'STOPPED-FLOW STUDIES OF THE OXIDATION OF ORGANIC SUBSTRATES BY CERIUM(IV), THALLIUM(III) AND VANADIUM(V)'

BY

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SUMMARY

The Cerium(IV) ion has been shown to exist in perchloric acid solution as a mixture of Ce^{4+} and $CeOH^{3+}$. The hydrolysis constant has been determined spectrophotometrically and compared with the existing data on tetravalent ions. From a spectrophotometric study, values of the molar extinction co-efficients of each ion have been determined over a wavelength range of 300-400 nm.

Two different types of apparatus utilizing the stopped-flow technique have been used to study the following reactions:

a) the cerium(IV) oxidation of α-hydroxy acids, malonic acid, L - cysteine and DL - penicillamine

b) the reaction of thiomalic acid with thallium(III) and

c) the vanadium(V) oxidation of thiourea.

Cerium(IV) has been shown to oxidise α-hydroxy acids (HL) in perchlorate media via well defined intermediate complexes. The ultraviolet spectra and the equilibrium constants of these complexes have been determined and a comparison made with the kinetically derived values and compared with other oxygen containing substrates. The rates of decomposition of the intermediate complex, CeL^{3+}, have been evaluated over a range of acidities (0.25 - 1.50M) and

temperatures (6.8 - 30°C) at an ionic strength of 1.50M and the thermodynamic data interpretted in terms of both enthalpy and entropy effects of the overall reaction. The increase in the rates of oxidation of these intermediate complexes has been attributed to the inductive effect of the substituent group. An inner-sphere mechanism has been suggested.

In the oxidation of malonic acid (H_2L) by cerium(IV) in perchlorate medium, decomposition of the intermediate complex has been shown to be the rate-determining step. At temperatures $\geq 25^\circ C$ the kinetic data suggest an apparent bimolecular reaction, whereas at lower temperatures intermediate complexes have been characterised and an acid catalysed reaction pathway has been proposed to account for the hydrogen ion dependence of the rate of reaction. In contrast to the oxidation of α-hydroxy acids, the CeH_2L^{4+} complex has been shown to be the kinetically important species. The hydrolysis constant of cerium(IV) has also been evaluated from the corresponding kinetic data.

The oxidation of L-cysteine and DL - penicillamine by cerium(IV) in perchlorate medium has been studied over the temperature range 6.85 to 25°C and at an ionic strength of 1.50M. In the $[H^+]$ range 0.25 to 1.50M the reaction has been interpretted in terms of both Ce^{4+} and $CeOH^{3+}$ being potential oxidants. No evidence of complex formation has been found.

Kinetic evidence has been provided in support of the suggestion that the reaction between thallium(III) and thiomalic acid (HRSH) in acid perchlorate solution proceeds via the formation of a relatively unstable intermediate complex, $TlHRS^{2+}$, for which unimolecular decomposition is the rate-determining step. All the kinetic data are apparently consistent with this mechanism.

Studies on the oxidation of thiourea by vanadium(V) in perchlorate medium have been made at 25°C. Several complex species have been suggested to exist in solution depending upon the $[H^+]$ and thiourea concentrations. The decomposition of intermediate complex(es) has been shown to involve a one electron transfer mechanism with vanadium(IV) thiourea complex(es) as the proposed reaction products.

Chapter 1

GENERAL INTRODUCTION

Studies of reaction mechanism began before 1900 and early investigations were generally undertaken by physical chemists who were testing the then current theories. Before 1915 these chemists studied the large number of inorganic systems, such as the decomposition of ozone and the reaction of hydrogen gas with chlorine gas. In recent years many new inorganic reactions have been studied and a wide variety of instrumental methods have become available. These new methods have given a firmer foundation to the study of kinetics. Inorganic reaction mechanisms can broadly be classified as substitution, free radical, oxidation-reduction, catalysis, etc., and have been widely reported[1-3].

Oxidation-Reduction Reactions

Interest in oxidation-reduction or electron transfer reactions has developed increasingly rapidly, largely as a result of the availability of the new experimental methods and instruments. In addition, the improvement in experimental capabilities has been paralleled by an increased consideration of theoretical treatments of such reactions by Marcus[4], Eyring[5], and Laidler[6].

In the reactions involving two metal ions, redox processes generally involve a single electron transfer step and much work has been done on the elucidation of the reaction mechanisms of such systems in solution. A classification which has been found useful for dealing with the mechanism of redox reactions is that of outer-sphere and inner-sphere activated complexes. In the outer-sphere activated complex the co-ordination spheres of the reactants remain intact, and the elctron given by the reducing agent must transfer from the primary bonding system of one complex to that of the oxidant. In an inner-sphere transition state complex a molecule is shared between the co-ordination sphere of both metal ions so that in effect, in the activated species the metal ions are part of a single primary bond system.

Electron transfer by both kinds of mechanism is subject to the restrictions of the Franck-Condon principle[7]. The principle states that the motion of the nuclei is slow compared with the motion of electrons and that electron transfer occurs without any appreciable movement of the nuclei. Before electron transfer from one centre to another can take place, the co-ordination spheres must adjust so that the energy of the system is unaltered on the electron transfer. The configurations which are appropriate for electron transfer represent a very small fraction of the total which are accessible to the system, and thus the rates of electron transfer can be very low. Where the adjustments required involve only small changes from the equilibrium dimensions, the probability of reaching a suitable configuration is high and rates tend to be rapid.

Examples of the outer-sphere type of reactions include: $Fe(CN)_6^{4-}$ - $Fe(CN)_6^{3-}$ [8], MnO_4^{2-} - MnO_4^{-} [9], $Mo(CN)_8^{3-}$ - $Mo(CN)_8^{2-}$ [10], $IrCl_6^{3-}$ - $IrCl_6^{2-}$ [11], and $Fe(phen)_3^{2+}$ - $Fe(phen)_3^{3+}$ [12]. From the detailed kinetic studies on these systems it has been suggested that in general, metal ions surrounded by unsaturated or large polarisable ligands of this type exchange electrons rapidly, usually much faster than the corresponding aquo-ions or ammine complexes.

The MnO_4^{2-} - MnO_4^{-} [9] exchange reaction has been found to be markedly sensitive to the presence of oppositely charged ions. A large increase in the rate is observed when Cs^+ replaces Na^+ which may be due to a rather specific bridging effect of Cs^+. It may be that the role of the positive ion is to aid in energy matching by moving along with the electron and thus reducing the unequal charge distribution and the reorganization needed. A postulate that a symmetric structure $[O_3MnO - Cs - OMnO_3]^{2-}$ forms between Cs^+ and two anions may be made.

The outer-sphere mechanism has been suggested to be operative even when one of the reactants is substitution labile. A typical example is the $Co(NH_3)_6^{2+}$ - $Co(NH_3)_6^{3+}$ exchange reaction[13]. One of the reacting species is labile (Co(II) in this case), but the observed rate law and poor bridging properties of the ligand make it likely that this reaction should be included in the outer-sphere category.

An important and useful method for correlating information obtained for outer-sphere mechanisms has been introduced by R.A. Marcus[14]. This correlation in a simplified form may be expressed by the equation

$$k_{12} = (k_{11}\ k_{22}\ K_{12})^{\frac{1}{2}} \qquad (1)$$

where k_{12} and K_{12} are the rate and equilibrium constants, respectively for the electron transfer reaction, and k_{11} and k_{22} are the appropriate exchange rate constants. For example, if k_{12} and K_{12} refer to the reaction

$$Fe(CN)_6^{4-} + Mo(CN)_8^{3-} \rightleftharpoons Fe(CN)_6^{3-} + Mo(CN)_8^{4-} \qquad (2),$$

then k_{11} and k_{22} refer to the exchange reactions

$$Fe(CN)_6^{4-} + Fe(CN)_6^{3-} \rightleftharpoons Fe(CN)_6^{3-} + Fe(CN)_6^{4-} \qquad (3)$$

and

$$Mo(CN)_8^{3-} + Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{4-} + Mo(CN)_8^{3-} \qquad (4)$$

respectively[8,10]. On the whole, the agreement of observed rates and those calculated from equation (1) is encouraging[15–17]. Exceptions are the Fe^{2+} - Ce(IV), Fe^{2+} - Co^{3+} and $Ru(NH_3)_6^{2+}$ - $Co(NH_3)_6^{3+}$ reactions[16,18,19]. Two of these reactions involve the Co(II) - Co(III) couple and it may be that spin multiplicity restrictions or other electronic factors are responsible for the anomalous behaviour of these systems. Moreover, the reactions of the aquo complexes may proceed via dinuclear intermediates. Apart from the above exceptions, the Marcus correlation is without doubt a powerful one, and in many instances predicts specific rate constants to within order of magnitude.

The inner-sphere or bridged-complex mechanism has been described by Taube and his co-workers. The essential feature of this mechanism is that one of the reactants undergoes substitution in the first co-ordination sphere by a ligand bound in the other reactant, which then bridges the reacting species. If after reaction the ligand can be shown to be present in the inner shell of the reducing ion, the bridge mechanism is established.

Actual systems which can be studied in this way are rather limited. $Cr(H_2O)_6^{2+}$ is an ideal reducing agent because it is labile to substitution and oxidises to $Cr(H_2O)_6^{3+}$, which is inert, so that a transfer of ligand must take in the activated complex, if at all. The demonstration of such a mechanism in which a firm ligand bridge was shown to be present at the time of electron transfer was made most elegantly by Taube[20]. The classical reaction was

$$Co(NH_3)_5Cl^{2+} + Cr(H_2O)_6^{2+} + 5H_3O^+ \longrightarrow Co(H_2O)_6^{2+} + 5NH_4^+ + ClCr(H_2O)_5^{2+} \qquad (5)$$

Careful isolation of the product showed that virtually all of the Cr(III) was in the form of $Cr(H_2O)_5Cl^{2+}$ and, working with the radioactive chloride, it could be shown that all of the chloride came from the original $Co(NH_3)_5Cl^{2+}$ and none from free chloride in solution.

It has been shown that groups not acting as bridging groups can also find their way into the Cr(III) product. For example in the reaction of $Co(NH_3)_5Cl^{2+}$ with $Cr(H_2O)_6^{2+}$ in the presence of $P_2O_7^{4-}$ both Cl^- and $P_2O_7{}^{4-}$ are found in the product[21]. The rates of reactions are also altered by such nonbridging ligands. One might postulate a bridged structure such as $(NH_3)_5CoClCr(H_2O)_4P_2O_7$ to explain these results.

Care must be taken not to assume that ligand transfer is necessarily an essential part of the electron transfer reaction. The bridging group may serve in various ways to facilitate the movement of electrons. A negatively charged ligand would serve to bring the metal atoms closer and reduce repulsions. If the ligand has mobile electrons (for example, because of π-bonding), then it may simply act as a 'conductor'. The reaction of $Cr(H_2O)_6^{2+}$ and $IrCl_6^{2-}$ yields $Cr(H_2O)_6^{3+}$ and $IrCl_6^{3-}$ even though a chloride bridge is believed to be involved. The binuclear intermediate simply undergoes a substitution more rapidly at the chromium-chlorine bond than at the iridium-chlorine bond.

The role of bridging ligands in inner-sphere reactions has been recently reviewed by Taube and Gould[22]. Studies of the reactions of Cr(II) with a large variety of carboxylatopentamminecobalt (III) complexes have shown that electron transfer is not very rapid unless the bridging ligand contains a conjugated bond system or unless it contains a group which is capable of binding the reducing agent. Electron transfer in these reactions has been shown to occur via either adjacent attack or adjacent attack with chelation, or by remote attack of the reducing agent.

The reactivity of metal ions is thus seen to be influenced by the presence of ligands in solution. Furthermore, the metal ion can undergo a redox reaction with the ligand. If the electron affinity of the ligand is not large it can be oxidised; alternatively, if its electron affinity is greater than that of the central atom, the oxidation of the latter may take place.

Reactions of the type

$$M^{n+} + L \rightleftharpoons ML^{n+} \longrightarrow ML^{(n-1)+} + P \quad (6)$$

will proceed from left to right if there is a decrease in free energy. The energy profile diagram for the overall reactions may be represented by Figure 1. In this diagram state A represents the energy of the reactants, B is the transition state, C is the energy minimum resulting from an intermediate after the transition state, D is the maximum of a small energy barrier between C and E, E is the energy of the final products and B' is the transition state if no

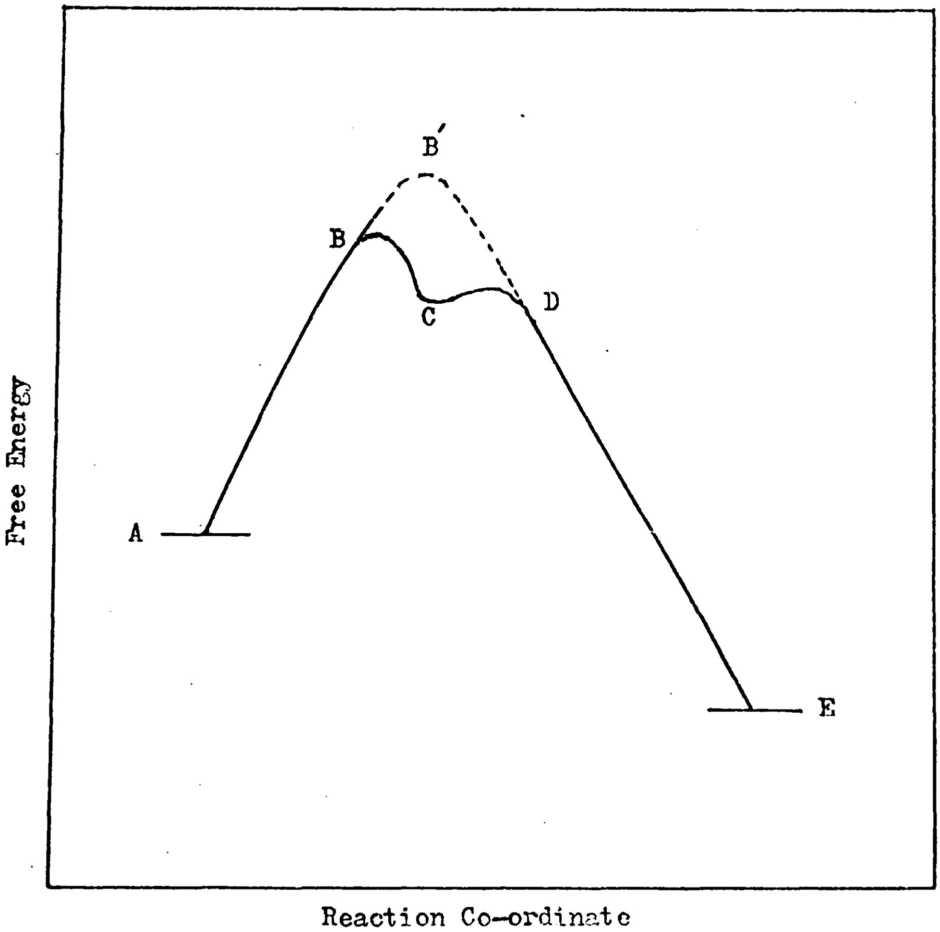


Figure 1.

complexation has occurred. The magnitude of $B'C$ will largely determine whether the reaction can be considered to be a concerted process involving the formation of ML^{n+} as a transition state, ie. when $B'C$ is small, or a two step reaction when an intermediate complex can be considered to be formed, ie. when $B'C$ is large. In the former case the equilibrium constant of ML^{n+} is small and a rate study may indicate strict second order kinetics. In the latter case, the rate law will be modified to incorporate a term in K, the equilibrium constant of the intermediate complex.

When $B'C$ is small there is little interaction between the reactants and an outer-sphere mechanism might be considered to be operating. The theoretical approach for outer-sphere reactions is somewhat simpler than for inner-sphere. No metal-ligand bonds are made or broken during the electron transfer step, and arbitrary parameters which occur in theoretical studies in chemical kinetics are therefore absent.

When $B'C$ is large (Figure 1) then the oxidation may be taking place by an inner-sphere mechanism. The theoretical investigation of inner-sphere electron transfer reactions is more difficult owing to several complications which do not exist in outer-sphere mechanisms. These are: (i)the close contact of the reactants that results in larger overlap in the electronic orbitals; (ii)the lower symmetry makes the calculations of the rearrangement free energy more difficult; (iii) the ligand cannot be considered to be a point charge or dipole, but its electronic orbitals significantly influence the electron transfer.

Extensive study of the oxidations of ligands by metal ions has established that these reactions generally proceed by an inner-sphere mechanism with the involvement, in some cases, of well characterised intermediates. The stopped-flow technique has been especially useful in studying these transient complexes. The formation of such inner-sphere complexes is more likely to take place where negatively charged or neutral substrates are involved than those with cationic reductants. There are three possible rate controlling factors in the overall formation of products:

i) the rate of formation of the intermediate
ii) the rate of electron transfer within the intermediate
iii) the rate of the breakdown of the intermediate

When the rate of formation of the intermediate is the rate controlling step the factors influencing the metal ion exchange may be important. Substitution reactions involving first row divalent transition metal aquo ions have been shown to be largely independent of the ligand and a common mechanism has been proposed, namely

$$M(H_2O)_6^{2+} + L \rightleftharpoons M(H_2O)_6^{2+}, L \longrightarrow M(H_2O)_5L^{2+} + H_2O \quad (7)$$

The first step, the diffusion controlled ion-pair formation, has a bimolecular rate constant of the order of $10^9 M^{-1} sec^{-1}$. The second step is rate controlling and corresponds to the loss of water molecule from the inner co-ordination sphere of the metal ion. A similar mechanism has been suggested to operate for some trivalent transition metal ions[24]. Recently Sassaki and Sykes[25] in the study on complexation reactions between Mo^{3+} and SCN^- and Cl^- have shown that these reactions proceed by an SN_2 mechanism. They also attempted to correlate their data with other trivalent metal ion systems. Since it is higher valence state transition metal ions which are usually oxidising agents, the mechanisms of such substitution reactions are most important.

When the rate of electron transfer controls the rate of reaction a theoretical approach, based on the relative electron affinity of the ligand, should be applicable. Such a theory would be similar to that of the outer-sphere mechanism already discussed and may explain why in the iron (II) oxidation by semiquinones[26,27], by an inner-sphere route, there is linear free energy relationship as predicted for an outer-sphere mechanism. It would appear that reactions of this type are more favoured when a single bond exists between the reactants since multiple bonding might lead to bond breaking becoming the rate controlling step. Many more experiments have to be carried out in order to determine which reactions occur by this route.

For the breakdown of the intermediate to be the rate determining step, the energy required for the homolytic cleavage of the metal ligand bond must be greater than that for the other reaction steps. The process may be modified by a ligand of denticity greater than one, when the breaking of a second bond between the reduced metal ion and radical ligand might become important. Other complications in such reactions are the driving force for the radical ligand to be stabilised by dimerisation and possible further electron transfer occurring between the metal ion oxidant and the radical ligand.

The detection of complex formation between oxidant and reductant does not in itself prove that this entity plays a direct role in the redox process[28]. There is a kinetic ambiguity which does not allow distinction to be made solely on the basis of the observed rate law, between whether or not a complex is a true intermediate. If such a complex is formed in measurable concentrations, however, the establishment of the existence of sequential process may be made spectrophotometrically, especially by the observation of induction periods and isobestic points.

Reactions of Oxyanions

It has been known for a long time that oxyanion reaction rates are markedly dependent on hydrogen ion concentration[29]. This is true for both ligand substitution and redox processes. The role of the proton is almost certainly the labilisation of the co-ordinated oxide and hydroxide anions by converting them to water. There is generally a close correlation between the rates of ligand exchange and electron transfer reactions of such compounds[29].

In any horizontal row of the periodic table, the rate of oxygen exchange in water decreases with an increase in oxidation state of the central atom[29].

$$H_2SiO_4^{2-} > HPO_4^{2-} > SO_4^{2-} > ClO_4^-$$

A similar oxidation state effect is observed for oxyanions of a single element[29]

$$ClO^- > ClO_2^- > ClO_3^- > ClO_4^- .$$

The size of the central atom also plays an important role[29]

$$IO_3^- > BrO_3^- > ClO_3^-$$

The two trends given above for the oxyhalides are also the trends for the rates of oxidation by these species[29]. This correlation has been discussed[30].

Perchlorate is an interesting example of a complex ion whose redox reactions are substitution controlled. When boiled in 9 M acid, the half-life of oxygen exchange with water is more than a century[31]; even the hydrated electron will not reduce it readily[32]. There is, however, a substantial thermodynamic driving force for the reduction of this species which has caused many spectacular explosions, often with tragic consequences[33]. Its kinetic inertness in aqueous solution renders it a useful inert constituent of the background electrolyte in studies of reactions in this medium, especially in view of its very poor co-ordinating properties[34].

Recent reviews[35–37] on fast reactions in solution indicate the extent of the activity in this field. Many electron transfer reactions can only be studied by fast reaction techniques. It is, therefore, of interest to investigate metal ion oxidations further, using fast reaction methods in order to gain more information about activated complexes. If an outer-sphere activated complex is formed it is important to further test the theoretical approach to this mechanism. If an inner-sphere activated complex is formed the interest is in the type of bonding which exists in the complex and thermodynamic parameters associated with its formation.

Chapter 2

THE STOPPED-FLOW APPARATUS

General Introduction

Prior to the last ten or fifteen years, chemical reactions could be divided into two groups: those whose rates could be measured and those whose rates were too fast to be measured. Too fast meant any reaction with a half-life of less than 10^{-3}sec. Almost no chemical reaction today is labelled 'immeasurably fast', since with the remarkable development in electronics and improved instrumentation, current experimental techniques now extend to reactions with half-lives approaching molecular vibrations and rotations. During the past decade a large number of reviews[38-41], monographs[42-45] and proceedings of several symposia[46-48] have been published to account for the interest and developments in the fast reaction techniques.

The problems associated with the study of fast chemical reactions are two fold. The first is the rapid initiation of reaction; the second is that of detecting the processes occurring during its course. It is obvious that to overcome the first difficulty the reactants must be brought together as quickly as possible. This has led to the development of what are termed 'rapid flow' methods. In this chapter various fast reaction techniques will be briefly discussed with special emphasis on stopped-flow method.

The Continuous - Flow Method

Two solutions are mixed and allowed to pass along an observation tube at a uniform velocity. The extent of reaction at various distances along the tube is found by measuring some physical property of the solution. With a flow velocity of 10 meters per second, a distance of 1cm corresponds to 1 millisec., and reactions with half-lives of this order can be observed. This technique enables reactions several times faster than the limit for the stopped-flow method to be measured. It has the major disadvantage that large volumes of reactants are required.

The Accelerated - Flow Method

This method resembles that of continuous-flow. It differs in that observations are made at a fixed point close to the mixing chamber, while the velocity of the liquid is varied continuously. The change in some physical property can be converted to a voltage change and displayed on an oscilloscope screen. The variation in velocity can be converted to voltage by using a variable potentiometer coupled to a driving syringe barrel, and in this way both velocity and physical property can be photographed together and the photograph later analysed. A stopped-flow apparatus can be converted to operate as an accelerated-flow device.

Relaxation Methods

For very fast reversible reactions in solution, relaxation methods, such as temperature-jump, have recently been developed[49-50]. By employing solutions where the reactants are already mixed these methods are obviously not subject to the limitations of flow techniques and provide a means of following the progress of reactions which are close to diffusion control[51]. These diffusion - controlled reactions almost invariably have second order rate constants in the range $10^{10} - 10^{11} M^{-1} sec^{-1}$ [51]. Although relaxation methods have been used in conjunction with the continuous-flow technique in the study of irreversible reactions[52,53] the considerable difficulties associated with this application make it desirable to use stopped-flow wherever it is a viable alternative. Reversible reactions in the stopped-flow time scale range are better suited to that technique in view of the much greater reproducibility afforded by it.

Photoelectric spectrophotometry is the most widely used technique for monitoring reactions in fast reaction devices[54] owing to fast response electronic detectors, the output of which is usually displayed on a cathode ray oscilloscope. Solution reactions are commonly accompanied by changes in the electronic spectrum of the reagents in solution. The linear relationship between optical density and concentration, in addition to the precision of measurement with photoelectric spectrophotometers are factors which account for popularity of this method. Where necessary, however, other physical properties have been monitored[45] and it is desirable for the same reaction to be followed, if possible, by two or more independent means.

The Stopped - Flow Method

In 1923 Hartridge and Roughton[55] showed that kinetic studies of fast reactions in solution could be accomplished using the continuous-flow method. With this method they were able to study reactions having half-lives as short as about 1 millisec. In 1940 Chance[56] introduced the stopped-flow method, its major advantage over the continuous-flow technique being the economical use of reactants. Since then many researchers, including Gibson and Milnes[57] sought ways to improve and add flexibility to the stopped-flow method. Although many variations have been reported since 1940, all, including those described in this chapter, have their roots in the original Chance design.

Principles:

In this technique, two reactant solutions are rapidly mixed by being forced through a mixing chamber, the mixed solution then flowing along an observation tube. The flow is suddenly stopped so that the solution comes to rest within several milliseconds. The element of solution about 1cm from the mixing chamber will have been mixed for a few milliseconds. The reaction taking place in this fixed element of solution is followed by making observations at this point using some rapid response technique such as photoelectric photometry. The output from this detection system can be applied to a cathode ray oscilloscope and using a time base of convenient value, a curve representing the extent of reaction against time will be displayed on the screen.

There are several factors which govern the reliability of a stopped-flow apparatus in its measurements of reaction rates and the value of the shortest reaction time accessible to it.

i) The flow velocity must be adequate: If the time elapsed is to be linearly related to the distance along the observation tube, a necessary condition is that the composition of the liquid is affectively uniform at any cross-section of the tube. Ideally this would require mass flow, with velocity uniform at all points on the tube. However, since there is a retardation at the wall, there will always be a maximum velocity at the centre of the tube. If the flow is laminar, the velocity profile across a diameter is parabolic and the ratio of the maximum velocity at the centre to the mean, is 2. A closer approach to mass flow is 'turbulent' flow, in which the distribution of velocity across the tube is more uniform, the ratio of maximum to mean velocity being about 1.25 for high rates of flow. Moreover, turbulent flow is accompanied by eddying, which will lead to improved mixing of the solution. The condition for turbulence is that the velocity must be above a critical value U_c (cm/sec), which has been empirically found to be related to the diameter d of the tube (cm) and the density ρ (g/ml) and viscosity η (poise) of the liquid, by the following equation

$$U_c = \eta R / \rho d \qquad (8)$$

The numerical factor R, known as Reynold's number is about 2000 for fairly short tubes with a stream-line entry[58]. For water the critical velocity at 20°C in a tube 2mm in diameter is about 4 metres/sec.

Thus the upper limit to solution velocities employed in flow devices is expected to be governed only by the technical difficulties involved in achievement of the necessarily very high push rates. In fact, however, a frequent limiting factor is the onset of cavitation[59], which is the formation of visible bubbles in solution. In most cases this imposes a limit of the order of 10–15 metres per second on flow rates[60].

Cavitation results when the external pressure on the solution falls below the vapour pressure of water[61]. The bubbles formed are in fact localised pockets of water vapour. Total internal reflections by these bubbles causes anomalous light transmission effects in solution.

ii) The reactant solutions must be thoroughly mixed: Although the degassing of solutions and the application of a positive back pressure while reactants are discharged have both been used successfully as methods for reducing or eliminating cavitation, consideration of this phenomenon nevertheless limits the scope of designs of mixing devices which provide optimum efficiency because mixers are often the principle sources of cavitation[59]. They must be constructed in such a way that they provide the means for maximum dissipation of energy by the reactant solutions in the mixing process. Since mixing efficiency increases with the number of jets incorporated in the mixer[62] it is obviously desirable to have a very large number of them. However, to minimise the pressure drop across the mixing chamber it is necessary to have an arrangement where the total cross-sectional area of the jets is approximately equal to that of the observation tube[63]. In view of the generally small bore of the latter, construction problems limit the number of jets which is practical. Also, the presence of a large number leads to such a great resistance to flow that high push rates become difficult to achieve[62]. Most mixers in general use do not incorporate more than eight jets. Gibson's pioneering stopped-flow apparatus utilised two four-jet mixers in series[64].

iii) Distance between observation point and mixing chamber: The observation point must be some millimetres from the mixing chamber to ensure that mixing is complete, but not too far away since the lost time between mixing and observation must be minimised.

iv) The flow must be stopped very quickly for the following reasons : the efficiency of mixing falls if the flow is too slow; consequently if the rate of flow was to decrease gradually, the liquid which ultimately comes to rest at the observation point might be incompletely mixed, and the apparent reaction rate would initially be too low. Moreover, the more sudden the stoppage, the faster the reactions that can be observed. Also, if stopping is slow the mixing efficiency will drop during the deceleration and the portion of solution observed will not be adequately mixed[64]. In addition, the rapid starting and stopping again promotes turbulence in solution. Gibson has developed a means of rapid stopping where the solution is driven against the plunger of a syringe. The plunger is halted abruptly when it encounters a block[64]. This method has the added advantage of providing back pressure which helps prevent cavitation.

Description of the Stopped - Flow Devices

Two types of stopped-flow apparatus were used, one for reactions having half-lives greater than 10 seconds, the other for all reactions faster than this. The stopped-flow apparatus which was used for slow reactions ($t_{\frac{1}{2}} > 10sec$) is shown schematically in Figure 2.

The drive - and reservoir - syringes, as well as the mixing device, were all thermostatted within a one cubic foot capacity plexiglass tank through which was circulated water from another larger tank by means of a B.T.L. Circon heater-pump. Temperature control within this tank was provided by means of a Circotherm Mk II Thermomix Series 769 (Shandon Southern, Cambridge) which incorporated a 27559/E contact thermometer (Braun,Melsungen). Cooling was achieved using a 'Tecam' dip-cooler refrigeration unit (Techne Ltd., Cambridge). Each of the two 10ml capacity pyrex glass drive syringes (Chance Brothers,

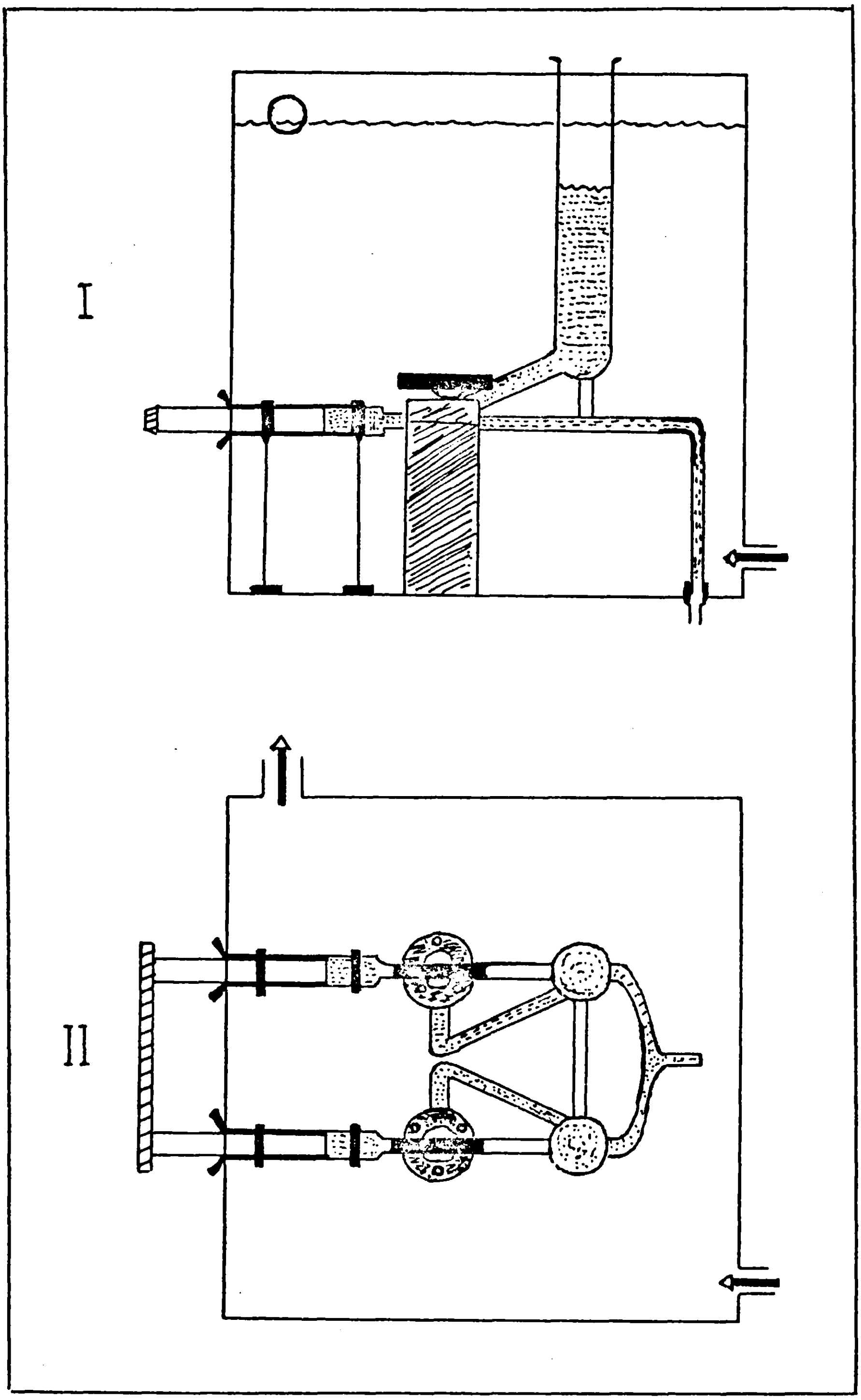


Figure 2 :- 'Slow'Stopped - Flow Apparatus

I · Side View;   II Plan View
1cm = 1 inch

Melvern Link), (fitted with specially constructed teflon plungers sealed with neoprene 'o' rings) was connected to a three-way teflon-barrelled stop-cock by short lengths of 'Portex' surgical tubing. The three-way taps were situated as shown and supported by perspex pillars. The glass reservoirs were specially blown, as was the mixer, which was of the type shown in Figure 3. A fused glass multibore network was placed downstream from this device in order to aid the efficiency of mixing. The plexiglass tank was situated above a Unicam S.P. 800D spectrophotometer which was fitted with S.P. 820 Series 2 contact wavenumber scan control and S.P. 850 scale expansion unit linked to a Servoscribe chart recorder. The mixed solution entered the cell compartment of the spectrometer which contained a 10mm path length quartz flow-through cell (Hellma Q.S.130).

Thermostatting was achieved by passage of water through the hollow cell-holder using the Circotherm heater-pump. Thermometers were used to monitor the temperature of the water in both tanks in addition to that of the cell-holder effluent. Overall temperature control was to within $\pm$ 0.2^{o}C.

The second type of stopped-flow apparatus used to study fast reactions ($t_{\frac{1}{2}} < 10$sec) is shown in Figure 4 and is described below.

The reactant solutions were delivered from two

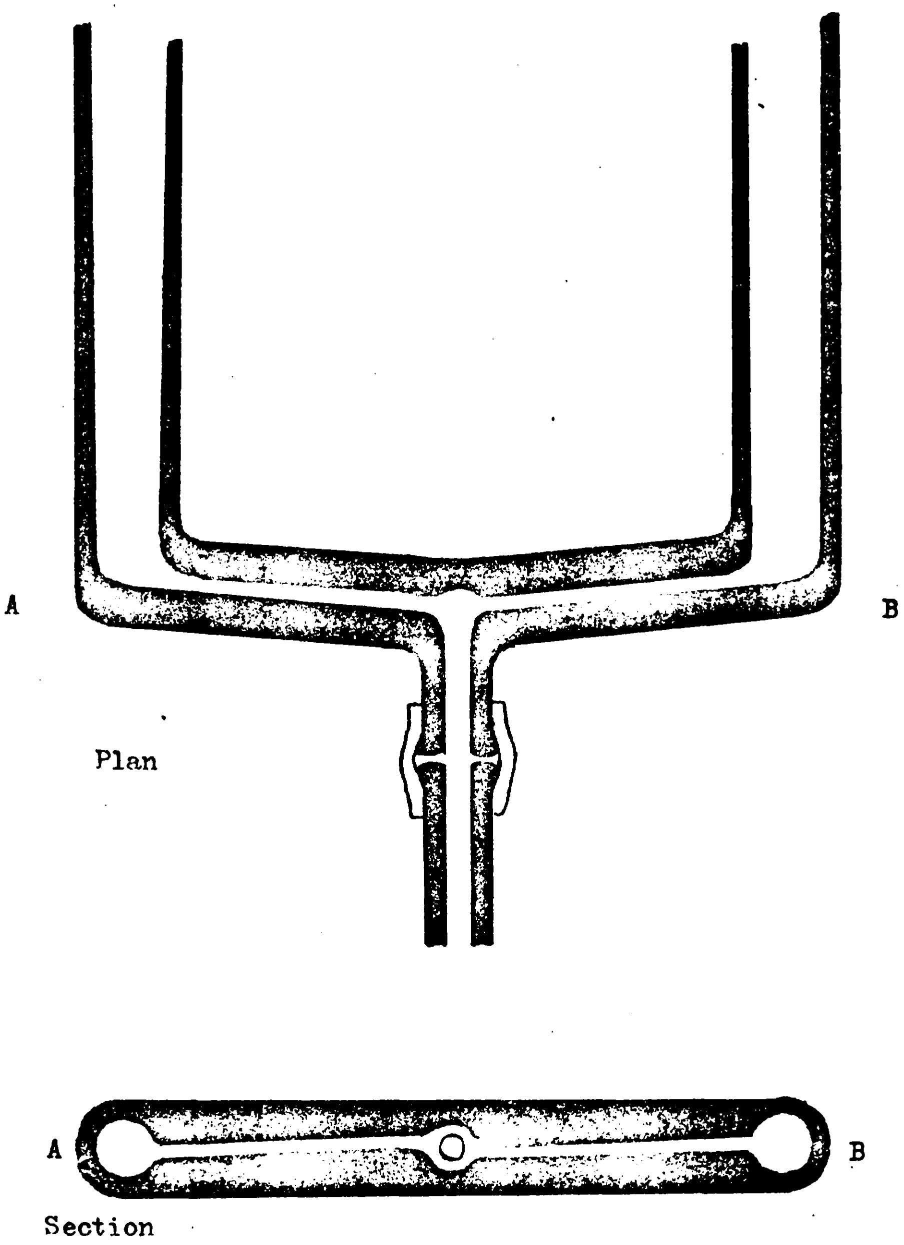
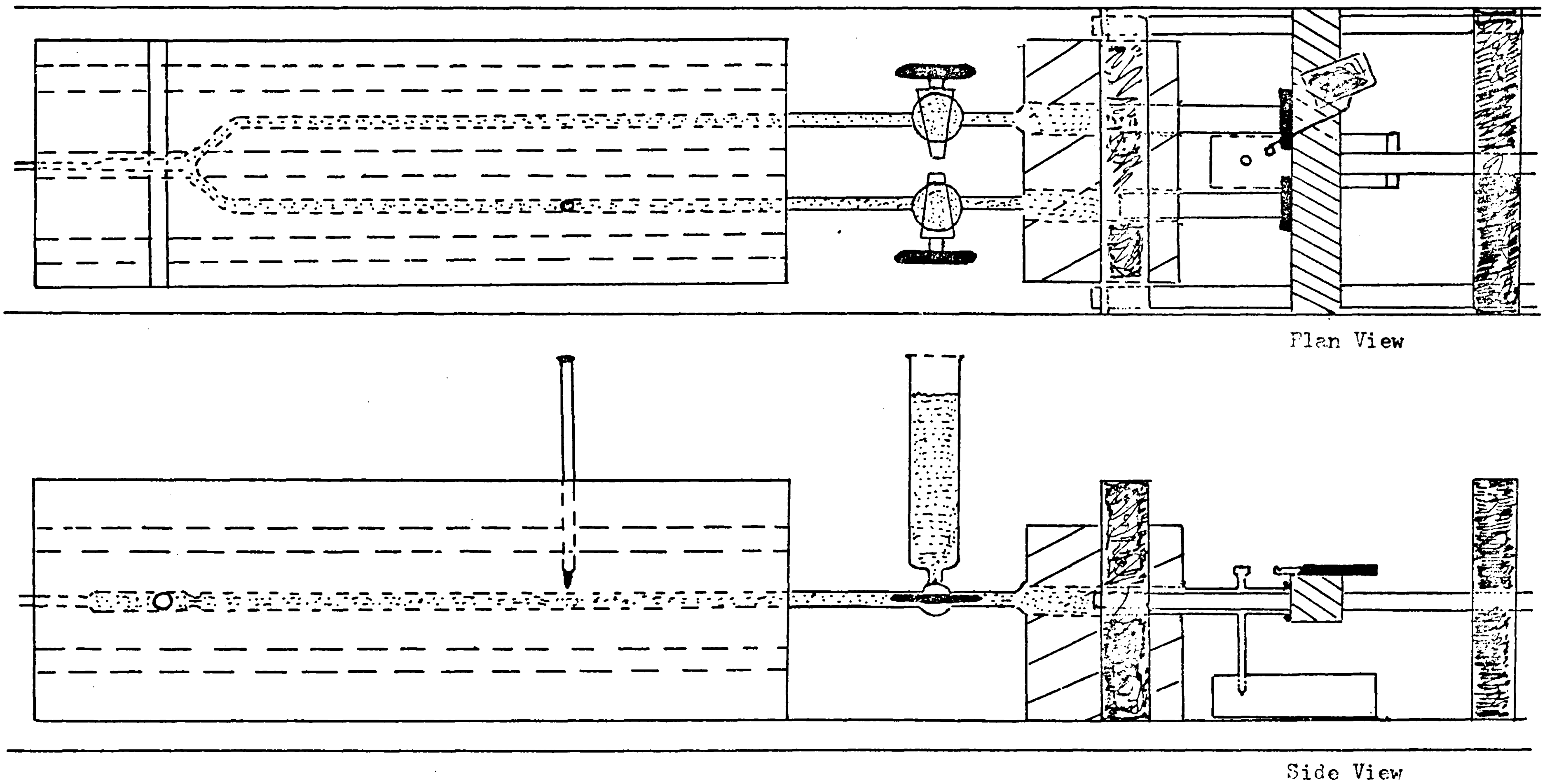


Figure 3:- All Glass Two Jet Tangential Mixer



Plan View

Side View

Figure 4 :- "Fast" Stopped Flow Apparatus

1 cm = 1 inch.

horizontal 'Zippette' pyrex glass syringes of 2ml capacity (Jencons, Hemel Hempstead). Specially constructed teflon plungers were used. These were fitted with flat brass screw-in heads which were incorporated into brass collars tapped into an aluminium pushing block. In order to achieve an effective seal within the drive-syringes, neoprene 'o' rings (Edward Vacuum Components Ltd., Crawley) were fitted to the plungers near their tips. Each of these syringes was connected to a three-way T-bore glass barrelled stop-cock (Springham, Harlow) either by glass blowing or by the use of short lengths of plastic tubing (Portex Surgical Tubing, Hythe, Kent) secured by windings of copper wire and embedded in plaster of Paris to prevent any expansion during pushes and consequent relaxation of solution when flow was stopped. The vertical reservoir syringes were glass pyrex with a capacity of 10ml. The nozzles of these syringes were lapped with glass to increase their external diameter and hence facilitate the connection to the main drive system. Solutions were transferred to the mixing device by way of glass tubing of 5mm internal diameter. The feed tubes were connected to the mixer by short lengths of 'Portex' plastic tubing which were secured by windings of copper wire. In instances where copper wire was used in this way it was not possible for solutions to be contaminated by contact with it.

The mixing chamber was an all-glass, two-jet mixer of the design shown in Figure 3. The 'spectrosil' type 134Q.S. flow-through spectrophotometer cell (Hellma Instruments, Southend-on-Sea) was fused to the observation tube very close to its exit from the mixer. This cell had a rectangular cross-section and 5mm path-length. In addition, another stopped-flow apparatus used was virtually identical in design, but differing only in the 'dead-times' of the apparatus. Reaction rates were found to be identical on both flow devices, well within the experimental error, indicating that the mixing efficiency of the two-jet device was not measurably inferior to that of the eight-jet mixer used in the previous design of this apparatus.

A metal rod projected horizontally from the rear of the pushing-block, which itself ran on iron rods. When compressed gas was released into 50ml 'Atlas' nylon syringe (Thackray Ltd., Leeds) by quickly turning a three-way tap (Fison Glassware, Loughborough), the plunger was driven out within the syringe and drove the pushing-block. Flow was stopped when the pushing-block encountered a vertical iron pin which was placed in one of several available holes in a brass block. This front-stopping method was used in preference to the conventional back-stopping system, as it was found to lessen the recoil which occurred when flow was stopped. Also, it provided greater operational flexibility in that by having a number of holes in series in the stopping-pin holder, it was possible to obtain several pushes without refilling the drive syringes. The solution finally travelled upwards into an inverted Dreschel-head fitted with a round bottom flask.

Thermostatting of solutions was achieved by incorporation of the feed-tubes, mixing chamber and observation cell all within a two-piece aluminium block through which water was circulated lengthwise via copper tubes, three in the top section, three in the bottom. A thermometer was placed in the cavity in the top block, providing contact of the bulb with one of the feed-tubes. Thermal contact between the flow system and both the thermometer and aluminium block was achieved by packing brass fillings into any air-spaces which existed. The thermostatting water was heated and was circulated from a tank by means of a Circotherm Mk II Thermomix series 769 (Shandon Southern, Camberley) which incorporated a 27559/E contact thermometer (Braun, Melsungen). Cooling was achieved using a 'Tecam' dip-cooler refrigeration unit (Techne Ltd., Cambridge). Overall temperature control was to within $\pm$ 0.1°C.

The power supplies and ancillary electronic equipment were operated from the mains via a type BTR - 5 A.C. automatic voltage stabiliser (Claude Lyons Ltd.) with an output of 240 volts at 50Hz.

One of the stopped-flow devices of the type described above used a S.P. 500 monochromator (Pye Unicam Ltd., Cambridge) as its light source. Visible radiation was provided by a tungsten lamp which was operated at 36 watts (6 volts, 6 amps) from a Unicam 115D power pack. Ultraviolet radiation was supplied by a deuterium lamp which utilised the standard Unicam power unit. The intensity of light leaving the spectrophotometer cell, which was masked with black tape to create an aperture approximately one millimetre in diameter, was monitored using an E.M.I. 6256S photomultiplier tube. Its operating voltage was supplied by an A.E.I. type R1184 power unit. The output of the photomultiplier tube was fed by way of a D.C. amplifier into one output of a Tektronix 2A63 differential amplifier which was incorporated in a Tektronix 564 storage oscilloscope. The D.C. amplifier circuit contained a number of resistor-capacitor filters. The decision regarding which one was used for a particular run was governed by a consideration of the magnitude of the time-constant of the filter compared with the half-life of the reaction. The other D.C. input signal to the oscilloscope differential amplifier was also provided by the D.C. amplifier circuit. The current could be varied by means of a calibrated helipot and enabled partial cancellation of the signal from the photomultiplier tube.

Current in the triggering circuit was drawn from the calibration voltage output of the oscilloscope to one terminal of a roller miniature microswitch (R.S. Components Ltd., London) which was mounted on top of the pushing-block. The other terminal was connected to the external trigger input of the 2B67 Tektronix time base. Triggering of the oscilloscope sweep took place when the microswitch was closed as it passed the stopping-pin shortly before flow stopped. Oscilloscope traces were photgraphed using a Shackman Super Seven Mk II oscilloscope camera fitted with a polaroid CB-40 Land back. Type 47 Polaroid Land film was used.

The other stopped-flow apparatus of similar design used as its light source a modified Hilger 'Uvispec' monochromator containing a 100 watt Osram tungsten lamp (6.6 amps, 15 volts). Its power pack was a Farnell stabilised voltage/current S-series type 15/106L unit. A glass lens was used to concentrate light on the cell. This limited this apparatus to operation in only the visible region of the spectrum. It used a Tektronix 5103N single-beam storage oscilloscope in conjunction with a Tektronix 5A20N differential amplifier and Tektronix 5B10N time base. Traces were photographed with a Tektronix C-5 oscilloscope camera using type 107 Polaroid film.

Calculation of Results

In order that a thorough kinetic analysis could be obtained with the two 'fast' stopped-flow devices, it was necessary to convert the oscilloscope displays of voltage as a function of time to the equivalent absorbance data which could be used, with knowledge of the appropriate molar extinction coefficients, as a direct measure of the way in which component concentrations varied during the course of reaction.

Optical density, O.D., can be expressed as in equation (9)

$$O.D._t = \log_{10}\frac{I_o}{I_t} \qquad (9)$$

where I_o is the intensity of light transmitted by an optically clear solution and I_t is the intensity of light transmitted by a solution of absorbance $O.D._t$ or A_t. For a calibrated photomultiplier tube where the output current, i, is linearly proportional to the intensity of incident light,

$$O.D._t = \log_{10}\frac{i_o}{i_t} \qquad (10)$$

The impedence of the system obviously does not change with absorbance. Hence,

$$O.D._t = \log_{10}\frac{V_o}{V_t} \qquad (11)$$

where V_o and V_t are as displayed on the oscilloscope screen.

Calibration of the helipot control entailed plotting its voltage output, as measured on the oscilloscope screen, against the corresponding readings on the control knob, see Figure 5. When the photomultiplier tube signal was exactly balanced by the signal from the back-off source, as illustrated in Figure 6, the horizontal line on the oscilloscope screen which represented zero volts of P.M.T. signal when no backing-off was applied, clearly then represented the voltage of P.M.T. output equal to that of the oppositely applied signal, with zero volts of light signal being as shown. V_t the P.M.T. voltage corresponding to any other horizontal line on the screen, could be computed simply by adding or subtracting the appropriate voltage, ΔV, with respect to this reference voltage $V_{B.O.}$. ΔV could be calculated simply by multiplying the vertical distance of separation, ΔR, by the oscilloscope gain setting.

The most common form of information collected was the exponential decrease in optical density resulting from the pseudo-first-order decay of a metal ion which absorbed more strongly than the substrate or products.

It can readily be shown that for such a situation a plot of $\log(A_t - A_\infty)$ against time, where A_t is the absorbance of the reaction mixture at any time, t, and A_∞ is the absorbance of solution when reaction has been completed, will be linear with a slope equal to k_{obs}. Thus/

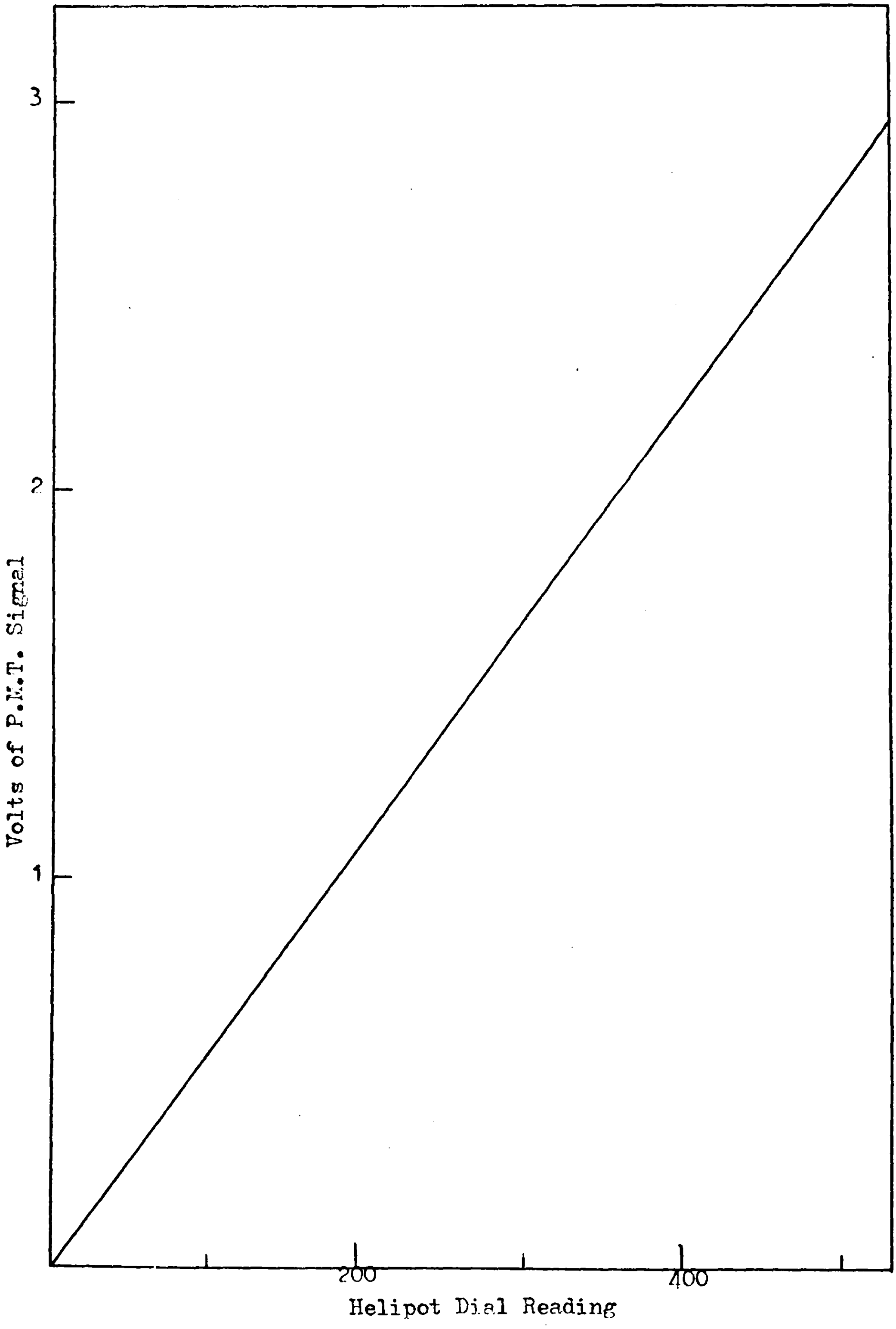


Figure 5 :- Calibration of Helipot Control.

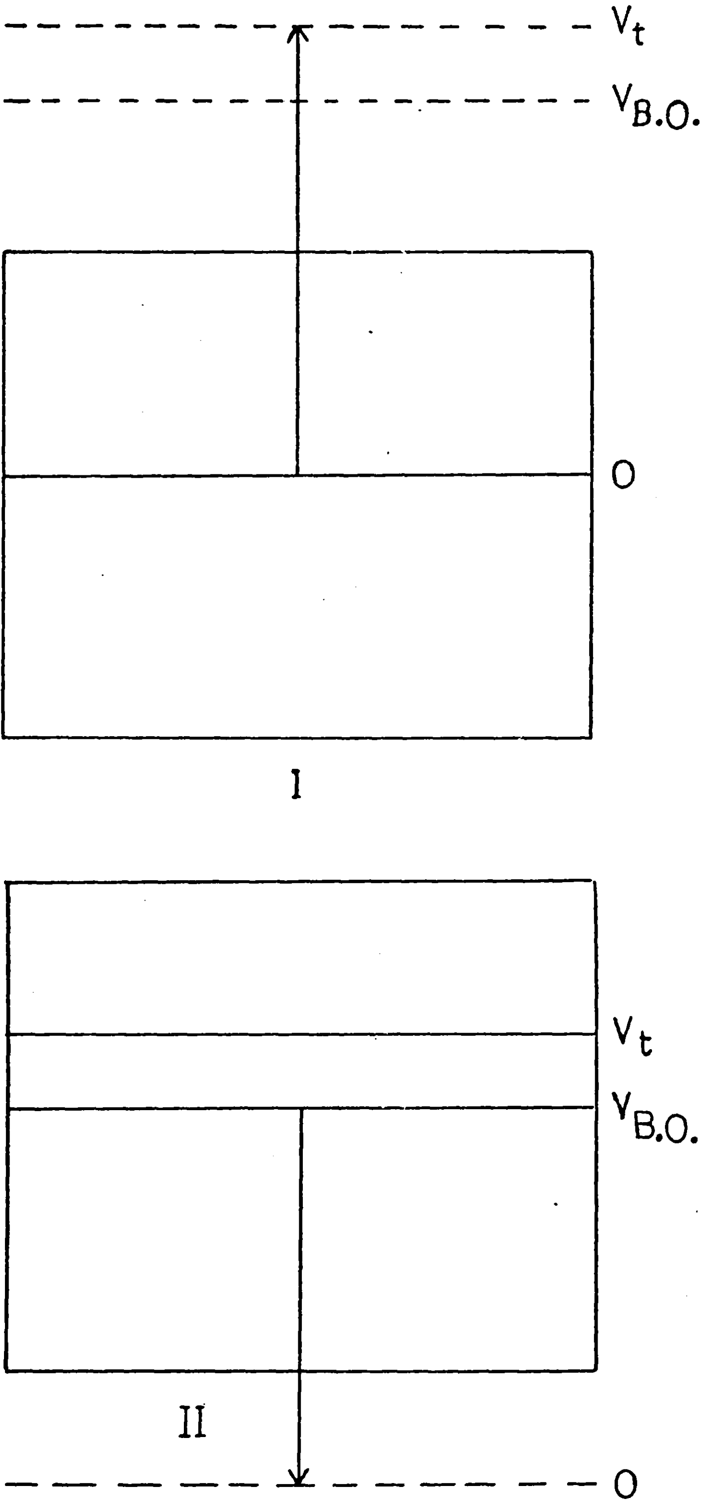


Figure 6 :- The Use of the "Back - Off" Helipot

I Volts of P.M.T. signal applied.
II $V_{B.O.}$ volts of helipot signal applied in opposite direction to "back-off" most of P.M.T. signal.

Thus:

$$A_t - A_\infty = \log_{10}\frac{I_o}{I_t} - \log_{10}\frac{I_o}{I_\infty}$$

$$= \log_{10}\frac{I_\infty}{I_t}$$

$$= \log_{10}\frac{V_\infty}{V_t}$$

$$= \log_{10}V_\infty - \log_{10}V_t \qquad (12)$$

An illustration of this procedure is provided by calculation of log $(A_t - A_\infty)$ for the point marked with the arrow in the hypothetical trace in Figure 7.

$$V_{B.O.} = B.O. \times 0.005575$$

$$= 538 \times 0.005575$$

$$= 3.00 \text{ volts}$$

The voltage corresponding to the bottom of the oscilloscope screen, ie. zero cm, V_z, is calculated by equation (13)

$$V_z = V_{B.O.} - \Delta V_{B.O.} \qquad (13)$$

$$\Delta V_{B.O.} = R_{B.O.} \times \text{Gain} \qquad (14)$$

$$= 4.00 \times 0.1$$

$$= 0.40 \text{ volts}$$

$$V_z = 2.60 \text{ volts}$$

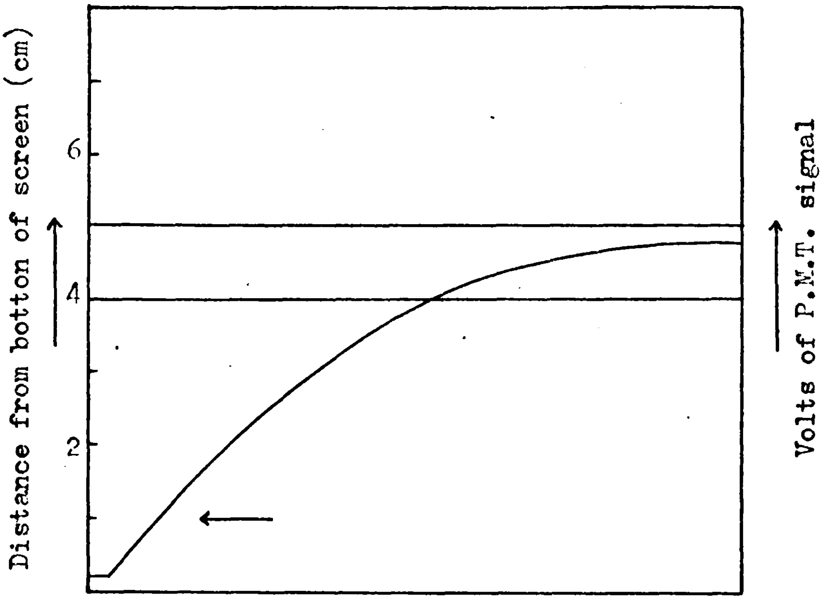


Figure 7 :- Hypothetical Oscilloscope Trace Representing an Absorbance Decrease.

Helipot dial reading = 538

The horizontal line at 4cm represents the zero setting of the oscilloscope, i.e. the display obtained in the absence of any applied signal.

$$\begin{aligned} \Delta V_t &= R_t \text{ x Gain} \\ &= 1.00 \text{ x } 0.1 \\ &= 0.10 \text{ volts} \end{aligned} \tag{15}$$

$$\begin{aligned} V_t &= V_z + \Delta V_t \\ &= 2.70 \text{ volts} \end{aligned}$$

$$\begin{aligned} V_\infty &= R_\infty \text{ x Gain} \\ &= 5.00 \text{ x } 0.1 \\ &= 0.50 \text{ volts} \end{aligned} \tag{16}$$

$$\begin{aligned} V_\infty &= V_z + V_\infty \\ &= 3.10 \text{ volts} \end{aligned} \tag{17}$$

$$\log_{10} V_\infty - \log_{10} V_t = 0.06$$

$$\log (A_t - A_\infty) = -2.81$$

When using the Tektronix 564 oscilloscope, account was taken of the parallax error which arose from the graticule being fractionally closer to the lens of the camera than was the screen. Thus distances as measured from photographs of traces were somewhat smaller than they actually were. This phenomenon is illustrated in Figure 8. It can easily by shown by the theorem of similar triangles that the necessary correlation factor is y/x. This was not, however, directly

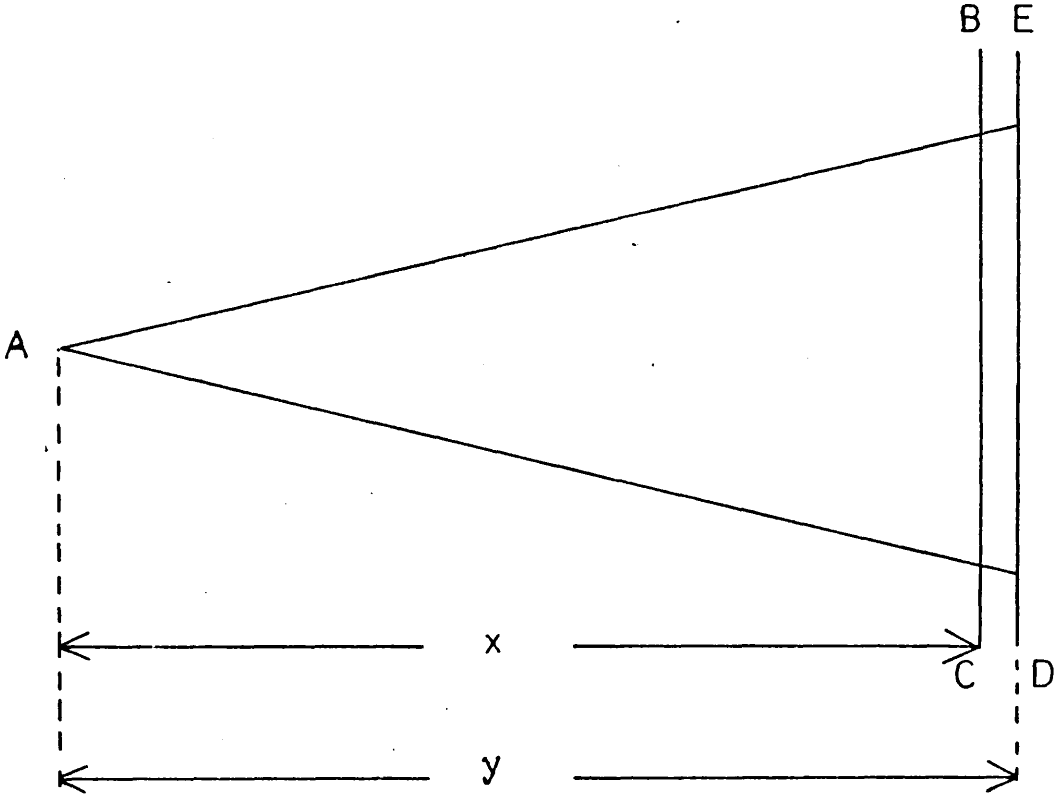


Figure 8 :- Illustration of the manner in which error can arise as a result of the graticule not being in the same plane as the oscilloscope display.

A : Camera aperture
BC : Graticule
ED : Oscilloscope screen

evaluated in this way. Instead, a plot was made of distances between horizontal lines as measured by eye as a function of the corresponding apparent distances as measured from photographs. y/x was found to be 1.032 ± 0.0006.

Operational Characteristics of the 'Fast' Stopped-Flow Apparatus

Although it would have been clearly preferable to employ greater gas pressures to drive the pushing-block, it was found that when more than 20 p.s.i. was used the shock caused by the stopping-pin being struck brought about undesirable optical effects in the initial portion of oscilloscope traces. (It is unlikely that these were the result of cavitation since they were also observed when degassed solutions were used).

In order to observe absorbance changes occurring during a push, and also to measure the flow rate, it was necessary to trigger the oscilloscope at the start of a push. This was achieved by keeping the microswitch closed while earthing the negative terminal of the switch using a short length of wire which was placed so that the current could flow to the trigger input of the oscilloscope time-base as soon as the pushing-block started to move.

The flow rate at 20p.s.i. was measured in this manner, using the Fe^{III}/SCN^- reaction to indicate the end of a push. The volume discharged could easily be measured quite accurately from the calibration markings on the reservoir syringes. It was possible to observe the flushing-out of the dead-space. A push-length equivalent to three times the distance between adjacent stopping-pin holes was 4-5 times longer than was necessary for this process and was adopted as standard. The duration of such a push was found to be 200 milliseconds, yielding a flow rate of 15 ± 1.5ml sec^{-1}.

Mixing efficiency was tested by the Schlieren method using water and 8M $NaClO_4$. Figure 9 illustrates the absorbance changes during and after a typical push; a line indicating the transmittance of water is superimposed. It is evident that multiple refractions which are found for incomplete mixing of liquids of differing refractive index, such as these, were, within 30 milliseconds after stopping, too small to be measurable.

Mixing ratios were determined by pushing a dilute solution of ferroin, $Fe(phen)_3^{2+}$, against water. The resultant optical density was compared with that obtained when the same concentration of ferroin was driven from both syringes. Absorbances were measured by evaluating the logarithm of the ratio of the voltage necessary to completely back off the P.M.T. signal for water to that necessary to do likewise for ferroin. The results, within experimental

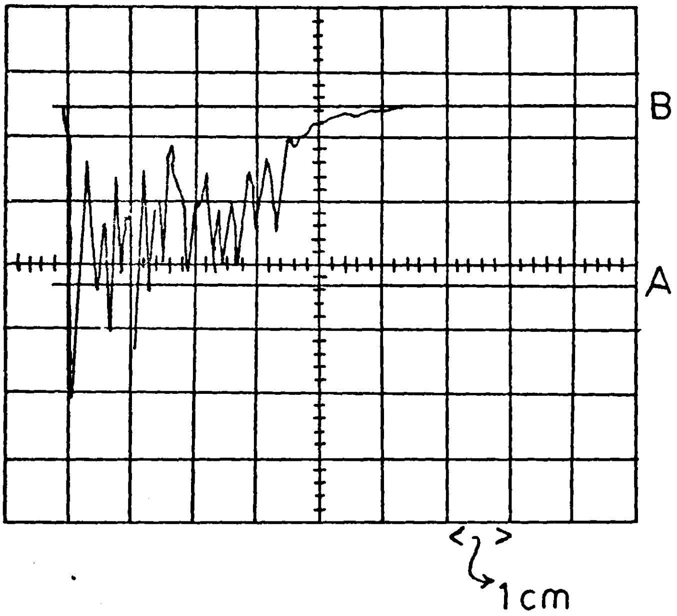


Figure 9 :- Oscilloscope display of the transmittance changes which occur in the course of Schlieren test.

Standard three-hole push: duration 200 millisec.

'Back-off' voltage = 2.84

gain = 0.2 volts/cm

sweep = 50 millisec/cm

Drive pressure = 20 p.s.i.

A = $R_{B.O.}$, the display obtained with no input

B = the transmittance of water

error, (± 1%), indicated a ratio of 1 : 1.

The dead-times were measured as shown schematically in Figure 10. Neither Fe^{3+} nor NH_4SCN absorb at 465nm when dissolved in 0.2 M-$HClO_4$. The formation of $FeNCS^{2+}$ was monitored, using excess iron (III) to give pseudo-first-order absorbance increases[65]. The dead-time is the time through which it was necessary to extrapolate a plot of $\log(A_\infty - A_t)$ vs. time to reach the value corresponding to A_o, which was derived from a superimposed water-line corresponding to the zero absorbance of a newly-formed mixture of reactants. The stopped-flow apparatus using the unicam S.P.500 monochromator was found to have a dead-time of 15 ± 1 milliseconds, while that of the other was 35 ± 2 milliseconds.

The mixing ratio of the 'slow' stopped-flow apparatus was determined as 1 : 1 by the method described above. Its dead-time was derived experimentally as 300 ± 15 milliseconds.

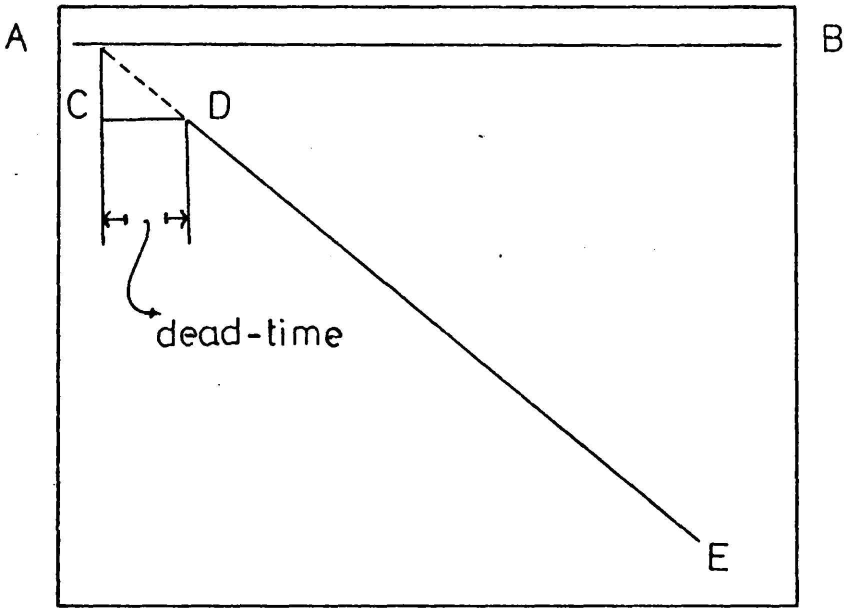


Figure 10 :- The calculation of the dead-time of a stopped - flow apparatus.

AB represents the transmittance of water

CD represents the transmittance observed at the start of the trace

DE represents a plot of $\log(A_{\infty} - A_t)$ versus time.

Chapter 3

THE HYDROLYSIS OF CERIUM(IV) IN ACID PERCHLORATE MEDIUM

INTRODUCTION

The use of cerium (IV) as an oxidant has long been known to the analyst in the determination of variety of organic compounds. Unlike many other transition metal ions, cerium (IV) as an oxidant has attractions of being somewhat unique in its behaviour towards mineral acids. Since most kinetic studies on the oxidation of organic and inorganic compounds depend on the acid medium employed, it is important to discuss the nature of various cerium (IV) species existing in such solutions. The marked ligand dependence[66] observed in the reduction potential of Ce(IV) - Ce(III) couple is shown in Table 1 and interpreted in terms of various equilibria discussed below.

Increasing the nitric acid concentration, the observed increase in potential has been attributed to the complex formation. From a potentiometric study it has been inferred that hydrolytic and polymeric species, as well as nitrato complexes, eg. $\left(Ce(NO_3)\ (OH)\right)^{2+}$, are present in solution. Under conditions of high nitrate concentrations, ion-exchange data are consistent with anionic complexes formed, presumably $Ce(NO_3)_6^{2-}$, among others. These phenomena are further reflected in the half cell potentials of cerium (IV) solutions as shown in Table 1. Available

TABLE 1

SINGLE ELECTRODE POTENTIAL VALUES, $Ce(IV) + e \rightleftharpoons Ce(III)$ IN VARIOUS CONCENTRATIONS OF HNO_3 , H_2SO_4, HCl, and $HClO_4$

E^o(volts)[a,b]

Acid/M	HNO_3	H_2SO_4	HCl	$HClO_4$
0.5		1.44		
1	1.61	1.44	1.28	1.70
2	1.62	1.43		1.71
4	1.61	1.42		1.75
6				1.82
8	1.56			1.87

a - electrode potentials with reference to the normal hydrogen electrode.

b - reference 66.

information on this subject has been correlated and discussed[67]. In a separate study[68] on cerium (IV) nitrate equilibria, the association between cerium (III) and nitrate has also been considered important. This provides an added factor in cerium (IV) oxidations where appreciable quantities of cerium (III)[68] are formed. A more recent spectrophotometric study[69] on the complexation of cerium (IV) with nitrate has shown that only one complex,$(CeNO_3)^{3+}$, is formed up to at least fifty fold excess of nitrate ions over cerium (IV), the equilibrium constant being 0.14M.

In sulphate solutions the predominant tendency is toward complex formation, with the result that hydrolysis and polymerisation are suppressed. Stability constants for the mono — , di — , and tri-sulphato complexes $Ce(SO_4)^{2+}$, $Ce(SO_4)$, and $Ce(SO_4)_3^{2-}$ may be defined in terms of the equilibrium of the type

$$Ce^{4+} + HSO_4^- \underset{}{\overset{K'}{\rightleftharpoons}} CeSO_4^{2+} + H^+ \qquad (18)$$

where $K' = [CeSO_4^{2+}]\ [H^+] \ / \ [Ce^{4+}]\ [HSO_4^-] = 3500$ and the corresponding K'' and K''' are 200 and 20 respectively[70] at 25°C.

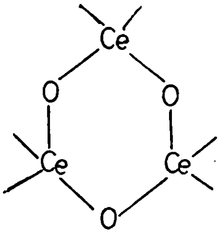
The reduction potential of the Ce(IV) - Ce(III) couple in hydrochloric acid is probably low (in the negative sense), because reaction at the platinum electrode is not reversible[67].

Recently Wiberg and Ford[71] have studied the cerium (IV) equilibria in aqueous acetic acid and postulated that the principle equilibrium is between a monomer and trimer

$$HOAc + 3\ CeOH^{3+} \overset{K_{ac}}{\rightleftharpoons} Ce_3O_3\ (HOAc)^{6+} + 3H^+ \qquad (19)$$

where $K_{ac} = 1.62 \times 10^5$ at 25°C.

The data clearly indicate that the trimer is the principle species in 5 - 90% acetic acid solution and the authors suggested the following cyclic structure



The formation of such a species has many analogies. Thus alcohols generally form trimers rather than dimers and these species probably involve six membered rings held together by hydrogen bonds[72].

The equilibria among cerium (IV) species in perchloric acid has been the subject of a number of studies. Smith and Goetz[73] found the oxidation potential of the Ce(III) - Ce(IV) couple to increase with increasing $HClO_4$. Sherrill, King and Spooner[74] showed that the increase in potential was independent of the perchlorate ion concentration and concluded that neither Ce(III) nor Ce(IV) reacts with perchlorate ion and Ce(IV) is hydrolysed even in strongly acidic solutions. They estimated an equilibrium constant for the second hydrolysis reaction

$$Ce(OH)^{3+} + H_2O \underset{}{\overset{K_{h_2}}{\rightleftharpoons}} Ce(OH)_2^{2+} + H^+ \qquad (20)$$

where $K_{h_2} = 0.6M$.

However, their data did not include corrections for the presence of polymerised Ce(IV) species which were observed in later studies. The presence of a dimer in the oxidation of water by Ce(IV) perchlorate was first reported by Heidt and Smith[75], which was later confirmed by King and Pandow[76] by observing deviations from Beer's law in the wavelength range $\lambda = 440 - 553$nm for 4×10^{-3} to 0.1M Ce(IV) in perchloric acid. Hardwick and Robertson[77] observed similar deviations at $\lambda = 395 - 430$nm, and reported the equilibrium constants derived from spectro-photometric measurements at three different acid concentrations in the range 0.2 to 2.0M $HClO_4$, for the reactions

$$Ce^{4+} + H_2O \overset{K_h}{\rightleftharpoons} Ce(OH)^{3+} + H^+ \qquad (21)$$

$$2Ce(OH)^{3+} \overset{K_d}{\rightleftharpoons} CeOCe^{6+} + H_2O \qquad (22)$$

where $K_h = 5.2M$ and $K_d = 16.2M^{-1}$ at 25°C.

Migration experiments confirmed the presence of positively charged cerium (IV) species in solution[77].

An indirect determination of the hydrolysis constants of Ce(IV) was reported by Baker, Newton and Kahn in connection with a kinetic study of the U(IV) - Ce(IV) reaction[78] in perchloric acid. Their estimated constants were $K_h > 15M$ and $K_{h_2} > 0.15M$ at 25°C.

More recently Offner and Skoog have determined spectrophotometrically[79] the hydrolysis constant of Ce(IV) in perchloric acid. From the Beer's law behaviour at various Ce(IV) concentrations it was concluded that polymerisation did not occur over the concentration range $1.0 - 10 \times 10^{-3}M$ Ce(IV), studied. The hydrolysis constant calculated was 0.20M at 25°C with no evidence for $Ce(OH)_2^{2+}$ species. Moreover, the hydrolysis constant was found to be independent of ionic strength.

The situation regarding the absolute value of this hydrolysis constant in perchloric acid is the more confusing in that some recent kinetic studies[80,81,82] support the value of Hardwick and Robertson[77]. A spectrophotometric study was thus undertaken to re-examine the conflicting values and results are presented in this chapter.

EXPERIMENTAL

Preparation of Cerium (IV) Solutions

Stock solutions of cerium (IV) in aqueous perchloric acid were obtained by the following two methods :

From an aqueous solution of ceric ammonium nitrate (B.D.H. Poole, AnalaR) cerium (IV) hydroxide was precipitated by slow addition of aqueous ammonia (B.D.H. AnalaR) till precipitation was complete. After the resultant precipitate had settled, the supernatant liquid was syphoned off with the aid of a water-suction pump. The precipitate was then washed with water which was in turn syphoned off. The last process was repeated until the supernatant liquid was found to be free of nitrate and ammonium ions whereupon syphoning was followed by dissolution of the hydroxide in 3 – 5M perchloric acid (Hopkin and Williams, AnalaR). The resultant solution was then treated with a slight excess of hydrogen peroxide (Hopkin and Williams, AnalaR) to reduce the Ce(IV) ions to oxidation state (III) followed by its electrolytic oxidation[83]. Such solutions (ca 0.025M Ce(IV) in 4M $HClO_4$) were kept at 0°C in dark to avoid any decomposition. It has been previously noted that cerium (IV) perchlorate solution obtained by dissolving cerium (IV) hydroxide (obtained by the above method) in 2M $HClO_4$ contains colloidal polymeric species and reacts slowly with hydrogen peroxide yielding a transient orange-red complex[84,85]. Electrolytic oxidation of cerium (III) perchlorate has previously been shown to yield only monomeric cerium (IV) species[85].

The second method of preparing cerium (IV) stock solutions involved the dissolution of ceric ammonium nitrate which had been dried at 87°C and stored in a dark bottle, in aqueous perchloric acid. Such solutions (ca.0.01M Ce(IV) in 3.0M $HClO_4$) were prepared the day any spectrophotometric or kinetic measurements were to be made and stored as described above.

The cerium (IV) content of stock solutions was determined by adding an excess of a standard ferrous ammonium sulphate and titrating the excess with standard potassium dichromate using N-phenylanthranilic acid as an indicator. The acid content of stock solution of cerium (IV) perchlorate was determined by titration of hot solution with freshly prepared 0.1M sodium hydroxide (Hopkin and Williams, Convol) which had been standardised using potassium hydrogen phthalate (Hopkin and Williams, AnalaR). Once coagulation of cerium (IV) hydroxide occurred, phenolphthalein was added and titration continued. In the calculation of the hydrogen ion concentration, allowance was made for the quantity of sodium hydroxide necessary to form cerium (IV) hydroxide.

Preparation of Standard Perchloric Acid and Sodium Perchlorate Solutions

Stock solutions of perchloric acid were standardised by titration against weighed samples of disodium tetraborate (Hopkin and Williams, AnalaR). The standardisation of stock solutions of sodium perchlorate (Fluka, Puriss p.a.) which was used to adjust the ionic strength, was carried out by evaporation of known volumes in an oven at 140°C and weighing the resultant anhydrous solid. Grade 'A' glassware was used whenever possible and all solutions were prepared using water obtained from an all-glass still.

Spectrophotometric Measurements

Appropriate dilutions were made using the stock cerium (IV) solution, standard perchloric acid and sodium perchlorate to give solutions of required cerium(IV) concentration, acidity and ionic strength. The solutions to be investigated were immersed in a bath at the required temperature for at least forty five minutes before use. Thermostatting of the bath was achieved as described in chapter 2. All optical density measurements were made with a Unicam S.P. 800D spectrphotometer equipped with a constant temperature cell compartment using a 10mm path-length quartz cell. A blank containing perchloric acid and sodium perchlorate solution appropriate to cerium (IV) solution was used as a reference.

RESULTS and DISCUSSION

In order to check that cerium (IV) stock solutions prepared by two different methods contain only monomeric species, optical density measurements were made with solutions containing differing concentrations of cerium (IV) at constant hydrogen ion concentration and ionic strength, and at various wavelengths. Such experiments have confirmed that cerium (IV) in the concentration range 2.5 - 15 x 10^{-4}M at λ =300 - 400nm strictly obeys Beer's law as illustrated in Figure 11.

The observed extinction coefficient of Ce(IV) calculated at λ = 400nm and $[H^+]$ = 0.20M is 149 $mol^{-1}cm^{-1}$ which is in excellent agreement with extinction coefficient value of 150 $mol^{-1}cm^{-1}$ obtained by Skoog and Offner[79] under the same experimental conditions. However, both these values differ somewhat from Hardwick and Robertson's reported value of 162 $mol^{-1}cm^{-1}$ under the same experimental conditions[77]. There may, however, be some polymeric species present in the solutions studied by these authors. The fact that, like Offner and Skoog[79], one also observed no deviations

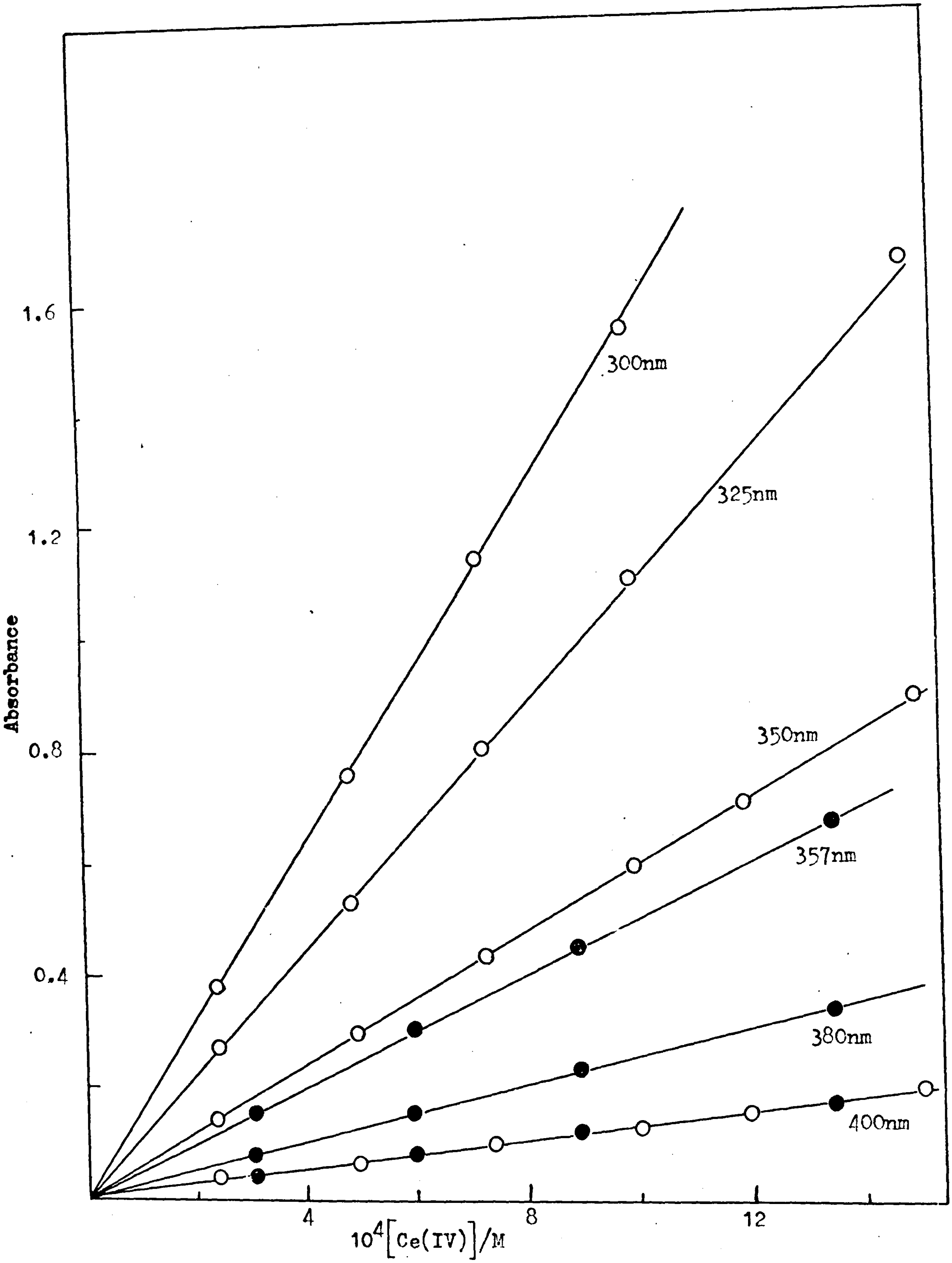


Figure 11 :- Absorbance as a function of cerium(IV) concentrations
(●)cerium(IV) perchlorate (electrolysed) $[H^+]$ = 0.50M,
I = 1.0M.
(○)cerium(IV) ammonium nitrate in perchloric acid,
$[H^+]$ = 0.60M, I = 1.50M.

from Beer's law and good agreement between the extinction coefficient values further substantiates the presence of only monomeric cerium (IV) species in solutions of this concentration range.

The following procedure was adopted to derive an expression relating experimental optical density values to the unknown hydrolysis constant, so that the latter may be calculated from experimental data.

If $[\mathrm{Ce(IV)}]_t$ represents the total cerium (IV) concentration present in solution, the measured optical density of a cerium (IV) solution may be written as

$$\mathrm{OD} = \varepsilon_{\mathrm{Ce}} \left[\mathrm{Ce}^{4+}\right] + \varepsilon_{\mathrm{CeOH}} \left[\mathrm{CeOH}^{3+}\right] \qquad (23)$$

and if no hydrolysis took place, the optical density

$$\mathrm{OD}_o = \varepsilon_{\mathrm{Ce}} \left[\mathrm{Ce(IV)}\right]_t \qquad (24)$$

Introducing the hydrolysis constant K_h

$$\mathrm{Ce}^{4+} + \mathrm{H_2O} \overset{K_h}{\rightleftharpoons} \mathrm{CeOH}^{3+} + \mathrm{H}^+ \qquad (21)$$

yields the expression

$$\mathrm{OD} = \frac{\left[\mathrm{H}^+\right] (\mathrm{OD}_o - \mathrm{OD})}{K_h} + \varepsilon_{\mathrm{CeOH}} \left[\mathrm{Ce(IV)}\right]_t \qquad (25)$$

where OD_o may be calculated from three different experimental optical density values (OD_n) at three differing hydrogen ion concentrations $\left[\mathrm{H}_n^+\right]$ since

$$\mathrm{OD}_o = \frac{\left[\mathrm{H}_1^+\right](\mathrm{OD}_1)(\mathrm{OD}_2 - \mathrm{OD}_3) + \left[\mathrm{H}_2^+\right](\mathrm{OD}_2)(\mathrm{OD}_3 - \mathrm{OD}_1) + \left[\mathrm{H}_3^+\right](\mathrm{OD}_3)(\mathrm{OD}_1 - \mathrm{OD}_2)}{\left[\mathrm{H}_1^+\right](\mathrm{OD}_2 - \mathrm{OD}_3) + \left[\mathrm{H}_2^+\right](\mathrm{OD}_3 - \mathrm{OD}_1) + \left[\mathrm{H}_3^+\right](\mathrm{OD}_1 - \mathrm{OD}_2)} \qquad (26)$$

Table 2 contains the optical density values of eight solutions in the acid range $[H^+]$ = 0.0848 - 0.9328M, and eight differing combinations of (OD_n) and $[H_n^+]$ yielding OD_o values to within ± 1%. A plot of $[H_n^+]$ $(OD_o - OD_n)$ against OD_n gave a straigth line (Figure 12) with a slope K_h^{-1}. This result (K_h = 0.169 ± 0.08M) was used to calculate ε_{Ce} and ε_{CeOH} values at all wavelengths using the following expression

$$OD_n = \varepsilon_{Ce}\left[Ce(IV)\right]_t \frac{[H_n^+]}{([H_n^+] + K_h)} + \frac{K_h}{([H_n^+] + K_h)}\varepsilon_{CeOH}\left[Ce(IV)\right]_t \qquad (27)$$

and these values are collected in Table 3. The spectra of Ce^{4+} and $CeOH^{3+}$ species are thus constructed and shown in Figure 13. Calculations of ε_{Ce} and ε_{CeOH} from data at longer wavelengths (>330nm) give rise to large errors as the difference between the observed extinction coefficient values is extremely small. However, attempts were made to calculate K_h values under the conditions, ($Ce(IV)_t$ = 2.5×10^{-4}M at λ = 357nm), used in kinetic studies (chapter 4) using a Unicam spectrophotometer equipped with expansion scale. Such data showed large errors associated with small optical density changes. Thus Robertson's reported value of the hydrolysis constant (K_h = 5.2M) involving measurements[77] at 400nm are perhaps subject to error from this source. As is obvious from Figure 13, the differences in the values of

TABLE 2

SPECTROPHOTOMETRIC DATA FOR K_h DETERMINATION

Temperature = 20.0°C   Ionic Strength = 1.50M

λ = 300nm $[Ce(IV)]_t = 1.014 \times 10^{-3}$M[a]

Sample	$10[HClO_4]$/M	OD	$[H^+](OD_o - OD)$
1	0.848	1.20	0.0594
2	1.908	1.43	0.0897
3	2.968	1.52	0.113
4	4.028	1.60	0.121
5	5.088	1.64	0.132
6	6.148	1.67	0.141
7	8.268	1.73	0.140
8	9.328	1.74	0.149

a – from stock prepared by dissolving ceric ammonium nitrate in aqueous perchloric acid (0.05071M Ce(IV) in 4.24M $HClO_4$).

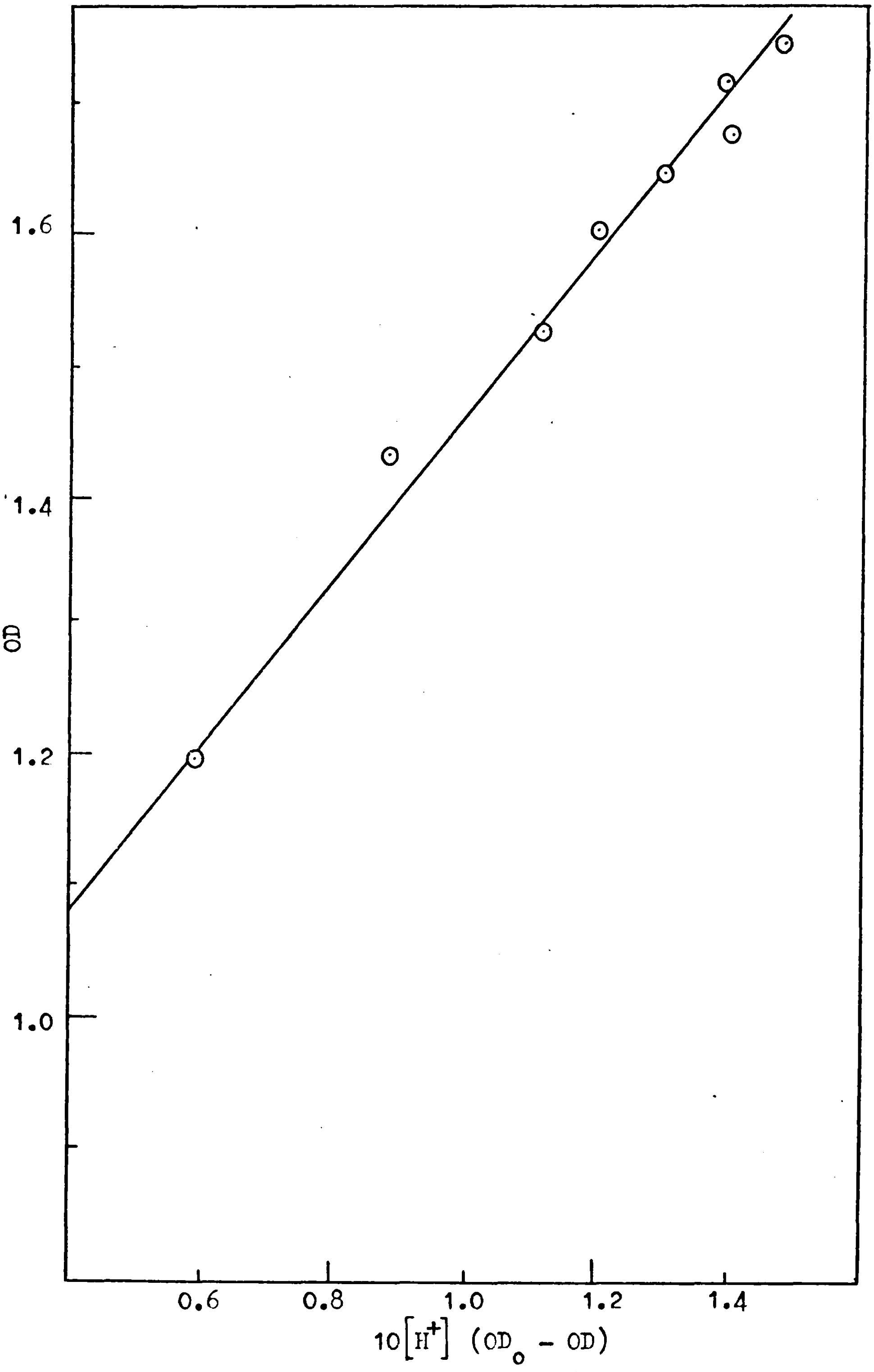


Figure 12 :- Plot of OD against $[H^+]$ $(OD_o - OD)$.

$T = 20.0^\circ C$, $\lambda = 300nm$, $I = 1.50M$,

$[Ce(IV)] = 1.014 \times 10^{-3}M$,

$[H^+] = 0.0848$ —— $0.9328M$

TABLE 3

MOLAR EXTINCTION COEFFICIENTS[a] of Ce^{4+} and $CeOH^{3+}$ [b]

λ(nm)	$10^{-1}\varepsilon_{Ce}$	$10^{-1}\varepsilon_{CeOH}$
260	167[d]	126[d]
270	170	106
280	183	91.9
290	192	84.6
300	187	84.3
305	178 (172)[c]	82.8 (78)[c]
310	169	84.5
320	142	82.8
330	113[e]	74.2[e]
340	86.9	62.1
350	62.4	49.9

a – units are $mol^{-1}\,l\,cm^{-1}$

b – calculated using equation (27)

c – derived from Skoog's data[79]

d – error 2–4%

e – error 5–8%

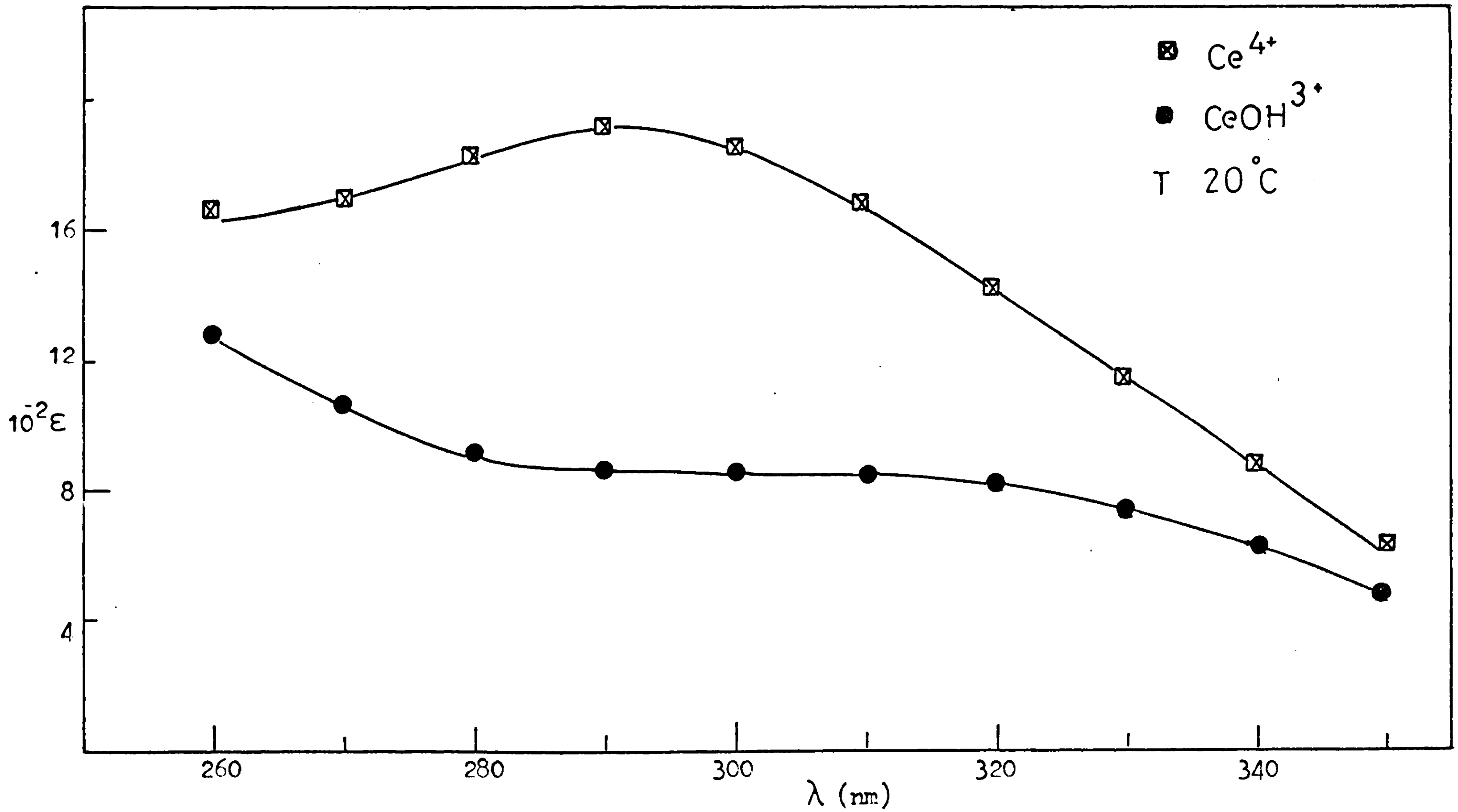


Figure 13 :- Spectra of the species present in cerium(IV) perchlorate solution

$[Ce(IV)] = 1.014 \times 10^{-3}M$, $[H^+] = 0.0848$ —— $0.9328M$, $I = 1.50M$.

ε_{Ce} and ε_{CeOH} at $\lambda = 300$nm used in the present study and also at $\lambda = 305$nm, are large enough to make accurate measurements, thus giving more reliable value of K_h. It may be added that the values of ε_{Ce} and ε_{CeOH} at $\lambda = 305$nm (Table 3) are 17.8×10^2 and 82.8×10 mol^{-1} cm^{-1} respectively, which are in good agreement with ε_{Ce} 17.2×10^2 $mol^{-1}cm^{-1}$ ε_{CeOH} 78×10 $mol^{-1}cm^{-1}$ derived from Skoog's data[79].

Two assumptions have been made in calculating K_h, ε_{Ce} and ε_{CeOH} values. First, only one hydrolysis form of Ce(IV) is considered present, ie. $CeOH^{3+}$. The formation of $Ce(OH)_2^{2+}$ is not excluded, but such an ion, if present, would either exist in small amounts or have a spectrum very similar to that of $CeOH^{3+}$. Second, the ions related by hydrolysis are considered to be Ce^{4+} – $CeOH^{3+}$. This could equally well be $CeOH^{3+}$ – $Ce(OH)_2^{2+}$ as far as mathematical interpretation of the work is concerned. However, with zirconium in 2M $HClO_4$, the average number of hydroxyl ions associated with zirconium is between zero and one[86]; with uranous ion in 2M $HClO_4$, ca. 98% is found to be in the U^{4+} state. From this work one calculates only 90% present as unassociated Ce^{4+} ion in 2M $HClO_4$. It is therefore quite likely that the hydrolysis couple Ce^{4+} – $CeOH^{3+}$ is the one involved. This is further substantiated by the non-linear plot obtained between $\left[H_n^+\right]^2$ $(OD_o - OD_n)$ vs OD_n using the data of Table 2.

Metal ions undergo hydrolysis because co-ordinated water is a stronger acid than free water since the metal-oxygen bond weakens the O-H bond, so that in aqueous systems the free water molecules behave as proton acceptors. The greater strength of metal oxygen bonds will depend largely upon the size and charge of the metal ion. Thus on this basis one can compare the experimental values of K_h with those of similar charged species. Hydrolysis constants of some metal ions are thus collected in Table 4 for comparison. In a series, Na^+, Cd^{2+}, Tl^{3+} and Ce^{4+}, pK_h values decrease with increasing charge on the metal ion (where ionic radii are approximately equal) as predicted. The agreement between the values of K_h obtained in this study with other tetravalent ions is also reasonably good and strongly suggests that previous reported values[77,78] for cerium (IV) are too high.

It must, however, be pointed out that such a comparison is only relative since it suffers two major disadvantages. First, the hydrolysis constants can be compared only with others which have been obtained at the same ionic strength and in the same medium, and unfortunately, different workers use different ionic strength. Second, too little is known about the variation of activity coefficients at constant ionic strength to permit reliable estimates of uncertainties for this source. But this is probably the lesser objection, since if the ions are present in sufficiently small

TABLE 4

HYDROLYSIS DATA FOR METAL IONS

ION	IONIC RADII(Å)	pK_h	T/°C	I/M	REF.
Hf^{4+}	0.81	1.09	25	4.0	a
Th^{4+}	0.95	3.82	25	0	b
U^{4+}	0.97	2.0	25	3.0	87
Ce^{4+}	1.01	-0.72	25	2.1	77
		0.70	25	1.33	79
		0.77(0.77)[c]	20	1.50	this work
Tl^{3+}	0.95	1.14	25	3.0	b
Cd^{2+}	0.99	9.0	25	3.0	b
Na^{+}	0.95	14.6	25	3.0	b

a – B. Noren, Acta.Chem. Scand., 27, 1369 (1973).

b – J.P. Hunt, 'Metal IOns in Aqueous Solution'
W.A. Benjamin, INC., New York, (1963), Chapter 4.

c – derived from Skoog's data[79].

concentrations relative to the background electrolyte, their activity coefficients will be constant within experimental error.

Perhaps one can overcome this problem by extrapolating such data to zero ionic strength where activity coefficients become unity. In practice, however, this approach is not easy. In conclusion it may be said that more data are required (especially at low ionic strength) for a complete understanding of such equilibria.

Chapter 4

CERIUM(IV) OXIDATION IN ACID PERCHLORATE MEDIUM OF

I α -Hydroxy Acids.

II Malonic Acid.

III L - Cysteine and DL - Penicillamine.

INTRODUCTION

During the past few decades the chemistry of cerium(IV) has received considerable attention. Probably the first publication leading to the proposal that cerium(IV) could be used as an analytical reagent in oxidation-reduction reactions was made by Lang[88]. Since then the oxidative properties of this metal ion have proved of considerable value both in volumetric analysis and synthetic organic chemistry. The diversity and complexity of its reactions have been discussed in recent reviews[66,89].

Oxidations of organic compounds by cerium(IV) are generally believed to involve initial transfer of a single electron. Two types of mechanisms can be distinguished depending on the nature of this interaction. In the first mechanism a relatively unstable co-ordination complex is formed between the cerium(IV) and the organic substrate, S, in a rapid preliminary equilibrium step. The intermediate complex then decomposes, unimolecularly, in the rate determining step forming Ce(III) and a free radical, S.

$$\mathrm{Ce(IV)} + \mathrm{S} \overset{K}{\rightleftharpoons} \text{Complex} \xrightarrow{k} \mathrm{Ce(III)} + \mathrm{H^+} + \mathrm{S} \qquad (28)$$

The free radical is further rapidly oxidised by a second molecule of Ce(IV)

$$\mathrm{Ce(IV)} + \mathrm{S} \xrightarrow{\text{fast}} \mathrm{Ce(III)} + \mathrm{H^+} + \text{Product} \qquad (29)$$

The second mechanism assumes that the substrate is oxidised directly by Ce(IV) via a simple bimolecular process. In this case the interaction takes place in the transition state

$$Ce(IV) + S \longrightarrow Ce(IV)......S \longrightarrow Ce(III) + H^{+} + S \quad (30)$$

The participation of intermediate complexes in the reaction mechanism can be evaluated from kinetic data. Duke[90] originally derived the general theory for oxidations involving co-ordination complexes and applied it to the cerium(IV) oxidations[83,91]. Recent developments have been discussed in detail[92] and so only general considerations are necessary here. In particular, it is important to point out that in the presence of large excess of substrate both the co-ordination complex and the direct bimolecular reactions are consistent with pseudo first order behaviour with respect to cerium(IV). However, the dependence of observed first order rate constant on substrate concentration is different for the two alternative mechanisms. The direct bimolecular mechanism (equation 30) predicts a linear relationship between observed rate constant and substrate and the slope of such a plot gives second order rate constant ($k = k_{obs}/[S]$). On the other hand, the co-ordination complex mechanism predicts that a plot of k_{obs} vs $[S]$ will be non linear, concave downward and pass through the origin. At differing substrate concentrations k_{obs} is related to the equilibrium constant for complex formation, K, and the rate constant, k, for the decomposition of complex by the expressions

$$Ce(IV) + S \underset{}{\overset{K}{\rightleftharpoons}} CeS$$

$$CeS \xrightarrow{k} Ce(III) + S + H^+$$

$$k_{obs} = kK[S] / 1 + K[S] \qquad (31)$$

The general features of equation (31) are (a) if $1 \gg K[S]$, then $k_{obs} = kK[S]$. Thus the apparent second order rate constant will be a composite term, kK, which cannot be distinguished from the second order rate constant, k ; (b) if $K[S] \gg 1$, equation (31) then predicts zero order dependence of rate on [S] and (c) if $K[S] \approx 1$, then a plot of k_{obs}^{-1} vs $[S]^{-1}$ should be linear with a positive intercept. From the values of the slope and intercept of such a reciprocal plot the equilibrium constant, K, and rate constant, k, can be calculated. The detection of such intermediate species does not in itself prove that these entities play a direct role in the redox process. This kinetic ambiguity has been discussed in chapter 1.

Although there are analytical difficulties associated with the spectroscopic study of such complexes, it is possible in many cases to calculate the equilibrium constant, K, from spectrophotometric measurements. Thus the comparison between K_{kin} and K_{spect} can be made and, as will be shown later, such a comparison is generally good.

a) Reactions with Organic Substrates Exhibiting a Second-Order Rate Law

During the last decade or so a large number of papers have appeared on the cerium(IV) oxidation of a variety of organic substrates in sulphuric acid. The primary products of such reactions are radicals which subsequently are oxidised to the stable isolable products. For example, cyclohexanol is oxidised to cyclohaxanone[93]. Polyhydric alcohols also undergo simple oxidations, pinacol[94] being quantitatively cleaved to acetone and glucose phenylostriazole[95] being oxidised to 2 - phenyl -1,2,3 - triazole-4 - carboxylic acid. The last two reactions are used as analytical methods for these alcohols.

Formaldehyde, as expected, requires two moles of cerium(IV) for oxidation to formic acid[96]. In addition, the rate is third-order in $\left[H_2SO_4\right]$, suggesting that the sulphate complexes of cerium(IV) are the oxidising species. It has also been suggested that when a high sulphate to cerium(IV) ratio is used, oxidations by cerium(IV) species with fewer than four sulphate ions are apparently unimportant[96].

Not all oxidations of cerium(IV) are as easily interpreted as the above examples and stoicheiometric studies indicate that in many cases several reactions occur concurrently, e.g. one mole of acetone requires 8.6 equivalents of cerium(IV) sulphate[97], and 1.4 moles of formic acid are produced. To account for this observation it has been suggested that 60% of the reaction proceeds via the reaction

$$CH_3COCH_3 \xrightarrow{2\ Ce(IV)} CH_3CO\ CH_2OH \xrightarrow{2\ Ce(IV)} CH_3COCHO \longrightarrow$$

$$\xrightarrow{2\ Ce(IV)} CH_3CO_2H + HCO_2H \qquad (32a)$$

and the remaining 40% by

$$CH_3COCH_3 \xrightarrow{2\ Ce(IV)} CH_3COCH_2OH \xrightarrow{8\ Ce(IV)} 2\ HCO_2H + CO_2 \qquad (32b)$$

Higher molecular weight ketones are extensively degraded. one mole of methyl n-amyl ketone consuming 18.2 equivalents of cerium(IV) sulphate[98], to produce 1.75 moles of formic acid, while isobutyraldehyde gives α- hydroxyisobutyraldehyde, isobutyric acid and acetone as products[99].

The oxidation of α - hydroxy acids has been the subject of a number of studies. Earlier investigations of the cerium(IV) oxidations of glycollic[100], malic[101], lactic[101] and mandelic acids[102] in sulphate media indicated a first order dependence on both cerium(IV) and organic substrates. Thus cerium(IV)–carboxylic acid complexes are not present in detectable concentrations. While the oxidation of mandelic acid requires only two equivalents of cerium(IV)being oxidised to benzaldehyde, glycollic, malic and lactic acids require 4.0, 8.5 and 7.5 equivalents of cerium(IV), respectively, to produce mixtures of carbon dioxide, formic acid and acetic acid. Although it was thought the mechanism for the oxidation of these α-hydroxy acids involved oxygen–hydrogen bond rupture, it has been shown[103] by kinetic isotopic studies that the hydrogen is lost from the carbon atom adjacent to this oxygen. The instability of the radical formed and the absence of a site on the molecule where delocalised radical formation is preferred presumably lead to complex stoicheiometrics observed in the above reactions.

In another reported investigation[104] on the oxidation of malic acid by cerium(IV) sulphate, C – C bond rupture was postulated to be rate determining. The measured stoicheiometry was consistent with the overall organic product being formic acid. In a further study[105] on the reactions of glycollic, lactic, methyl lactic and mandelic acids by cerium(IV) sulphate it was shown that two equivalents of cerium(IV) are consumed in each case with the formation of formaldehyde, acetyldehyde, acetone and benzaldehyde, respectively. Again C – C bond fission was considered important.

The oxidation of sulphur containing systems has been investigated in sulphate media using fast reaction techniques[106,107]. Where the substrate is either an α – mercapto carboxylic acid or a thiourea the kinetics are shown to be strictly second order with no evidence for complex formation, and in both cases the thermodynamic parameters are fairly similar. The reaction rates are substantially slower than for the corresponding oxygen analogues.

The greater stability of the sulphur containing radicals is demonstrated by the fact that in all cases in large excess of substrate, disulphides are formed as reaction products. In the oxygen analogues, however, delocalisation of the electron takes place and the radical may now interact with another cerium(IV) molecule with subsequent rapid decomposition of the intermediate involving decarboxylation and the formation of either a lower aldehyde or its corresponding acid.

b) Reactions with Organic Substrates Occurring via Transient Complexes

Metal ion complexes formed as intermediate during oxidation of organic substrates by metal ions have now been well characterised. Unlike the comparable reactions in sulphate media which are generally slower, and where there may be competition between the sulphate ions and other ligands for positions in the primary co-ordination sphere of the metal ion, in the presence of perchlorate ions it should be possible to identify any intermediate complexes in solution and so substantiate an inner-sphere mechanism.

The appearance of a red-shift in the visible spectrum on the addition of ethanol to a cerium(IV) solution, which is indicative of complex formation, has long been known as a colourimetric test for ethanol[108,109]. Recent kinetic studies on a variety of monofunctional alcohols with cerium(IV) perchlorate have confirmed the presence of such transient complexes[80,110,111,112,113]. Aldehydes and ketones are the final products which are quite resistant to further oxidation. Although in the oxidation of benzyl alcohol[80] by cerium(IV) perchlorate, spectrophotometric evidence indicates complex formation the overall reaction is simple bimolecular suggesting that the equilibrium constant is very small.

The formation of such transient complexes is not restricted to monofunctional alcohols where 1 : 1 complex species have been assumed; complexes of higher composition have been suggested in the oxidation of polyfunctional alcohols. For example, with cerium(IV) perchlorate kinetic evidence indicates that both glycerol[114] and 2,3-butanediol[83] are oxidised via complex formation. The glycerol complexes have also been identified spectrophotometrically and a 1 : 2 complex has been postulated at high alcohol concentration[114]. Increasing the hydrogen ion concentration increases the equilibrium constant for Ce(IV) - 2,3-butanediol complex formation, which also indicates that the complex formed is between Ce^{4+} and 2,3-butanediol, rather than with the metal hydroxocation[83]. A similar result is also observed in the cerium(IV) perchlorate oxidation of glycerol[114] as well as of monofunctional alcohols[80,110-113]. Unlike the corresponding reaction in sulphate media the oxidation of 2,3-butanediol by cerium(IV) nitrate has been shown to proceed through complex formation[91], thus confirming the greater thermodynamic stability of cerium(IV)-sulphate complexes.

The oxidation kinetics of isopropanol[110], sec-butanol[111], and cyclohexanol[111] by cerium(IV) perchlorate have recently been studied in more detail. Unlike previous studies, the increase in rate with increasing $[H^+]$ has been interpreted in terms of the proton equilibria between $CeR_1R_2COH^{4+}$ and $CeR_1R_2CO^{3+}$. Furthermore, the latter species has been shown to be formed not by the interaction of $CeOH^{3+}$ and R_1R_2CHOH, but from the deprotonation of $CeR_1R_2CHOH^{4+}$.

The oxidation of formic acid in perchloric acid media has been investigated spectrophotometrically[115], the reaction being so slow that it was not followed to completion. There is, however, evidence for an inner-sphere reaction, in that in the presence of increasing concentrations of formic acid the optical density increases progressively, the effect being confirmed by extrapolation of the plots to zero time. The rate of disappearance of the oxidant is first order, the pseudo first order rate constant increases with $[HCO_2H]$ to a value independent of substrate concentration. In this region the rate constant is dependent on perchloric acid concentration. On the basis of these observations, it is considered that both $CeHCOOH^{4+}$ and $Ce\ HCOO^{3+}$ complexes are formed with only the latter acting as an oxidising agent. A similar mechanism has also been suggested in the cerium(IV) oxidation of acetic acid and substituted acetic acid[81].

I Interaction of Cerium(IV) with α-Hydroxy Acids in Acid Perchlorate Media

From the above discussion it is evident that extensive kinetic data on the cerium(IV) oxidation of α-hydroxy acids have so far been accumulated in sulphate media. There are very few results reported on these systems in perchlorate acid solutions, where extensive complexation occurs and it is of interest to investigate these reactions in order to compare reaction products, rate parameters, and equilibrium constants with those previously reported.

The α-hydroxy acids chosen for this study were glycollic, lactic, methyl lactic, mandelic and malic acids, details of which are given in Table 5.

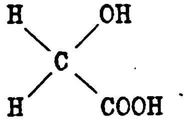
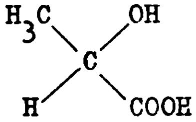
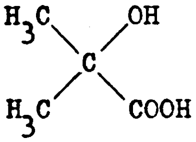
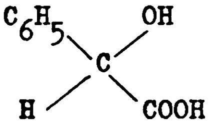
EXPERIMENTAL

Materials:

Stock solutions of cerium(IV) perchlorate, sodium perchlorate and perchloric acid were prepared and standardised as described in chapter 3. Mixtures of sodium/lithium perchlorate and perchloric acid were used to maintain a constant ionic strength of 1.50M at varying hydrogen ion concentrations.

TABLE 5

STRUCTURES AND IONISATION CONSTANTS[a] OF α-HYDROXY ACIDS, $T=25^{\circ}C$

α-Hydroxy Acid	Structure	$K_a 10^5$/M
Glycollic		15
Lactic		14
Methyl Lactic		10.6
Mandelic		43

a – Dictionary of Organic Compounds. Eyre and Spottiswoode, London. (1965).

Lithium perchlorate was prepared by slow addition of anhydrous lithium carbonate (Hopkin and Williams, Reagent Grade) to AnalaR concentrated perchloric acid at 80°C. The pH was then adjusted to pH 5.5 by addition of necessary quantity of either of the reagents. The hot solution was then filtered and cooled slowly and finally allowed to stand at 0°C. The isolated solid product was recrystallised three times from distilled water. Appropriate chemical tests demonstrated the absence of chloride or sulphate ions. Stock solutions of lithium perchlorate were standardised either by the same procedure as that for sodium perchlorate or by titration, with standard base, of the eluent of a cation exchange column in the hydrogen-ion form which had been charged with a known volume of a stock solution. Both methods yielded identical results.

Glycollic acid (Hopkin and Williams, AnalaR) and methyl lactic acid (Eastman Organic Chemicals, Reagent Grade) were twice recrystallised from hot methanol-water mixture (1 : 1), dried under vacuum and analysed (C and H, University of Glasgow Analytical Services)

	Found	Literature
Glycollic acid	C = 31.8%	C = 31.6%
	H = 5.26%	H = 5.26%
Methyl lactic acid	C = 46.3%	C = 46.1%
	H = 7.75%	H = 7.68%

Lactic acid (B.D.H. Poole, AnalaR), malic acid and mandelic acids (B.D.H. Poole, Reagent Grade) were used without further purification. Sodium nitrate (Hopkin and Williams, AnalaR) and cerium(III) nitrate (B.D.H. Poole, Reagent Grade) were used as provided. All solutions were prepared with water obtained from an all-glass still.

Stoicheiometric Measurements

The oxidation of malic acid by cerium(IV) yielded exclusively formic acid. Under the experimental conditions ie. $[Ce(IV)] = 3.2 \times 10^{-4}$ moles and $[\text{malic acid}] = 3.93 \times 10^{-3}$ moles in $\backsim$ 0.2M $HClO_4$, formic acid was quantitatively determined[116] by further oxidation to carbon dioxide in the presence of Hg(II) chloride, the Hg(I) chloride formed being the evaluated using an iodine-thiosulphate titration.

The oxidation of glycollic, lactic, methyl lactic, and mandelic acids by cerium(IV) in perchloric acid afforded formaldehyde, acetaldehyde, acetone, and benzaldehyde respectively, as the main oxidation products. The aldehydes and acetone were converted to their respective hydrazones[117] by adding a slight excess of saturated solution of 2,4 dinitrophenylhydrazine in 2N HCl, to the reacted solutions. Typical reactants concentrations employed were: $Ce(IV) = 2.34 \times 10^{-4}$ moles and 2.4×10^{-3} moles of α-hydroxy acid in ~0.4M $HClO_4$. No interference in the above reaction was observed from either cerium(III) or the unreacted α-hydroxy acid.

Kinetic Measurements

Kinetic studies were made under conditions of excess of substrate on both the 'fast' and 'slow' stopped-flow apparatus, described in chapter 2. In a typical kinetic experiment, the cerium(IV) solution was prepared immediately prior to kinetic measurements being made. Comparison of optical density of blank solutions at $\lambda = 357$nm, in which cerium(IV) was rapidly diluted with acid perchlorate solution, with those where α-hydroxy acid was present, indicated formation of a complex within the time of mixing and the subsequent redox reactions were monitored at the same wavelength. The $[H^+]$ range employed was 0.25 - 1.50M at total ionic strength of 1.50M. The temperature was varied between 6.4 - 30.1°C. The presence of sufficient excess of reductant ensured pseudo first order reaction conditions. For each kinetic experiment reactant solutions were allowed to equilibrate at the appropriate temperature for at least thirty minutes before any rate measurements were made. From the photographs of the oscilloscope traces the decrease in optical density as a function of time was calculated using a Nova 1200 Computer. Each kinetic run was repeated at least three times, with replicate measurements usually agreeing to ± 2%.

RESULTS AND DISCUSSION

(a) Stoicheiometry

Differing values for the stoicheiometry of reactions of cerium(IV) with malic acid were derived in sulphate media[101,104], possibly as a result of the presence of excess of oxidant in the determinations made previously. In order to overcome this problem it was considered desirable to measure the stoicheiometry of this reaction under conditions related directly to the kinetic data.

The determination of formic acid was found to be quantitative only in buffered solutions and small corrections were made using blank comparisons in the presence of malic acid. Four determinations gave a stoicheiometry of 9.5 ± .2 moles of cerium(IV) reacting per mole of reductant, consistent with (33),

$$10\ \mathrm{Ce(IV)} + \mathrm{HOOC.CH_2.CH(OH)\ COOH} \xrightarrow{H_2O} 10\ \mathrm{Ce(III)} + 10\mathrm{H^+} + \mathrm{HCOOH} + 3\mathrm{CO_2} \qquad (33)$$

The stoicheiometric measurements in the reactions involving cerium(IV) and glycollic, lactic, methyl lactic, and mandelic acids established that in each case two moles of cerium(IV) reacted with one mole of α-hydroxy acid. Thus the overall reaction may be written as

$$RR'C(OH)COOH + 2\ Ce(IV) \longrightarrow RR'CO + 2\ Ce(III) + 2H^+ + CO_2 \qquad (34)$$

where $R' = H-$, CH_3- , and $R = H-$, CH_3-, C_6H_5-.

Elemental analyses of respective hydrazones are given in Table 6.

Since previous stoicheiometric measurements[100-102,105], unlike the present, were made in sulphate media and in the presence of an excess of oxidant, the discrepency observed in these values could possibly be explained on the basis of over oxidation of reaction products, i.e. aldehyde or ketone. It is unlikely, although possible, that the reaction medium is responsible for such an ambiguity.

(b) Nature of Reactant Species

From the discussion in the last chapter the only cerium(IV) species present in perchlorate media are Ce^{4+} and $CeOH^{3+}$.

Using the K_a values (Table 5) it is possible to calculate the concentrations of undissociated acid present

TABLE 6

ELEMENTAL ANALYSIS OF 2,4-DINITROPHENYLHYDRAZONES

Product	Found(%)	Literature(%)	M.P./°C
formaldehyde	C = 39.7 H = 2.88	C = 40.0 H = 2.86	165 (166)[a]
acetaldehyde	C = 42.5 H = 3.50	C = 42.8 H = 3.57	158 (157)[a]
acetone	C = 45.6 H = 4.25	C = 45.4 H = 4.20	128 (128)[a]

(a) - literature value.

at various hydrogen ion concentrations. Such calculations indicate that under the experimental conditions used, the undissociated acid is the major species and the contribution of hydrogen ion produced from such equilibria to the total hydrogen concentration employed, is also negligible.

(c) Formation of the Intermediate Species

i) Spectra

No absorbance changes were detected when solutions of cerium(IV) were mixed under typical reaction conditions with 'blank' solutions containing no α-hydroxy acid. Superimposition of an oscilloscope trace from such an experiment on one obtained from a normal run showed the initial optical density, OD_1 of the latter trace (when extrapolated to t = 0 sec.) to be greater than that of cerium(IV). A typical example is illustrated in Figure 14. If OD_2 is the optical density value in the presence of substrate, then $(OD_2 - OD_1)$ defined as ΔOD, represents a measure of the extent of formation of intermediate species. Using the method described in chapter 2, OD_2 and OD_1 can easily be calculated from the stopped-flow traces. From ΔOD values at suitable wavelengths under normal reaction conditions it was possible to compile the spectra

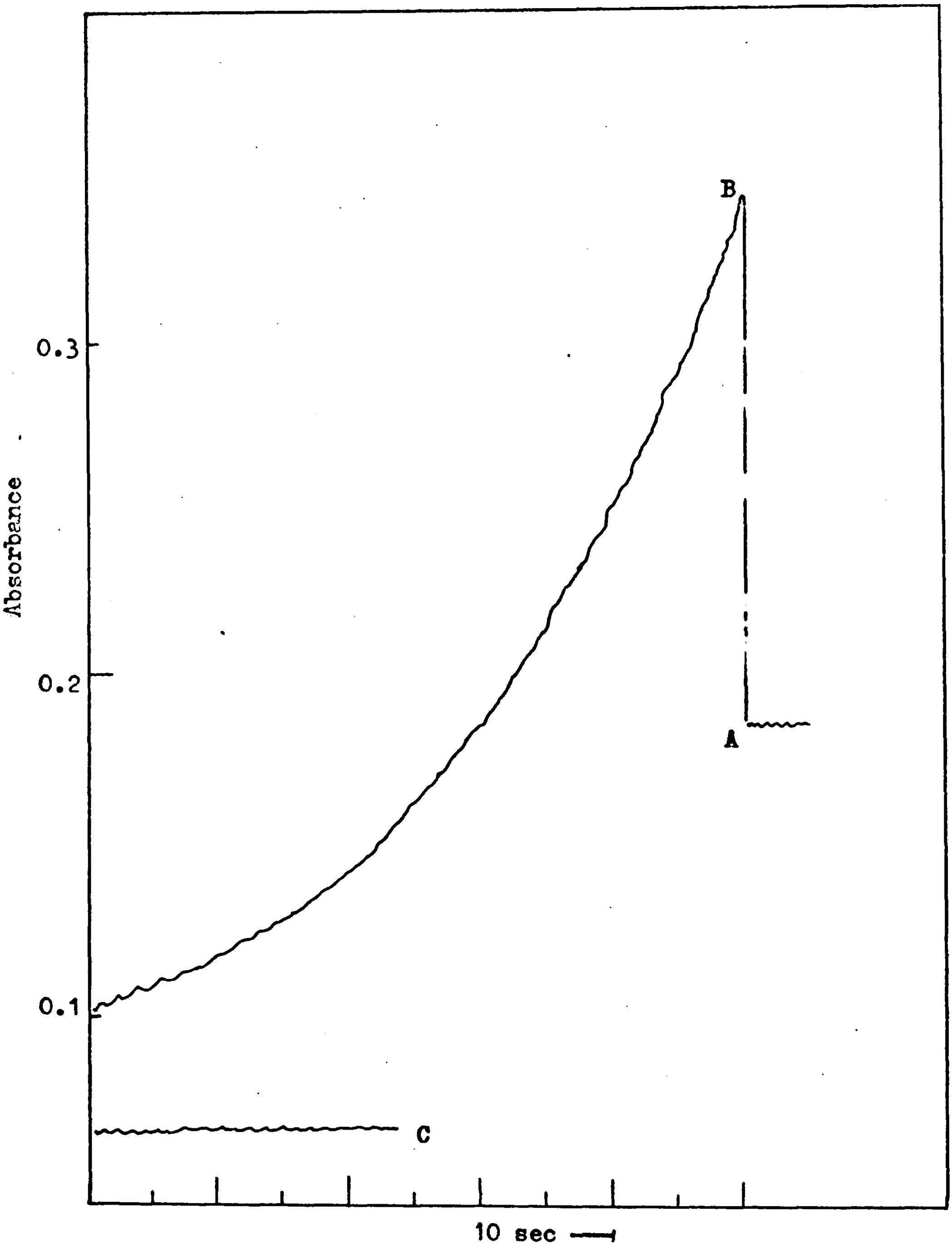


Figure 14 :- Typical 'slow' stopped - flow trace

Cerium(IV) absorbance changes in time,
$[\mathrm{Ce(IV)}] = 2.5 \times 10^{-4}$M (A);
Ce(IV) + glycollic acid (1.316×10^{-2}M) (B);
at the end of reaction (C), at $\lambda = 28{,}000\,\mathrm{cm}^{-1}$,
$[\mathrm{H}^+] = 0.30$M, I = 1.50M and T = 11.4°C.

of the red-brown species. λ_{max} were found to be between 355 - 360nm as shown in Figure 15, and collected in Table 7. Previous kinetic studies on the oxidation of these α-hydroxy acids in sulphate media[100-102,104-105,118] indicated an absence of such transient complexes. Spectrophotometric measurements[118] were, however, atte,pted in perchloric acid media and bands were observed between 245 - 255 nm, which might correspond to second absorption maximum. Such measurements at longer wavelengths were not possible in these studies[118] because of very low reactant concentrations which were employed to slow down the redox reactions. In another investigation λ_{max} = 405 nm has been reported for the intermediate[80] formed in the oxidation of monofunctional alcohols by cerium(IV) perchlorate. However, the position of the maximum (Table 7) observed in the present studies seems to be markedly different from this value and this may be due to chelate formation. In fact, these workers[80] have unambiguously assigned the shoulder observed in the spectrum of complex to λ_{max} and did not attempt any measurement below 370 nm. When the spectrum of Ce(IV) - Ethanol complex was run, a peak ~ 360 - 370 nm resembling very much that with Ce(IV) -α- hydroxy acid complex (Figure 15), was observed. These spectra, however, are markedly different from those observed in the spectrophotometric studies of

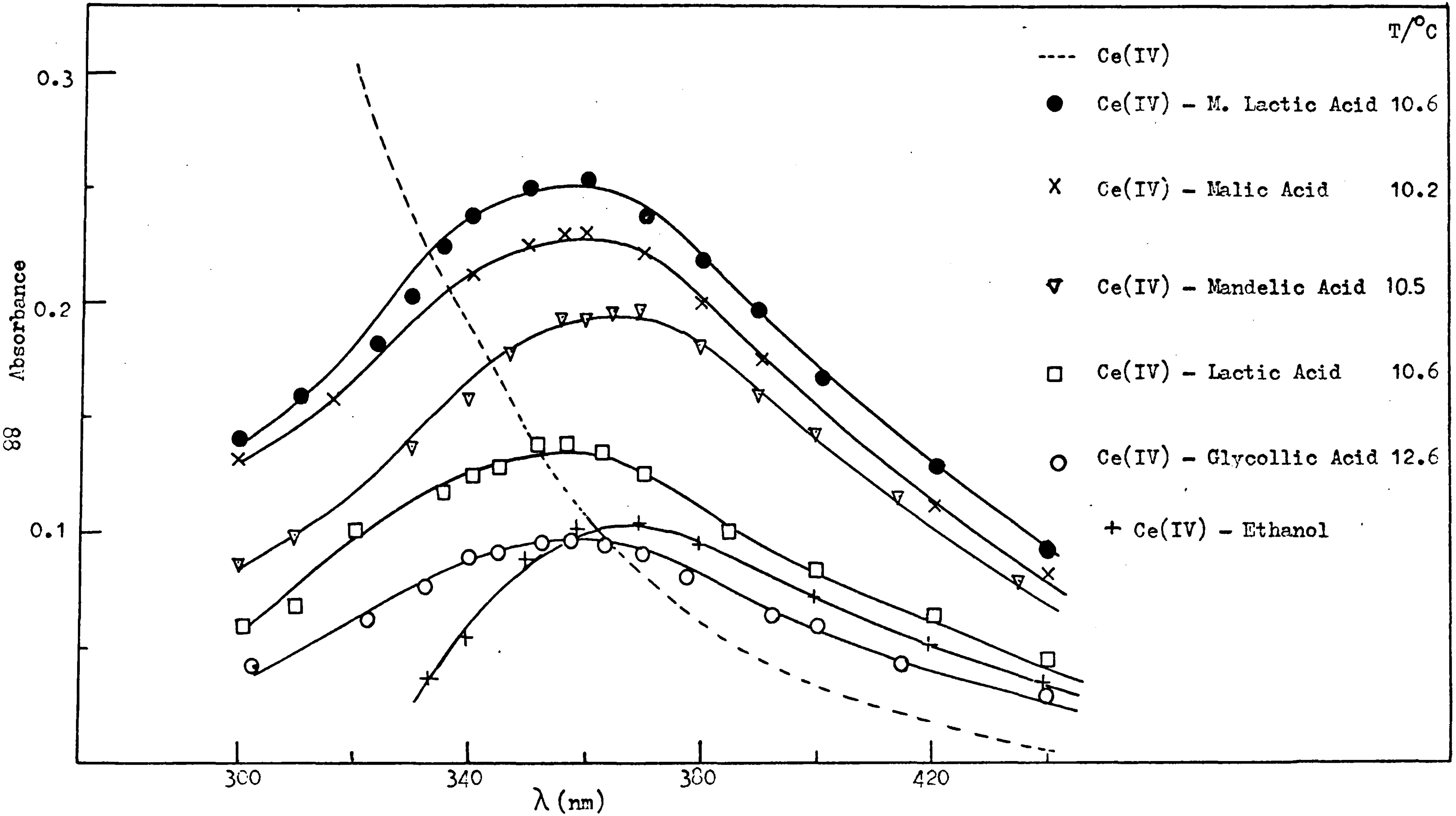


Figure 15 :- Spectra of cerium(IV) – α-hydroxy acid intermediate complexes.

$10^2[HL]/M$, $[H^+]/M$; (●) 1.01, 0.605; (X) 0.99, 0.728; (▽) 0.55, 1.08
(□) 1.03, 0.862; (○) 1.08, 0.60; (+) 20, 1.0.

TABLE 7

PARAMETERS$^{(a)}$ RELATING TO INTERMEDIATE COMPLEXES FORMED IN THE COURSE OF THE REDUCTION OF Ce(IV) BY α-HYDROXY ACIDS AT 1.50M IONIC STRENGTH AND IN AQUEOUS PERCHLORIC ACID MEDIA

α-Hydroxy Acid	T/°C	$K_1^{(b)}$	K_2K_h	$10^3\ {}_{CeHL}^{(c)}$	$10^3\ {}_{CeL}^{(c)}$	λ_{max}/nm
Glycollic	11.4	33±5	40±6	2.12	2.05	
	17.6	25±6	30±5	2.51	1.69	
	25.2	22±5	25±6	2.47	1.93	
	30.1	23±4	18±4	2.81	1.77	
						355-358
Lactic	10.0	31±5	70±10	2.15	1.52	
	20.0	25±6	55±7	2.57	1.41	
	25.0	15±4	40±6	2.75	1.72	
	30.0	21±7	23±9	2.49	1.29	
						357
Methyl Lactic	11.3	52±15	205±28	1.52	1.92	
	16.1	90±20	170±22	1.91	1.44	
	20.7	77±21	145±20	1.77	1.85	
	25.0	40±12	110±18	2.11	1.62	
						356
Malic	10.6	50±30	175±25	2.41	2.12	
	16.0	35±15	220±15	2.25	1.79	
	20.0	25±10	200±20	2.57	1.88	
	25.0	16±10	145±25	2.32	2.22	
						355

(a) - calculated using equation (39)

(b) - units of M^{-1}

(c) - units of $M^{-1}cm^{-1}$

formic, acetic and malonic acids (Figure 40 in Section II).

ii) Extinction Coefficients and Equilibrium Constants

Using the scheme (HL = α-hydroxy acid) in reactions (21), (35)-(37)

$$Ce^{4+} + H_2O \xrightleftharpoons{K_h} CeOH^{3+} + H^+ \qquad (21)$$

$$Ce^{4+} + HL \xrightleftharpoons{K_1} CeHL^{4+} \qquad (35)$$

$$CeOH^{3+} + HL \xrightleftharpoons{K_2} CeL^{3+} + H_2O \qquad (36)$$

$$CeHL^{4+} \xrightleftharpoons{K_3} CeL^{3+} + H^+ \qquad (37)$$

the observed extinction coefficients, ε'_{obs}, of a solution containing cerium(IV) and α-hydroxy acid may be written as

$$\varepsilon'_{obs} = \frac{\varepsilon_{Ce} + \varepsilon_{CeOH}\frac{K_h}{[H^+]} + \varepsilon_{CeHL}K_1[HL] + \varepsilon_{CeL}\frac{K_2K_h[HL]}{[H^+]}}{1 + \frac{K_h}{[H^+]} + K_1[HL] + \frac{K_2K_h[HL]}{[H^+]}} \qquad (38)$$

This equation may be rearranged to give equation (39)

$$\alpha[HL]^{-1} = \varepsilon'_{obs}(K_1[H^+] + K_2K_h) - (\varepsilon_{CeHL}K_1[H^+] + \varepsilon_{CeL}K_2K_h) \qquad (39)$$

where $\alpha = \varepsilon_{Ce}[H^+] + \varepsilon_{CeOH}K_h - \varepsilon'_{obs}([H^+] + K_h)$.

At the wavelength used for the kinetic measurements (357nm),

$\varepsilon_{Ce} \backsim \varepsilon_{CeOH}$ and, from a knowledge of K_h, α can be calculated. Plots of $\alpha\,[HL]^{-1}$ against ε'_{obs} at fixed $[H^+]$ were linear with positive gradients (G) and negative intercepts (I). The data at 25°C and 20.7°C for lactic and methyl lactic acids, and at 30°C, 10.6°C for glycollic and malic acid respectively, derived from initial optical density changes are shown in Figures 16 - 19 respectively. Similar plots were also obtained at other temperatures. From equation (39) it may be seen that $G = K_1\,[H^+] + K_2K_h$ and $I = -(\varepsilon_{CcHL}\,K_1\,[H^+] + \varepsilon_{CeL}\,K_2K_h)$, so that plots of G against $[H^+]$ and I against $[H^+]$ yield K_1, K_2K_h, $\varepsilon_{CeHL}\,K_1$, and $\varepsilon_{CeL}\,K_2K_h$ from which the extinction coefficients of the complexes may be calculated. Typical plots of G and I against $[H^+]$ for glycollic, lactic, methyl lactic and malic acids are shown in Figures 20 and 21. The equilibrium constants and extinction coefficients are collected in Table 7. Consideration of values will be left until after discussion of kinetic data.

(d) Kinetics and Mechanism

First order plots of $\ln(A_t - A_\infty)$ vs time, where A_t and A_∞ are measured optical densities at times t and after several half-lives, respectively, were linear for at least 85 - 90% reaction in the presence of a ten fold or

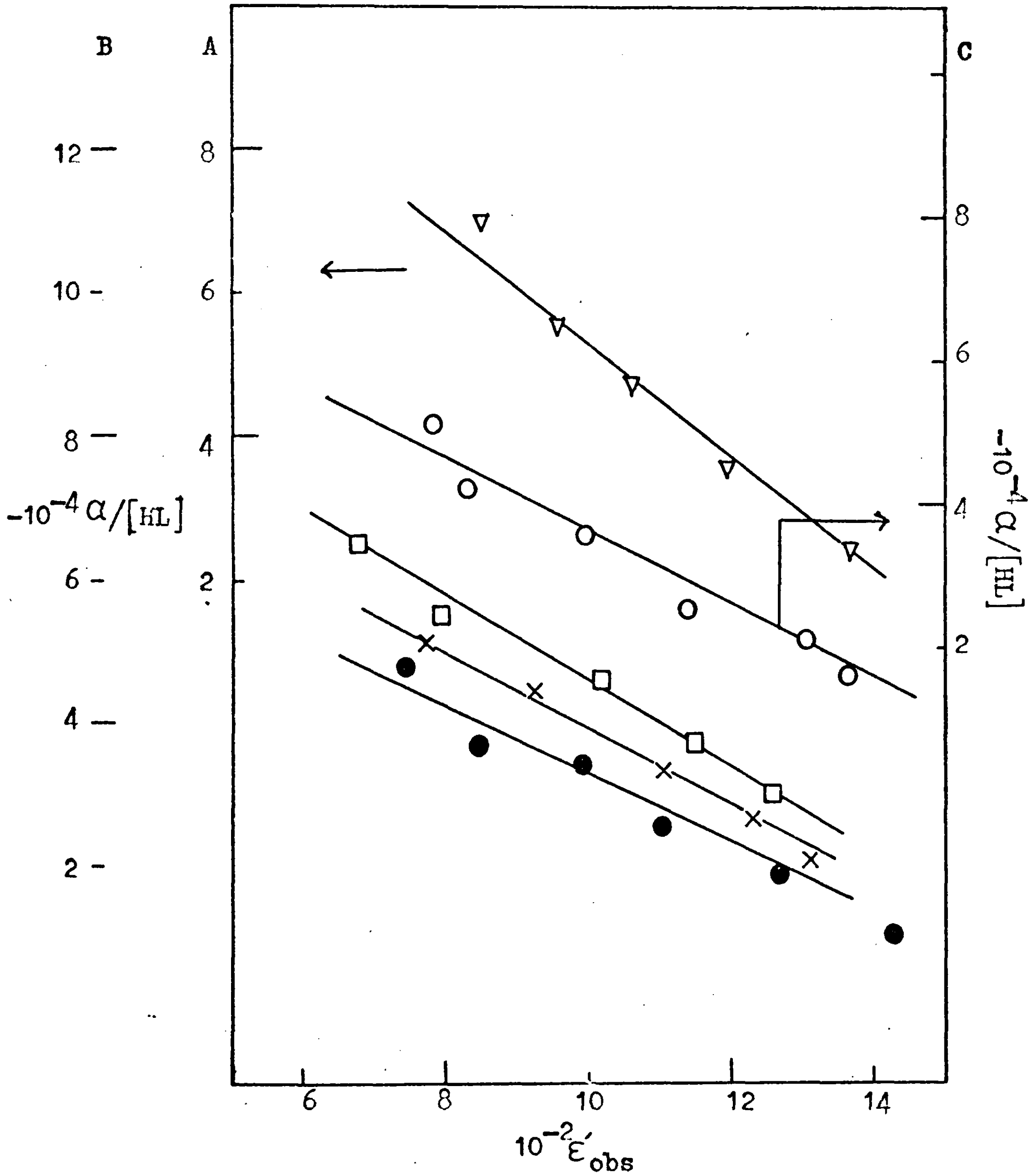


Figure 16 :- Plots of $\alpha/[HL]$ against $\acute{\varepsilon}_{obs}$ (equation 39) for lactic acid.

$[H^+]$ = (∇) 1.50M (scale A); (□) 1.25, (X) 0.75, (●) 0.25 (scale B); (O) 0.50M (scale C)
T = 25°C, λ = 357nm, I = 1.50M.

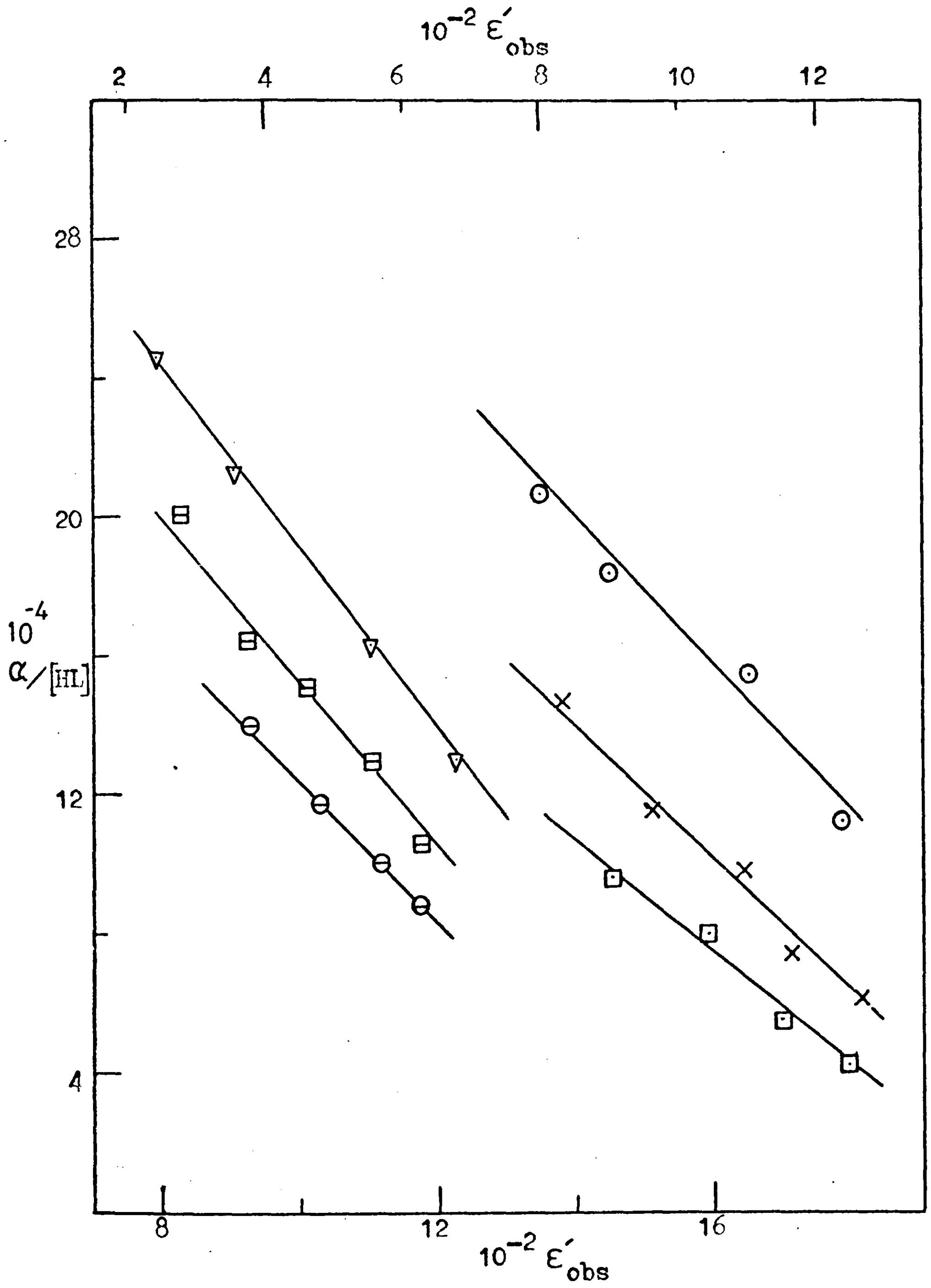


Figure 17 :- Plots of $\alpha/[HL]$ against ε'_{obs} (equation 39) for methyl lactic acid.

$[H^+]/M$ = (▽) 1.25, (⊟) 1.0, (⊖) 0.50 lower scale;
(O) 1.50, (X) 0.75, (□) 0.35,
T = 20.7°C, I = 1.50M, λ = 357nm.

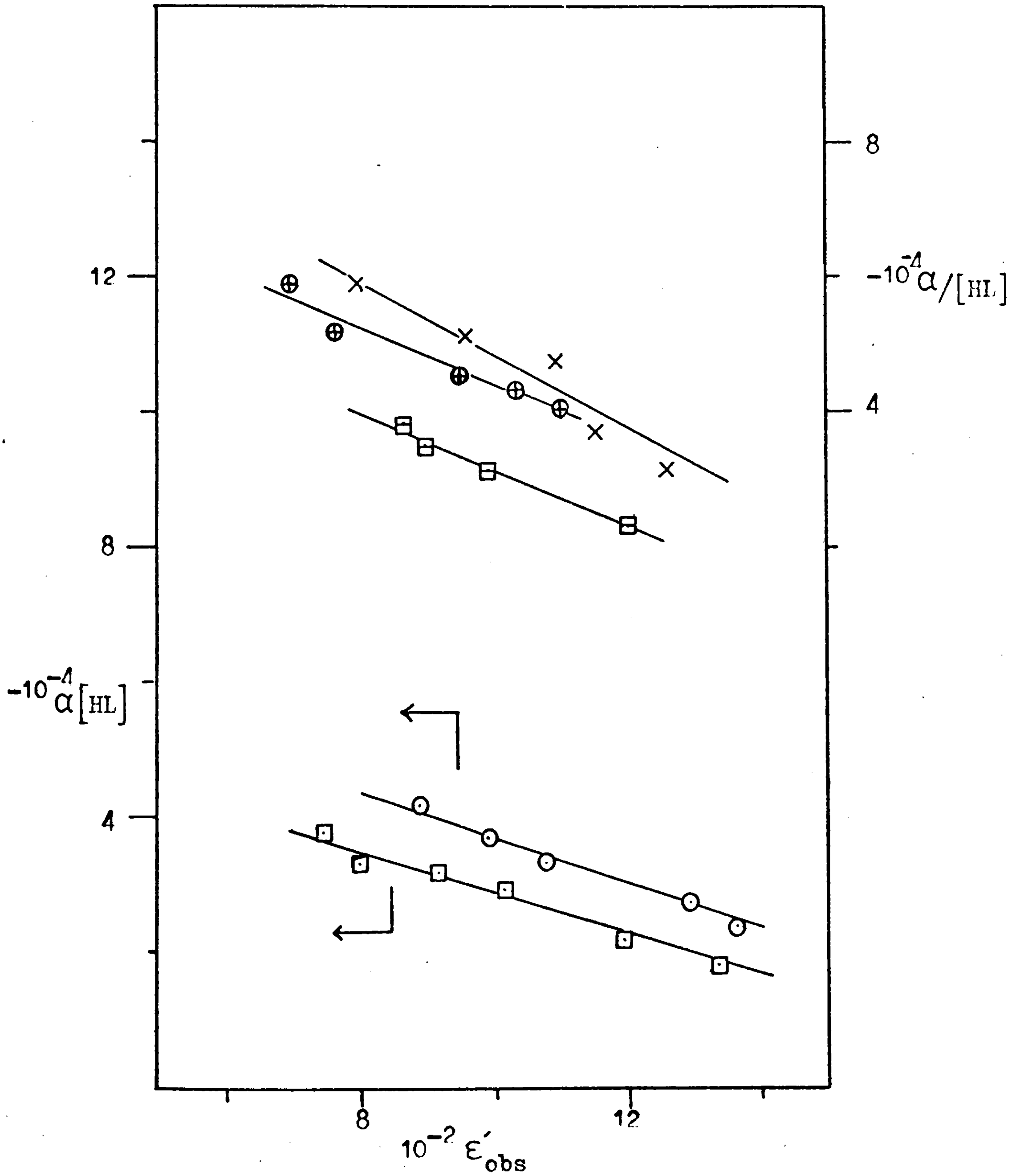


Figure 18:- Plots of $\alpha/[HL]$ against ε'_{obs} (equation 39) for glycollic acid.
at T = 30.1°C, I = 1.50M, $[H^{+}]/M$ = (⊙)0.75, (⊡) 0.35, (⊟) 0.60M, (X) 1.25, (⊕) 1.0.

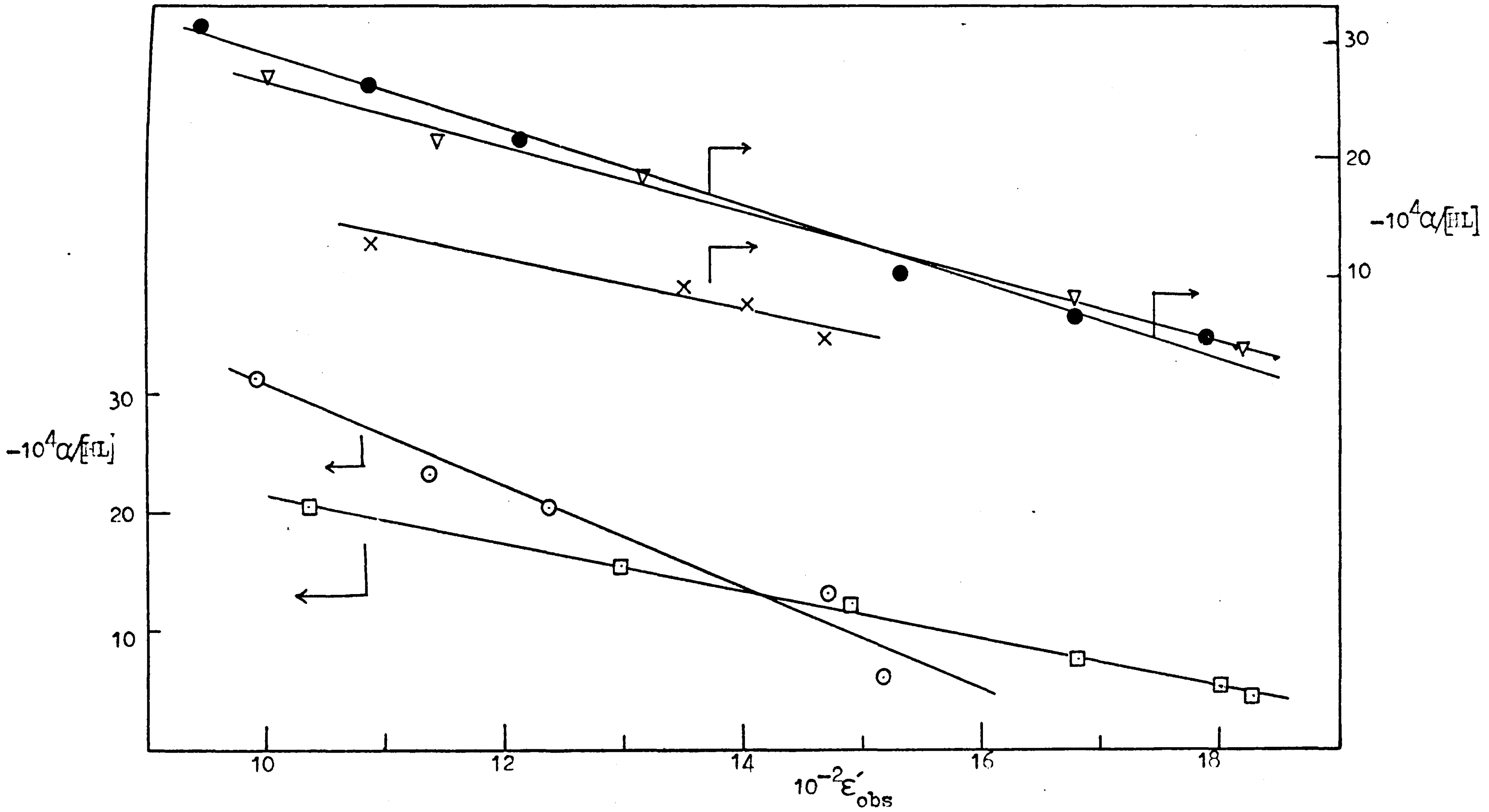


Figure 19 :- Plots of $\alpha/[HL]$ versus ε'_{obs} for malic acid
$[H^+]/M$ = (□) 0.50, (O) 1.45, (X) 0.25, (●) 1.0, (▽) 0.75
T = 10.6°C, I = 1.50M.

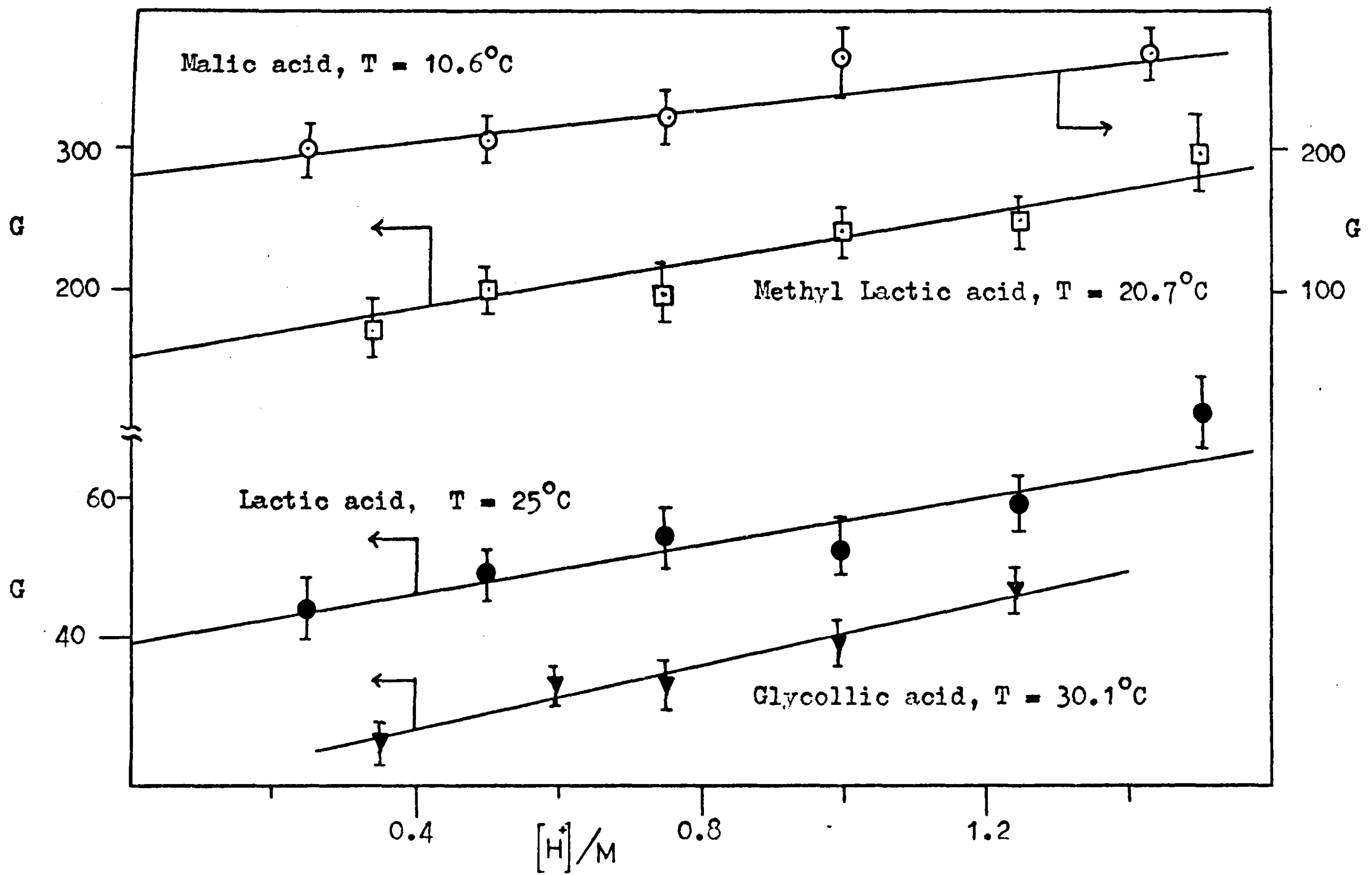


Figure 20 :- Plots of gradients, G, (Figures 16 – 19), against $[H^+]$ for α-hydroxy acids.

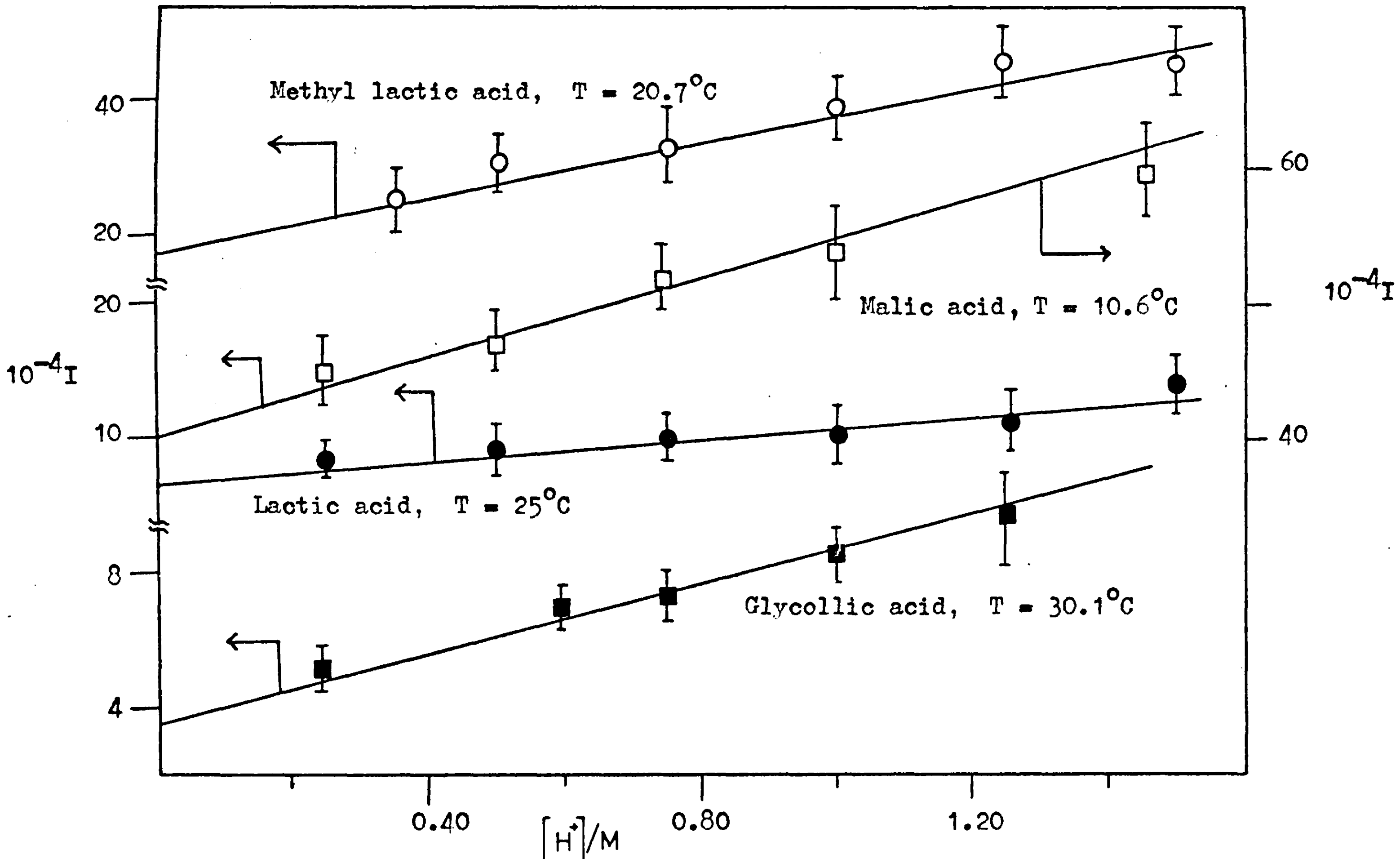


Figure 21 :- Plots of intercept, I, (Figures 16 – 19) against $[H^+]$ for α- hydroxy acids.

greater excess of α-hydroxy acid, establishing a first order dependence of the rate on cerium(IV). Typical reaction curves and plots of $\ln(A_t - A_\infty)$ against time for each system are shown in Figures 22 and 23 respectively. Similar plots were obtained under all experimental conditions. The pseudo first order rate constants, k_{obs}, obtained as the solpes of these plots were found to be independent of the wavelength at which measurements were made (Table 8). Since in most of these kinetic runs, the nitrate complex of cerium(IV) was used, it was necessary to establish whether nitrate ions had any effect on the rate. The results of experiments carried out in nitrate ion concentrations up to one hunderd times that of the oxidant concentration (Table 9) showed no effect on the observed rate. Similar runs with cerium(III) showed no effect on the observed rate up to a fifty fold excess. Both these observations suggest that neither any nitrato complexes[66,69] of cerium(IV) nor the hydroxy radicals[75] produced in a possible equilibrium

$$Ce^{4+} + H_2O \rightleftharpoons Ce^{3+} + H^+ + OH^{\cdot} \qquad (40)$$

are playing any important role in the oxidation of α-hydroxy acids by cerium(IV). Moreover, in kinetic runs where cerium(IV) perchlorate was used in place of its nitrate complex (Table 10), no change was observed on the

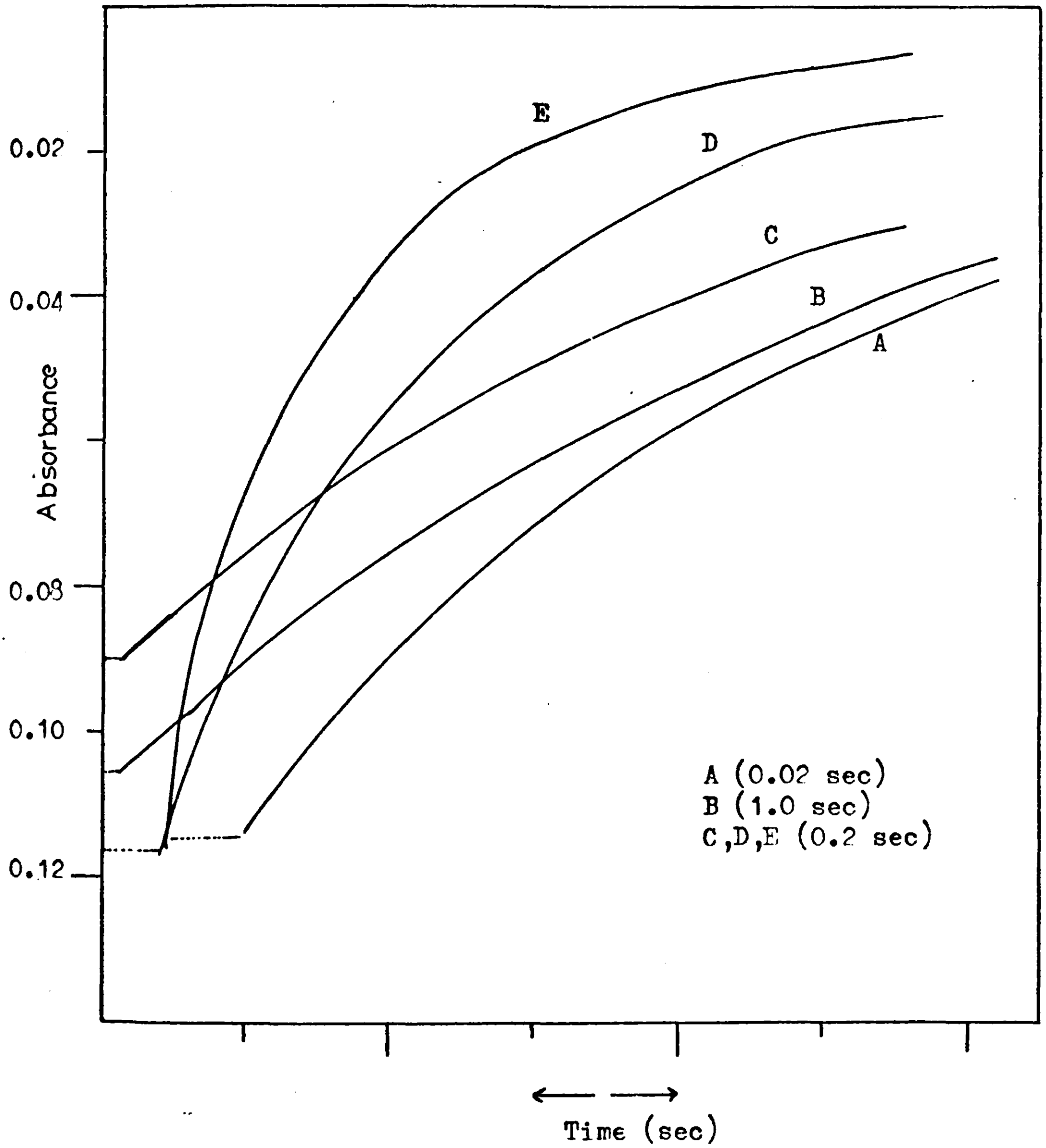


Figure 22:- Oscilloscope traces for the Ce(IV) - HL reactions

at I = 1.50M, [Ce(IV)] = 2.5×10^{-4}M and λ = 357nm.

A [Mandelic Acid] = 5.0×10^{-3}M, [H^+] = 1.00M, T=12.5°

B [Glycollic Acid] = 7.46×10^{-3}M, [H^+] = 0.70M, T=25.2°

C [Lactic Acid] = 7.50×10^{-3}M, [H^+] = 0.75M, T = 25°

D [Malic Acid] = 5.0×10^{-3}M, [H^+] = 0.80M, T = 25°

E [Methyl Lactic Acid] = 6.25×10^{-3}M, [H^+] = 0.75M, T = 25°

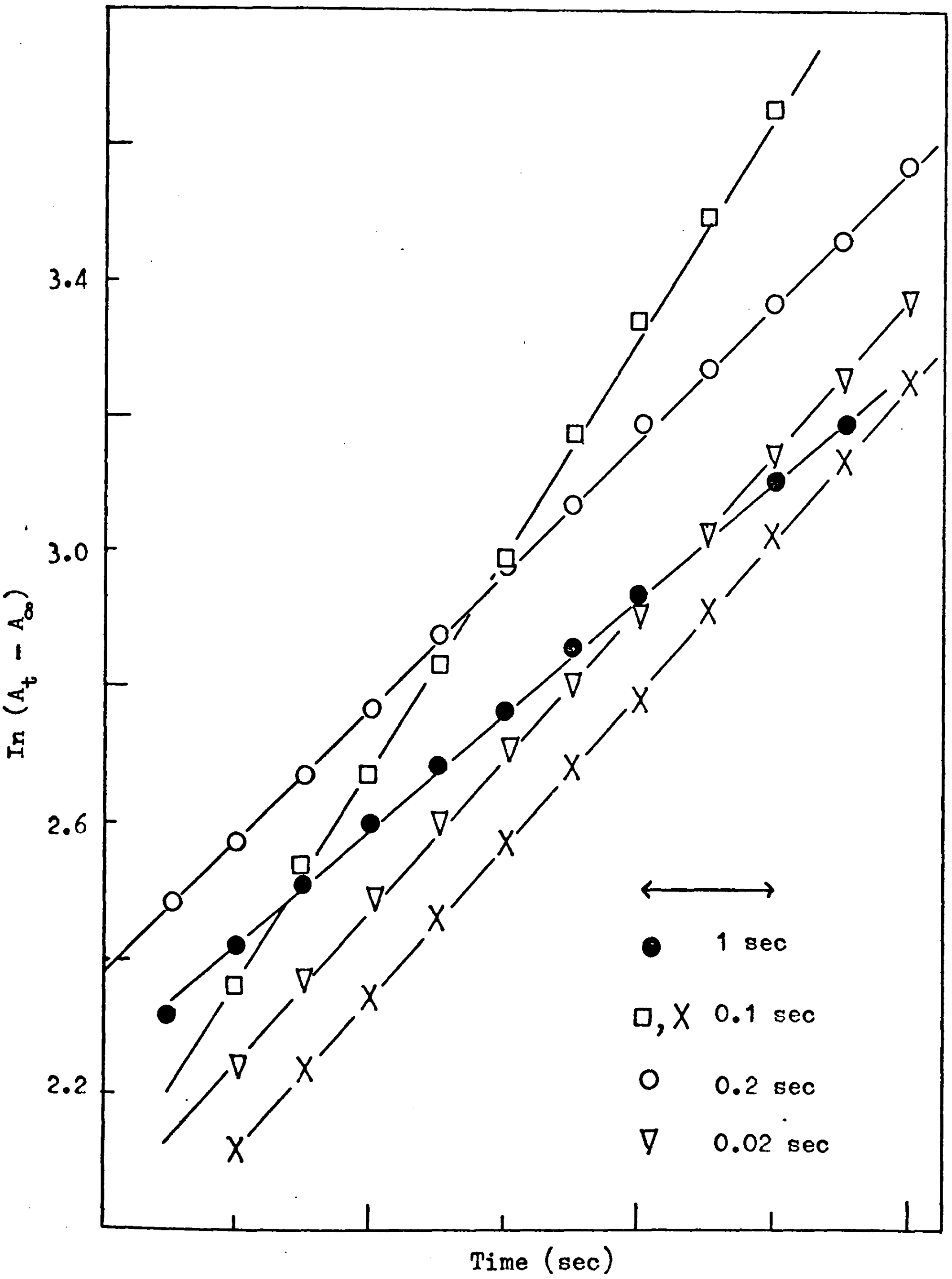


Figure 23 :- First order decay of Ce(IV) at λ = 357nm, T = 25°C, I = 1.50M with $10^2[HL]/M$, $[H^+]/M$, as follows:

(●) glycollic acid = 0.75, 0.70;

(□) methyl lactic acid = 0.625, 0.75;

(X) malic acid = 0.5, 0.80;

(O) lactic acid = 0.75, 0.75;

(▽) mandelic acid = 0.5, 1.0, (12.5°)

TABLE 8

OBSERVED RATE CONSTANTS FOR THE REACTION OF CERIUM(IV) WITH α-HYDROXY ACIDS AT VARYING WAVELENGTHS

$[\mathrm{Ce(IV)}] = 2.50 \times 10^{-4}$M   Ionic Strength = 1.50M

$[\text{Glycollic Acid}] = 7.48 \times 10^{-3}$M $[\mathrm{H}^{+}] = 0.70$M   T = 25.0°C

λ/nm	$10k_{obs}/s^{-1}$	λ/nm	$10k_{obs}/s^{-1}$
400	1.17	340	1.16
380	1.15	330	1.15
370	1.18	320	1.19
360	1.18	300	1.16

$[\text{Lactic Acid}] = 1.00 \times 10^{-2}$M $[\mathrm{H}^{+}] \mp 0.75$M   T = 25.0°C

λ/nm	$10k_{obs}/s^{-1}$	λ/nm	$10k_{obs}/s^{-1}$
400	11.8	340	11.9
380	11.5	330	11.6
370	11.4	320	11.4
360	11.9	300	11.5

$[\text{Methyl Lactic Acid}] = 5.0 \times 10^{-3}$M $[\mathrm{H}^{+}] = 0.60$M   T = 25.0°C

λ/nm	$10k_{obs}/s^{-1}$	λ/nm	$10k_{obs}/s^{-1}$
400	32.0	340	31.8
380	32.4	320	31.6
360	32.2	300	31.4

TABLE 9

EFFECT OF Ce(III) AND NITRATE IONS ON THE REACTION RATE OF Ce(IV) WITH α-HYDROXY ACIDS

$\left[\mathrm{Ce(IV)}\right] = 2.50 \times 10^{-4}\mathrm{M}$, $\lambda = 357\mathrm{nm}$, Ionic Strength = 1.50M

$\left[\text{Glycollic Acid}\right] = 6.066 \times 10^{-3}\mathrm{M}$, $\left[\mathrm{H}^{+}\right] = 0.430\mathrm{M}$, $T = 11.3^{\circ}\mathrm{C}$

$10^{3}\left[\mathrm{Ce(III)}\right]/\mathrm{M}$	$10k_{obs}/s^{-1}$	$10^{3}\left[\mathrm{NO_3^-}\right]/\mathrm{M}$	$10k_{obs}/s^{-1}$
0.0	2.25	0.0	2.25
0.249	2.25	0.251	2.26
0.746	2.27	0.752	2.24
2.240	2.27	2.254	2.23
4.977	2.22	5.010	2.22

$\left[\text{Lactic Acid}\right] = 9.90 \times 10^{-3}\mathrm{M}$, $\left[\mathrm{H}^{+}\right] = 0.0605\mathrm{M}$, $T = 7.8^{\circ}\mathrm{C}$

$10^{3}\left[\mathrm{Ce(III)}\right]/\mathrm{M}$	$10k_{obs}/s^{-1}$	$10^{3}\left[\mathrm{NO_3^-}\right]/\mathrm{M}$	$10k_{obs}/s^{-1}$
0.0	1.35	0.0	1.35
0.250	1.38	0.250	1.36
0.750	1.36	0.750	1.34
2.25	1.34	1.875	1.37
5.00	1.34	2.50	1.35

continued/

TABLE 9 continued:

$[\mathrm{Ce(IV)}] = 2.50 \times 10^{-4}\mathrm{M}$, = 357nm, Ionic Strength = 1.50M

$[\text{Methyl Lactic Acid}] = 9.63 \times 10^{-3}\mathrm{M}$, $[\mathrm{H^+}] = 0.605\mathrm{M}$, T = 7.8°C

$10^3[\mathrm{Ce(III)}]/\mathrm{M}$	$10k_{obs}/s^{-1}$	$10^3[\mathrm{NO_3^-}]/\mathrm{M}$	$10k_{obs}/s^{-1}$
0.0	4.59	0.0	4.59
0.250	4.55	0.250	4.55
0.750	4.63	0.750	4.60
2.25	4.54	1.875	4.53
5.00	4.58	5.00	4.61

$[\text{Mandelic Acid}] = 2.50 \times 10^{-3}\mathrm{M}$, $[\mathrm{H^+}] = 1.00\mathrm{M}$, T = 6.4°C

$10^3[\mathrm{Ce(III)}]/\mathrm{M}$	k_{obs}/s^{-1}	$10^3[\mathrm{NO_3}]/\mathrm{M}$	k_{obs}/s^{-1}
0.0	3.58	0.0	3.58
0.250	3.56	0.250	3.55
0.750	3.55	0.750	3.57
2.25	3.55	5.00	3.58

$[\text{Malic Acid}] = 5.00 \times 10^{-3}\mathrm{M}$, $[\mathrm{H^+}] = 1.00\mathrm{M}$, T = 20.0°C

$10^3[\mathrm{Ce(III)}]/\mathrm{M}$	k_{obs}/s^{-1}	$10^3[\mathrm{NO_3}]/\mathrm{M}$	k_{obs}/s^{-1}
0.0	1.05	0.0	1.05
		0.50	1.07
0.250	1.05	1.00	1.06
1.00	1.04	2.00	1.06
2.50	1.06	5.00	1.08
12.50	1.03	25.00	1.04

rate constant. A similar effect was noted in a recent study[81] on the oxidation of acetic acid by cerium(IV) in perchloric acid which is also believed to occur via transient complex. The k_{obs} for all the α-hydroxy acids at different temperatures are collected in Table 10, where it may be seen that, unlike other oxygen containing substrates, ie. alcohols, ketone, mono and di-carboxylic acids, at constant temperature, ionic strength and α-hydroxy acid concentration, the rate of the reaction decreases with increasing $[H^+]$. Kinetic substrate dependences (Figure 24) showed a deviation from a first order behaviour (equation (31). P69). This observation together with spectrophotometric evidence, further confirms the presence of transient complexes in the present systems.

The following scheme is consistent with the experimental observations

$$Ce^{4+} + H_2O \overset{K_h}{\rightleftharpoons} CeOH^{3+} + H^+ \qquad (21)$$

$$Ce^{4+} + HL \overset{K_1}{\rightleftharpoons} CeHL^{4+} \qquad (35)$$

$$CeOH^{3+} + HL \overset{K_2}{\rightleftharpoons} CeL^{3+} + H_2O \qquad (36)$$

$$CeHL^{4+} \overset{K_3}{\rightleftharpoons} CeL^{3+} + H^+ \qquad (37)$$

TABLE 10

OBSERVED RATE CONSTANTS AT VARYING α-HYDROXY ACID AND HYDROGEN-ION CONCENTRATIONS, $[\mathrm{Ce(IV)}]_T$ = 2.5×10^{-4}M, I = 1.50M, λ = 357nm Slopes (S)$^{(a)}$ AND INTERCEPTS (I)$^{(b)}$ WERE DERIVED FROM PLOTS ACCORDING TO EQUATION (45)

T/°C	$[H^+]$/M	10^2[Glycollic Acid]/M	$10k_{obs}/s^{-1}$
30.1	0.35	0.50	1.92
		0.75	2.62
		1.25	3.94
		1.50	4.38
		2.50	5.43
		3.62	6.33
	10^2S = 2.13 ± 0.05	I = 0.933 ± 0.06	
	0.60	0.75	1.99
		1.00	2.50
		1.50	3.33
		2.00	3.89
		3.50	5.20
	10^2S = 2.95 ± 0.036	I = 1.069 ± 0.03	
	0.75	0.50	1.19
		1.50	2.82
		2.00	3.35
		2.50	3.95
		3.75	4.90
		5.00	5.03
	10^2S = 3.62 ± 0.053	I = 1.148 ± 0.05	

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Glycollic Acid}]/M$	$10k_{obs}/s^{-1}$
30.1	1.00	0.25	0.588
		0.375	0.880
		0.50	1.09
		0.625	1.31
		0.938	1.81
		1.25	2.22
		1.88	3.01

$10^2S = 3.91 \pm 0.06$ $I = 1.29 \pm 0.13$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Glycollic Acid}]/M$	$10k_{obs}/s^{-1}$
	1.25	0.50	0.925
		1.50	2.02
		2.00	2.69
		2.50	3.06
		3.75	3.50
		5.00	4.19

$10^2S = 4.65 \pm 0.12$ $I = 1.53 \pm 0.12$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Glycollic Acid}]/M$	$10k_{obs}/s^{-1}$
25.2	0.35	0.5808	1.34
		0.9127	1.82
		1.245	2.15
		1.659	2.67
		2.323	3.12
		3.319	3.53

$10^2S = 3.29 \pm 0.08$ $I = 1.84 \pm 0.08$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Glycollic Acid}]/M$	$10k_{obs}/s^{-1}$
	0.70	0.746	1.15
		1.245	1.70
		1.659	2.03
		2.323	2.43
		3.319	2.79

$10^2S = 4.96 \pm 0.11$ $I = 1.99 \pm 0.086$

T/°C	$[H^+]$/M	10^2[Glycollic Acid]/M	$10k_{obs}/s^{-1}$
25.2	0.85	0.664	0.862
		0.8297	1.09
		0.9957	1.21
		1.328	1.48
		1.991	1.86
		3.319	2.37

$10^2S = 5.96 \pm 0.23$ $I = 2.33 \pm 0.22$

17.6	0.70	0.5392	0.328
		0.8088	0.462
		0.944	0.502
		1.092	0.541
		2.696	0.861

$10^2S = 12.6 \pm 0.5$ $I = 6.65 \pm 0.55$

	1.00	0.5392	0.248
		0.8088	0.338
		1.085	0.422
		1.348	0.488
		1.890	0.592
		2.696	0.693

$10^2S = 17.6 \pm 0.2$ $I = 7.64 \pm 0.17$

	1.25	0.5392	0.213
		0.8088	0.295
		1.078	0.379
		1.348	0.436
		1.901	0.500
		2.696	0.622

$10^2S = 20.6 \pm 0.6$ $I = 8.21 \pm 0.68$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Glycollic Acid}]/M$	$10k_{obs}/s^{-1}$
11.4	0.30	0.666	0.295
		0.9747	0.365
		1.316	0.412
		1.624	0.433
		2.599	0.502

$10^2S = 12.4 \pm 0.4$ $I = 15.1 \pm 0.39$

	0.50	0.6497	0.216
		0.9747	0.272
		1.316	0.327
		2.274	0.396
		3.249	0.428

$10^2S = 18.9 \pm 0.62$ $I = 17.0 \pm 0.6$

	0.70	0.5037	0.151
		0.731	0.195
		1.137	0.254
		1.624	0.295
		2.355	0.346

$10^2S = 23.8 \pm 0.3$ $I = 18.8 \pm 0.3$

	0.90	0.4878	0.124
		0.731	0.167
		1.137	0.218
		1.624	0.262
		2.355	0.308

$10^2S = 29.5 \pm 0.2$ $I = 19.9 \pm 0.2$

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Glycollic Acid}]/M$	$10k_{obs}/s^{-1}$
11.4	1.25	0.4878	0.0899
		0.731	0.122
		1.624	0.204
		2.355	0.239
		3.980	0.279

$10^2S = 42.3 \pm 0.7$ $I = 24.2 \pm 0.8$

		$10^2[\text{Lactic Acid}]/M$	
30.0	0.50	0.375	11.4
		0.500	14.4
		0.625	17.2
		1.00	24.2
		1.75	33.9

$10^3S = 2.78 \pm 0.02$ $I = 0.136 \pm 0.001$

	0.75	0.625	14.9
		1.00	20.8
		1.75	32.4

$10^3S = 3.49 \pm 0.04$ $I = 0.117 \pm 0.026$

	1.00	0.375	8.21
		0.50	10.1
		0.625	12.6
		1.00	17.8
		1.75	25.6

$10^3S = 4.00 \pm 0.10$ $I = 0.160 \pm 0.018$

T/°C	$[H^+]$/M	10^2[Lactic Acid]/M	$10k_{obs}/s^{-1}$
30.0	1.50	0.50	7.41
		1.00	13.0
		1.50	19.4

$10^3S = 5.84 \pm 0.03$ $\quad$ $I = 0.183 \pm 0.004$

T/°C	$[H^+]$/M	10^2[Lactic Acid]/M	$10k_{obs}/s^{-1}$
25.0	0.25	0.789	16.2
		1.018	19.9
		1.527	24.0
		2.545	26.4
		5.091	31.5

$10^3S = 2.66 \pm 0.12$ $\quad$ $I = 0.260 \pm 0.019$

T/°C	$[H^+]$/M	10^2[Lactic Acid]/M	$10k_{obs}/s^{-1}$
	0.50	0.50	9.35
		0.75	12.3
		1.00	14.7
		1.50	19.4
		2.50	23.9
		3.50	26.0
		5.00	28.3

$10^3S = 4.05 \pm 0.07$ $\quad$ $I = 0.264 \pm 0.007$

T/°C	$[H^+]$/M	10^2[Lactic Acid]/M	$10k_{obs}/s^{-1}$
	0.75	0.50	7.13
		0.75	9.72
		1.00	11.6
		2.50	19.9
		3.50	23.3
		5.00	25.3

$10^3S = 5.64 \pm 0.074$ $\quad$ $I = 0.279 \pm 0.008$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
25.0	1.25	0.50	4.98
		1.00	8.53
		1.50	11.4
		2.50	15.0
		3.50	18.1
		5.00	20.5
	$10^3S = 8.46 \pm 0.05$	$I = 0.318 \pm 0.005$	
	1.50	0.764	6.11
		1.018	7.45
		1.527	10.2
		3.054	14.8
		5.091	18.2
		7.632	19.3
	$10^3S = 9.73 \pm 0.19$	$I = 0.366 \pm 0.014$	
20.0	0.30	0.375	5.20
		0.513	6.65
		1.00	9.48
		1.75	12.5
		3.00	14.2
	$10^3S = 5.20 \pm 0.12$	$I = 0.516 \pm 0.019$	
	0.60	0.375	3.62
		0.50	4.69
		1.00	7.67
		1.75	9.70
		3.00	12.1
	$10^3S = 8.20 \pm 0.2$	$I = 0.531 \pm 0.04$	

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
20.0	1.25	0.50	2.99
		0.75	4.16
		1.00	5.01
		1.50	6.63
		2.50	8.91
		3.50	9.79
		5.00	10.8

$10^2S = 1.35 \pm 0.019$ $I = 0.622 \pm 0.02$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
	1.50	0.50	2.41
		0.75	3.34
		1.00	4.22
		2.00	6.46
		4.00	9.53
		5.00	9.80
		7.50	10.4

$10^2S = 1.73 \pm 0.02$ $I = 0.673 \pm 0.02$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
10.0	0.40	0.388	1.42
		0.50	1.60
		0.75	1.99
		1.00	2.33
		1.75	2.73

$10^2S = 1.73 \pm 0.07$ $I = 2.66 \pm 0.12$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
	0.70	0.375	1.05
		0.50	1.26
		0.75	1.63
		1.12	2.00

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
10.0	0.70	1.75	2.32
		2.50	2.56
		3.75	2.86

$10^2S = 2.50 \pm 0.03$ $\quad$ $I = 2.87 \pm 0.04$

	1.20	0.438	0.805
		0.563	0.968
		0.75	1.17
		1.013	1.37
		1.25	1.51
		1.76	1.90
		3.00	2.31

$10^2S = 4.09 \pm 0.09$ $\quad$ $I = 3.11 \pm 0.12$

	1.50	0.438	0.771
		0.563	0.945
		0.875	1.20
		1.125	1.43
		1.50	1.62
		2.00	1.95

$10^2S = 4.28 \pm 0.13$ $\quad$ $I = 3.19 \pm 0.18$

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Methyl Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
25.0	0.60	0.25	19.2
		0.375	26.1
		0.50	31.8
		0.625	35.1
		0.875	40.7
		1.25	47.3

$10^3S = 0.961 \pm 0.025$ $\quad$ $I = 0.131 \pm 0.005$

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Methyl Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
25.0	0.75	0.25	17.3
		0.375	22.7
		0.50	28.2
		0.625	32.3
		0.875	37.8
		1.25	46.5
	$10^3S = 1.13 \pm 0.025$	$I = 0.13 \pm 0.005$	
	0.90	0.25	15.1
		0.375	20.8
		0.50	24.6
		0.625	27.8
		0.875	33.0
		1.25	39.6
	$10^3S = 1.26 \pm 0.02$	$I = 0.154 \pm 0.005$	
	1.20	0.256	12.4
		0.375	16.9
		0.50	20.3
		0.625	23.3
		0.875	28.5
		1.25	35.8
	$10^3S = 1.66 \pm 0.03$	$I = 0.156 \pm 0.007$	
	1.35	0.25	10.8
		0.375	15.0
		0.50	18.4
		0.625	20.8
		0.875	24.8
		1.25	30.8
	$10^3S = 1.85 \pm 0.033$	$I = 0.181 \pm 0.007$	

$T/^{\circ}C$	$[H^+]$	$10^2[\text{Methyl Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
25.0	1.50	0.258	9.95
		0.377	13.2
		0.532	16.6
		0.629	19.1
		0.755	21.3
		0.881	22.8
		1.258	26.9
	$10^3S = 2.09 \pm 0.03$	$I = 0.196 \pm 0.006$	
20.7	0.35	0.256	17.4
		0.384	21.0
		0.640	26.5
		0.902	30.7
		1.281	32.3
	$10^3S = 0.874 \pm 0.034$	$I = 0.238 \pm 0.008$	
	0.50	0.228	14.0
		0.344	18.2
		0.464	21.1
		0.608	23.2
		0.760	25.3
		1.064	29.1
	$10^2S = 1.05 \pm 0.024$	$I = 0.251 \pm 0.006$	
	0.75	0.262	11.0
		0.384	14.2
		0.576	17.8
		0.768	20.4
		1.152	22.8
		1.568	25.3
	$10^3S = 1.58 \pm 0.026$	$I = 0.292 \pm 0.005$	

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Methyl Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
20.7	1.00	0.228	8.14
		0.608	15.3
		0.760	16.7
		1.064	20.1

$10^3S = 2.10 \pm 0.04$ $I = 0.309 \pm 0.01$

	1.25	0.228	6.92
		0.342	9.06
		0.456	10.6
		0.760	14.0
		1.102	17.0

$10^3S = 2.42 \pm 0.069$ $I = 0.39 \pm 0.018$

	1.50	0.312	7.60
		0.456	9.63
		0.608	11.5
		0.912	14.3
		1.521	16.9

$10^3S = 2.90 \pm 0.053$ $I = 0.394 \pm 0.01$

16.1	0.50	0.256	9.49
		0.375	11.4
		0.50	13.2
		0.625	14.0
		0.875	16.0
		1.25	16.9

$10^3S = 1.51 \pm 0.042$ $I = 0.465 \pm 0.011$

$T/^{\circ}C$	$[H^+]/M$	10^2[Methyl Lactic Acid]$/M$	$10k_{obs}/s^{-1}$
16.1	0.75	0.250	7.40
		0.381	9.68
		0.50	10.6
		0.625	11.5
		0.881	13.1
		1.25	14.2

$10^3S = 1.99 \pm 0.073$ $\quad I = 0.54 \pm 0.017$

	1.00	0.25	5.75
		0.50	8.36
		0.625	9.47
		0.875	10.7
		1.25	11.8

$10^3S = 2.81 \pm 0.049$ $\quad I = 0.62 \pm 0.011$

	1.25	0.375	6.44
		0.50	7.68
		0.625	8.36
		1.25	10.7

$10^3S = 3.26 \pm 0.13$ $\quad I = 0.67 \pm 0.025$

	1.50	0.25	4.02
		0.375	5.39
		0.75	7.54
		1.25	9.19
		1.875	10.3

$10^3S = 4.29 \pm 0.09$ $\quad I = 0.742 \pm 0.02$

T/°C	$[H^+]/M$	$10^2[\text{Methyl Lactic Acid}]/M$	$10k_{obs}/s^{-1}$
11.3	0.50	0.262	5.20
		0.375	6.22
		0.50	6.88
		0.625	7.47
		0.875	7.98
		1.25	8.32

$10^3S = 2.43 \pm 0.093$ $I = 0.975 \pm 0.02$

	0.75	0.25	4.02
		0.375	5.03
		0.50	5.74
		0.625	6.34
		0.875	6.90
		1.25	7.47

$10^3S = 3.62 \pm 0.078$ $I = 1.03 \pm 0.018$

	1.00	0.25	2.96
		0.375	3.80
		0.50	4.45
		0.625	4.90
		0.875	5.53
		1.25	6.15

$10^3S = 5.48 \pm 0.065$ $I = 1.17 \pm 0.015$

	1.50	0.224	1.86
		0.288	2.25
		0.512	3.17
		0.768	3.79
		1.28	4.59

$10^3S = 8.65 \pm 0.13$ $I = 1.49 \pm 0.04$

$T/^{o}C$	$[H^+]/M$	10^2[Malic Acid]$/M$	$10k_{obs}/s^{-1}$
25.0	0.60$^{(c)}$	0.25	16.0
		0.375	20.5
		0.500	23.9
		2.50	39.4
		3.75	39.8
	$10^3S = 1.012 \pm 0.03$	$I = 0.218 \pm 0.004$	
	0.80$^{(d)}$	0.50	22.0
		1.50	36.0
		2.50	40.2
		3.75	40.0
	$10^3S = 1.24 \pm 0.03$	$I = 0.205 \pm 0.006$	
	1.00$^{(d)}$	1.00	35.9
		2.50	37.3
		3.00	38.5
		3.50	40.0
		5.00	42.5
	$10^3S = 1.44 \pm 0.01$	$I = 0.209 \pm 0.004$	
	1.25$^{(d)}$	0.25	10.7
		0.50	17.4
		1.00	25.0
		1.50	30.4
		2.00	33.4
		2.50	36.4
		3.75	37.3
	$10^3S = 1.82 \pm 0.02$	$I = 0.211 \pm 0.004$	

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Malic Acid}]/M$	$10k_{obs}/s^{-1}$
25.0	1.45(d)	0.25	9.50
		0.388	13.1
		0.50	15.9
		0.75	20.5
		1.50	27.6
		2.50	31.4
		3.75	35.8
	$10^3S = 2.06 \pm 0.025$	$I = 0.225 \pm 0.005$	
20.0	0.50	0.312	11.8
		0.375	13.2
		0.50	14.9
		0.75	16.8
		1.50	20.1
		2.50	21.2
	$10^3S = 1.32 \pm 0.03$	$I = 0.414 \pm 0.006$	
	0.75	0.25	8.40
		0.375	11.0
		0.50	13.1
		0.75	14.9
		1.50	19.0
		2.50	20.4
		3.75	20.9
	$10^3S = 1.86 \pm 0.04$	$I = 0.413 \pm 0.008$	
	1.00	0.25	6.92
		0.50	10.3
		0.75	12.0

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Malic Acid}]/M$	$10k_{obs}/s^{-1}$
20.0	1.00	2.50	18.0
		3.75	19.4
	$10^3S = 2.46 \pm 0.08$	$I = 0.468 \pm 0.018$	
	1.25	0.25	6.30
		0.375	8.30
		0.50	9.55
		0.75	12.0
		1.50	15.2
		2.50	17.1
		3.75	18.7
	$10^3S = 2.80 \pm 0.04$	$I = 0.468 \pm 0.009$	
	1.50	0.25	5.40
		0.375	7.41
		0.50	8.70
		0.75	10.4
		1.50	14.0
		3.75	18.6
	$10^3S = 3.42 \pm 0.09$	$I = 0.470 \pm 0.019$	
16.0	0.30	0.312	8.30
		0.500	9.75
		0.75	11.0
		1.50	12.0
	$10^3S = 1.48 \pm 0.066$	$I = 0.727 \pm 0.013$	

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Malic Acid}]/M$	$10k_{obs}/s^{-1}$
16.0	0.90	0.375	6.17
		0.50	7.14
		0.75	8.40
		1.50	10.5
		2.50	11.8
	$10^3S = 3.39 \pm 0.066$	$I = 0.722 \pm 0.01$	
	1.25	0.25	3.87
		0.375	5.02
		0.50	6.10
		0.75	7.25
		1.50	9.43
		2.50	10.6
		3.75	10.9
	$10^3S = 4.51 \pm 0.03$	$I = 0.771 \pm 0.01$	
	1.50	0.25	3.38
		0.375	4.54
		0.50	5.45
		0.75	6.40
		1.50	8.93
		2.50	10.1
		3.75	10.9
	$10^3S = 5.44 \pm 0.09$	$I = 0.78 \pm 0.02$	
10.6	0.25	0.25	4.08
		0.437	4.95
		0.625	5.43
		1.25	5.81
		1.88	5.80
	$10^3S = 2.05 \pm 0.19$	$I = 1.58 \pm 0.04$	

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Malic Acid}]/M$	$10k_{obs}/s^{-1}$
10.6	0.50	0.25	3.19
		0.437	4.17
		0.625	4.67
		1.25	5.53
		1.83	5.95
		2.50	6.10

$10^3S = 4.07 \pm 0.07$ $I = 1.41 \pm 0.005$

	0.75	0.25	2.75
		0.375	3.46
		0.50	3.89
		0.75	4.58
		1.50	5.53
		2.50	6.10
		3.75	6.37

$10^3S = 5.51 \pm 0.06$ $I = 1.44 \pm 0.01$

	1.00	0.25	2.38
		0.375	3.07
		0.50	3.60
		0.75	4.07
		1.50	5.10
		2.50	5.60
		3.75	5.97

$10^3S = 6.65 \pm 0.13$ $I = 1.51 \pm 0.26$

	1.45	0.25	1.91
		0.375	2.54
		0.50	2.87

T/°C	$[H^+]$/M	10^2[Malic Acid]/M	$10k_{obs}/s^{-1}$
10.6	1.45	0.75	3.40
		1.50	4.43
		3.75	5.31

$10^3S = 8.87 \pm 0.23$ $I = 1.68 \pm 0.05$

T/°C	$[H^+]$/M	10^2[Mandelic Acid]/M	$10k_{obs}/S^{-1}$
17.5	0.75	0.25	145
		0.375	196
		0.50	225
		0.625	252

$10^4S = 1.22 \pm 0.056$ $10^2I = 1.97 \pm 0.15$

	1.00	0.25	109
		0.375	146
		0.50	178
		0.625	203
		1.25	262

$10^4S = 1.69 \pm 0.05$ $10^2I = 2.32 \pm 0.12$

	1.25	0.25	95.5
		0.50	144
		0.625	171
		1.25	243

$10^4S = 2.04 \pm 0.04$ $10^2I = 2.59 \pm 0.25$

$T/^{o}C$	$[H^+]/M$	10^2[Mandelic Acid]/M	$10k_{obs}/s^{-1}$
12.5	0.50	0.25	106
		0.375	136
		0.50	151
		0.625	170
		1.25	199

$10^4S = 1.39 \pm 0.06$ $10^2I = 3.79 \pm 0.15$

	0.75	0.25	80.5
		0.375	101
		0.50	122
		0.625	134
		1.875	185

$10^4S = 2.04 \pm 0.06$ $10^2I = 4.25 \pm 0.14$

	1.00	0.25	67.3
		0.375	85.8
		0.50	103
		0.625	116
		1.875	148

$10^4S = 2.58 \pm 0.06$ $10^2I = 4.62 \pm 0.15$

	1.25	0.25	55.8
		0.50	88.4
		0.625	100
		1.25	136

$10^4S = 3.29 \pm 0.03$ $10^2I = 4.72 \pm 0.06$

$T/^{o}C$	$[H^{+}]/M$	$10^{2}[\text{Mandelic Acid}]/M$	$10k_{obs}/s^{-1}$
6.4	0.25	0.25	74.0
		0.375	83.9
		0.50	96.0
		0.625	98.5
	$10^{4}S = 1.44 \pm 0.15$	$10^{2}I = 7.80 \pm 0.42$	
	0.50	0.25	59.0
		0.375	68.3
		0.625	83.7
		1.25	96.5
	$10^{4}S = 2.05 \pm 0.09$	$10^{2}I = 8.85 \pm 0.25$	
	0.75	0.25	42.8
		0.375	55.3
		0.50	59.6
		0.625	65.9
		1.25	77.3
	$10^{4}S = 3.24 \pm 0.19$	$10^{2}I = 10.1 \pm 0.46$	
	1.00	0.25	35.8
		0.375	44.5
		0.50	52.5
		0.625	58.0
		1.25	69.8
	$10^{4}S = 4.34 \pm 0.14$	$10^{2}I = 10.6 \pm 0.35$	

$T/^{o}C$	$[H^+]/M$	10^2[Mandelic Acid]/M	$10k_{obs}/s^{-1}$
6.4	1.35	0.25	27.0
		0.375	35.1
		0.50	40.8
		1.25	59.7

$10^4S = 6.33 \pm 0.05$ $10^2I = 11.7 \pm 0.13$

$T/^{o}C$	$[H^+]/M$	10^2[Mandelic Acid]/M	$10k_{obs}/s^{-1}$
	1.50	0.221	24.1
		0.299	28.5
		0.377	33.3

$10^4S = 6.52 \pm 0.32$ $10^2I = 12.5 \pm 1$

(a) - units of mol $^{-1}$ s

(b) - units of s

(c) - the nitrate salt of Ce(IV) was used

(d) - the perchlorate salt of Ce(IV) was used

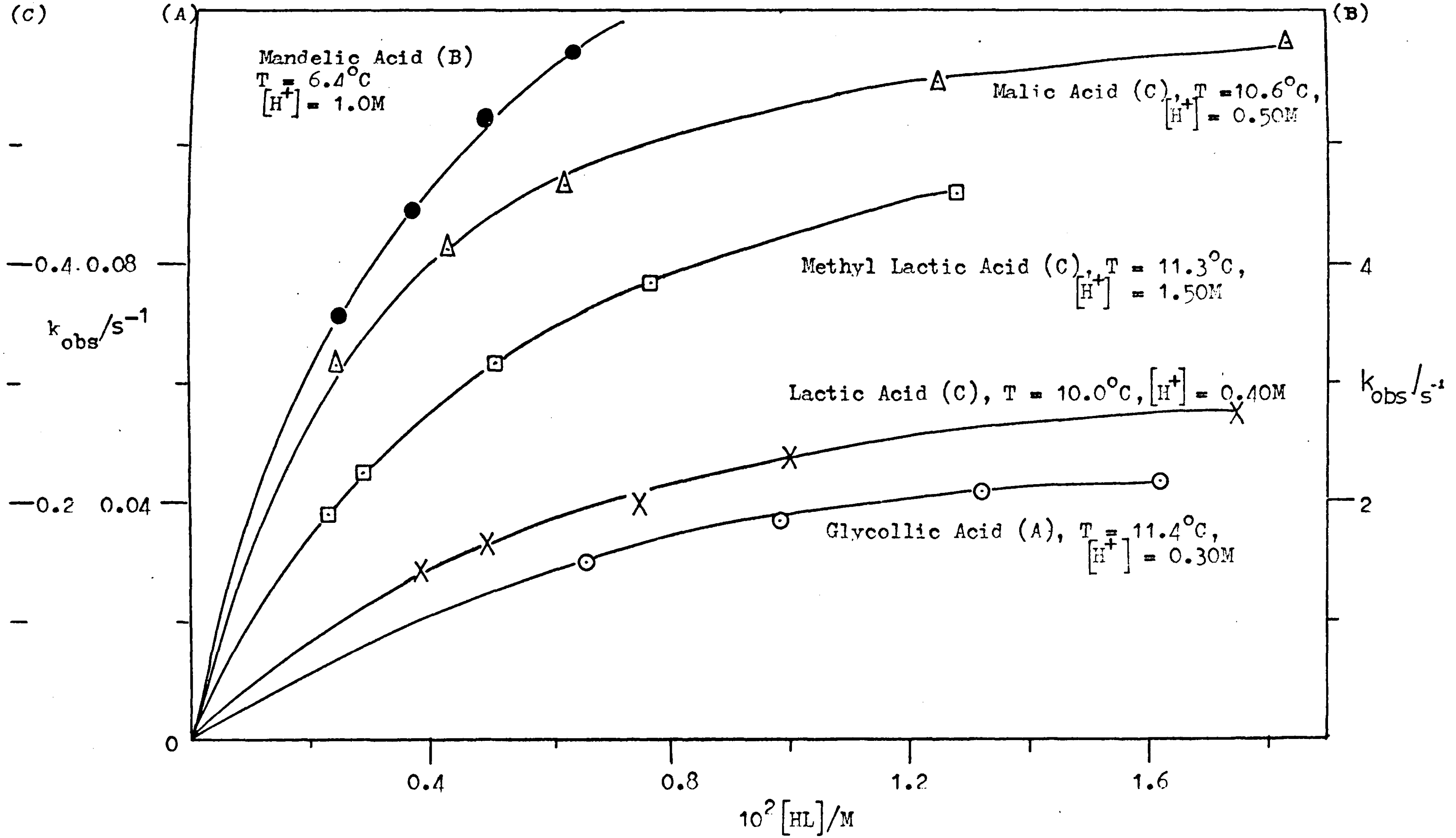


Figure 24:- Plots of the pseudo first order rate constant against $[\mathrm{HL}]$ at $\lambda = 357\,\mathrm{nm}$, $I = 1.50\,\mathrm{M}$.

$$CeHL^{4+} \xrightarrow{k_1} Ce(III) + L + H^+ \qquad (41)$$

$$CeL^{3+} \xrightarrow{k_2} Ce(III) + L \qquad (42)$$

$$Ce(IV) + L \xrightarrow{k_3} Ce(III) + \text{product/radical} \qquad (43)$$

In these equations $CeHL^{4+}$ and CeL^{3+} represent the intermediate complexes, L the radical produced by unimolecular decomposition of these complexes which further reacts with another molecule of cerium(IV) to give stable products or another reducing radical in case of malic acid. The oxidation of these radicals will continue until stable products are formed. It is assumed that such redox reactions are much faster ($k_3 \gg k_1, k_2$) than the rate-determining steps. Furthermore, it is also assumed that all the pre-equilibria are rapidly established compared with (41) and (42) and the possible alternative pathways (36) and (37) for the formation of complex, CeL^{3+}, are kinetically indistinguishable. Allowing for the overall stoicheiometry, the rate of loss of total cerium(IV) may be expressed as

$$\frac{-d\,[Ce(IV)]_T}{dt} = n\,k_1\,[CeHL^{4+}] + n\,k_2\,[CeHL^{3+}] \qquad (44)$$

and the observed first order rate constant, k_{obs}, may be written as

$$\frac{1}{k_{obs}} = \frac{[H^+] + K_h}{n(k_1K_1[H^+] + k_2K_2K_h)\ HL} + \frac{K_1[H^+] + K_2K_h}{n(k_1K_1[H^+] + k_2K_2K_h)} \qquad (45)$$

where n = stoicheiometry factor (10 for malic and 2 for other α-hydroxy acids), so that a plot of k_{obs}^{-1} against $[HL]^{-1}$ should be linear. Treatment of the kinetic data (Table 10) in this way showed excellent linearity as illustrated in Figures 25 - 29 for glycollic, lactic, methyl lactic, mandelic and malic acids, respectively. The considerable variation of these intercepts with $[H^+]$ observed (Figures 25-29) for the wide variation of conditions shows that equilibrium (37) exists with α-hydroxy acids. In earlier investigations on the oxidation of monofunctional alcohols[80,112,113], as well as polyfunctional alcohols[91,114] and ketone[119], a common intercept, in each case, was observed at varying hydrogen ion concentrations. This has been interpreted in terms of only one complex namely, $CeHL^{4+}$, undergoing redox; recent studies, however, on isopropanol[110], sec-butanol[111] and cyclohexanol[111] have shown that, in fact, equilibrium such as (37) is also important. An analysis of these data will be made later in the discussion. Thus the relative magnitudes of K_3, k_1 and k_2 seem to be the controlling factors in such mechanisms. For example, if K_3 is very small, i.e. only one complex, namely $CeHL^{4+}$ predominant, exists, or if $k_1 = k_2$ (which is considered unlikely) there will be no variation of intercept with $[H^+]$.

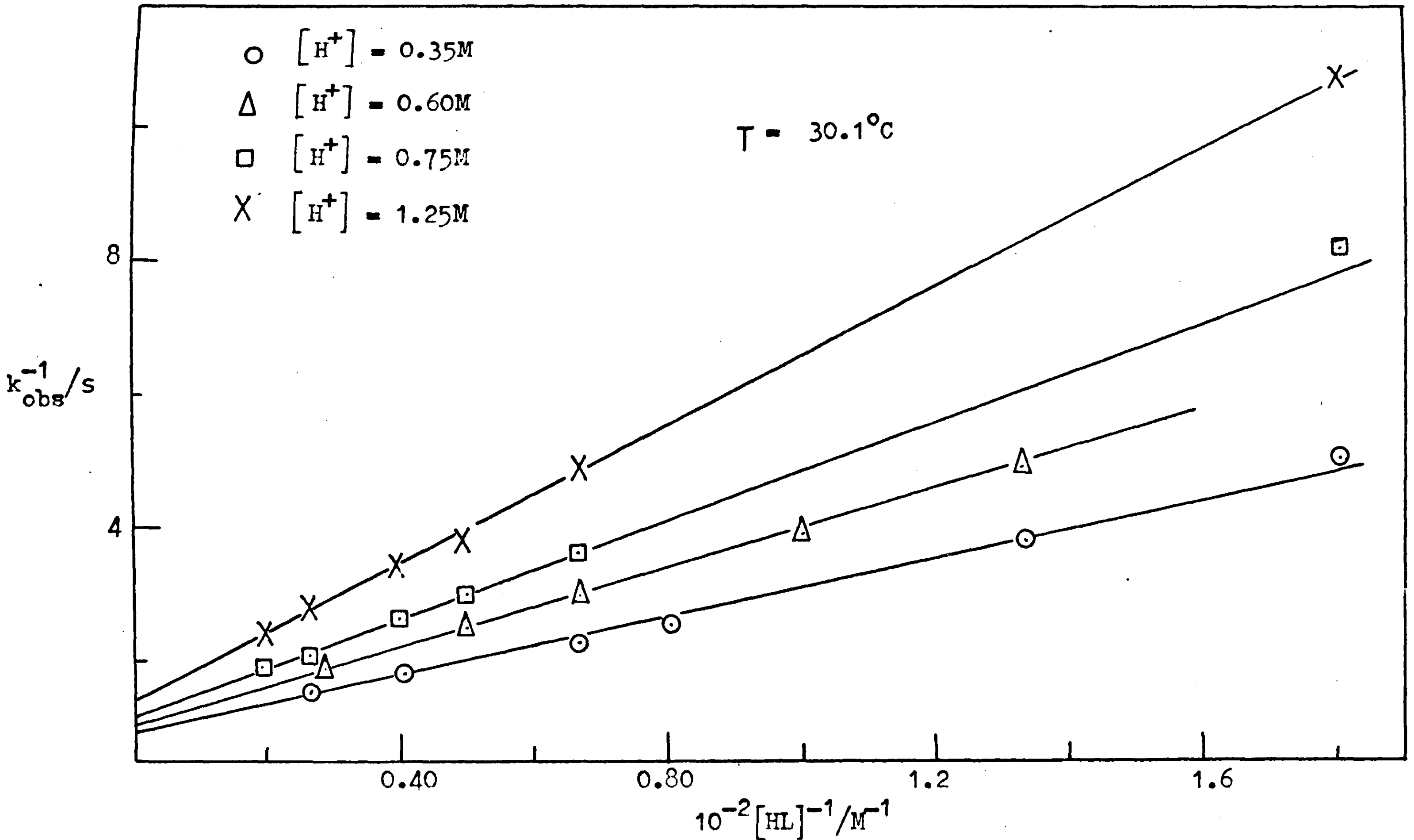


Figure 25 :- Plots of k_{obs}^{-1} versus $[\text{glycollic acid}]^{-1}$ (equation 45) at $\lambda = 357nm$ and I = 1.50M

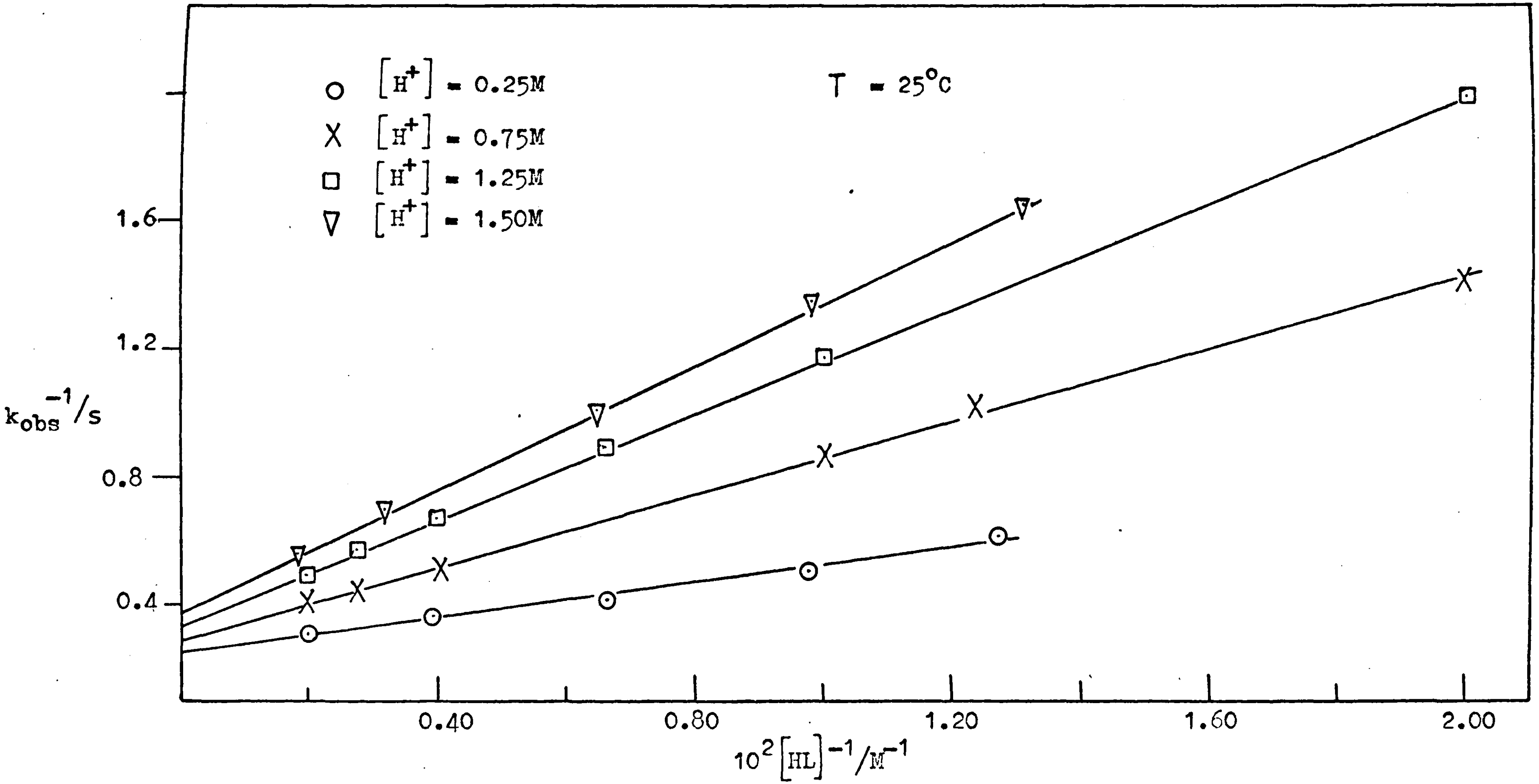


Figure 26 :- Plots of k_{obs}^{-1} versus $[\text{lactic acid}]^{-1}$ (equation 45) at λ = 357nm and I = 1.50M.

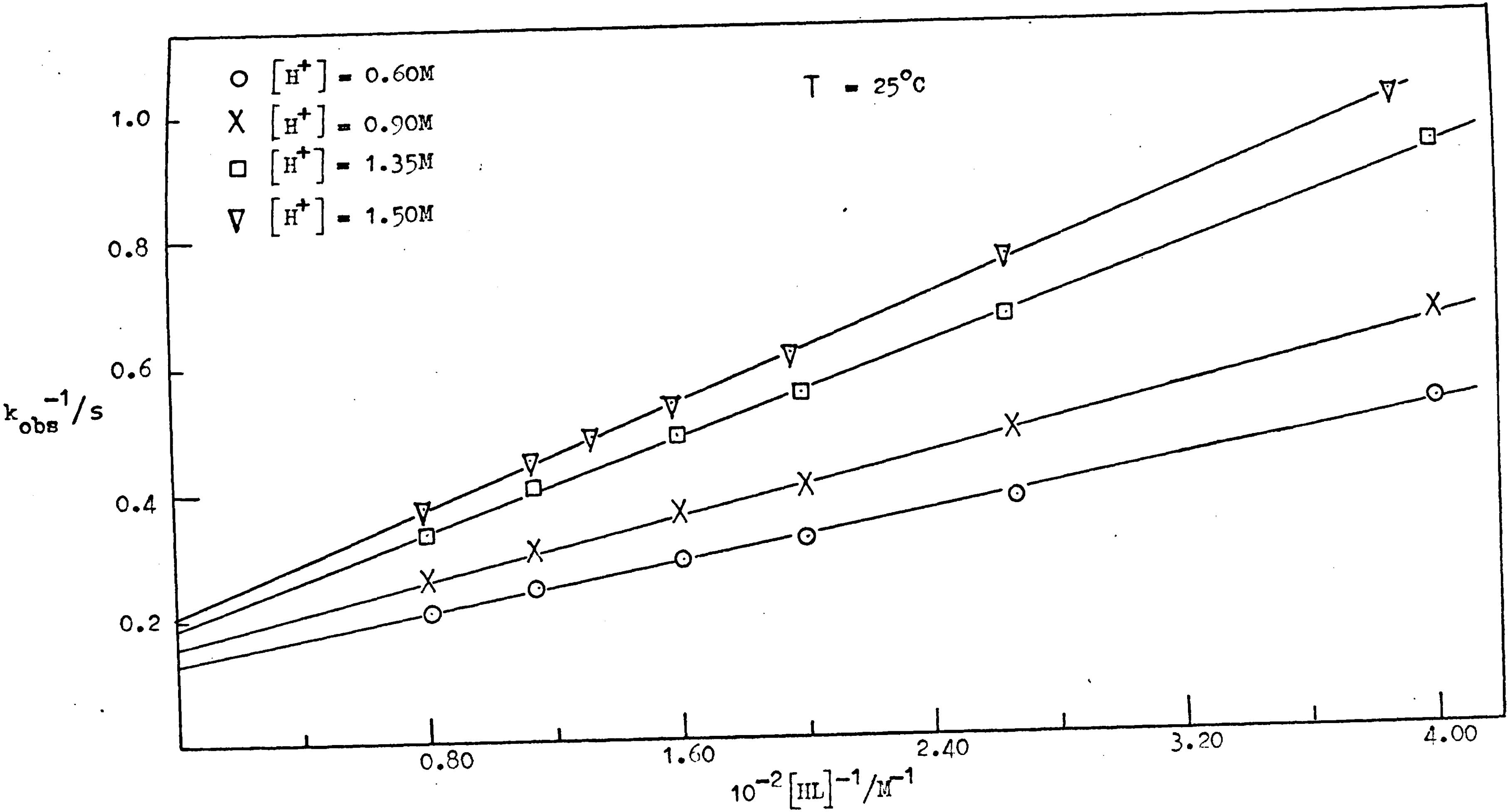


Figure 27 :- Plots of k_{obs}^{-1} versus $[\text{methyl lactic acid}]^{-1}$ (equation 45), at λ = 357nm and I = 1.50M.

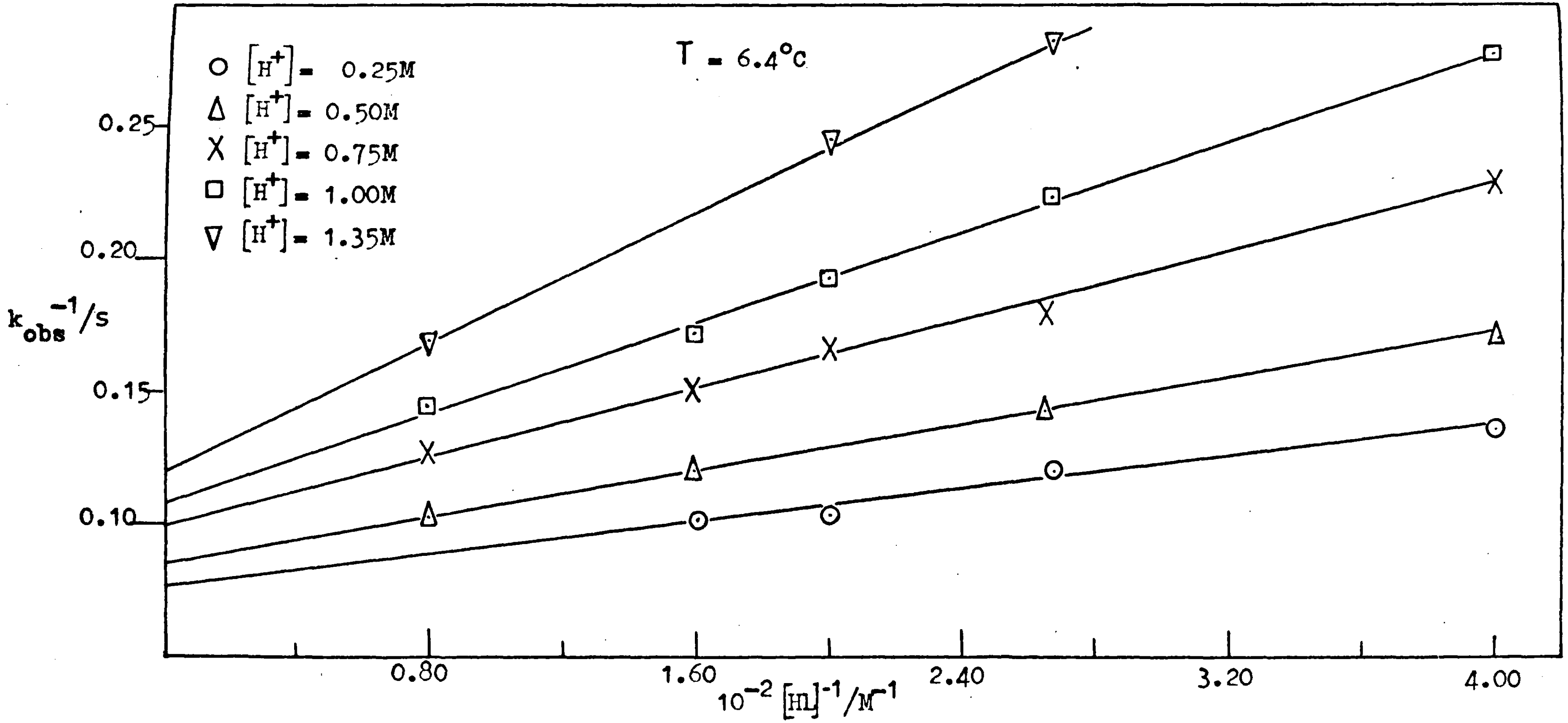


Figure 28 :- Plots of k_{obs}^{-1} versus $[\text{mandelic acid}]^{-1}$ (equation 45) at λ = 357nm and I = 1.50M.

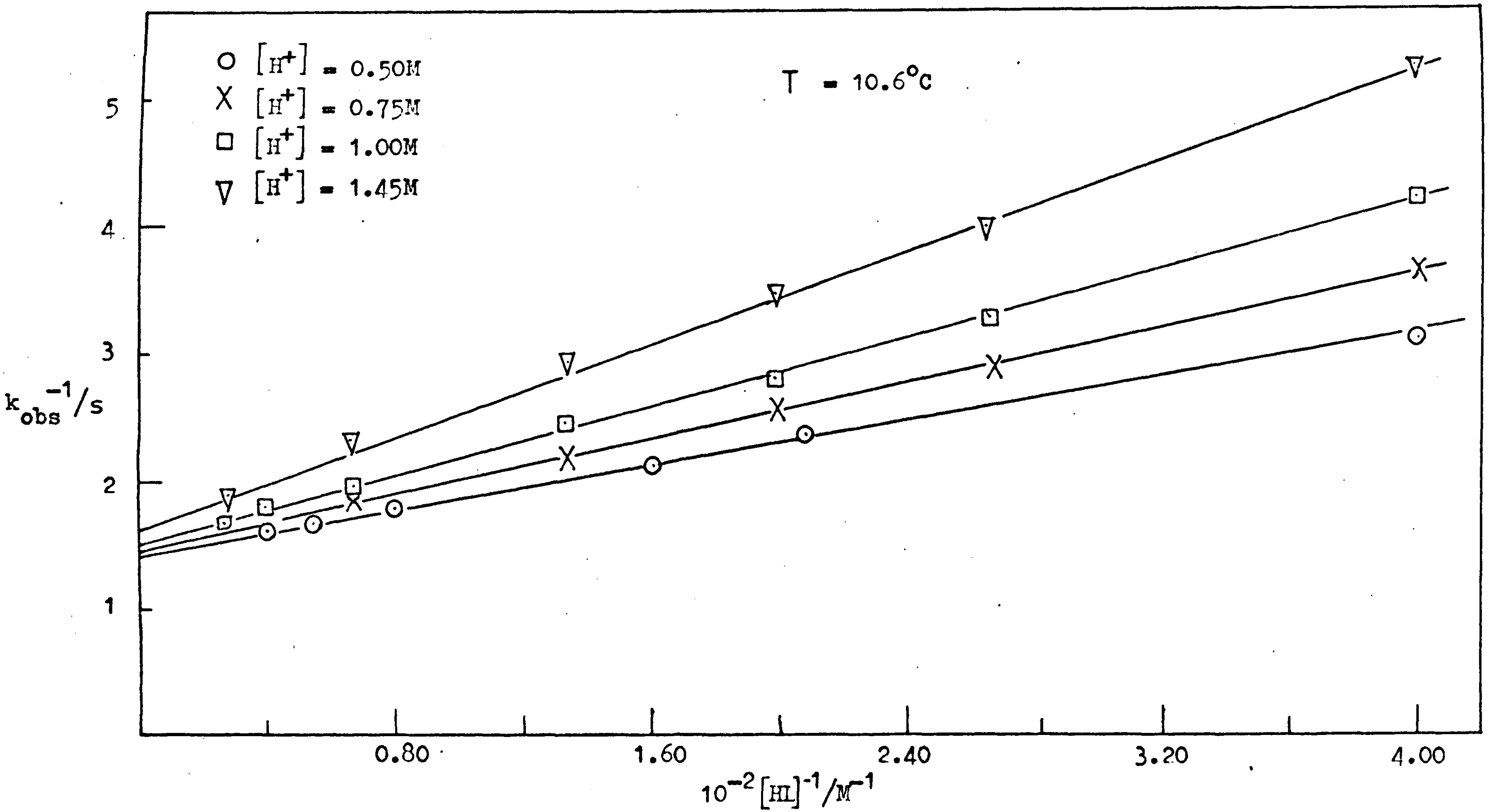


Figure 29 :- Plots of k_{obs}^{-1} versus $[\text{malic acid}]^{-1}$ (equation 45), at λ = 357nm and I = 1.50M.

(e) Evaluation of Equilibrium Constants

Equation (46) follows from (45) and the slopes and intercepts of the plots of k_{obs}^{-1} vs $[HL]^{-1}$

$$\frac{([H^+] + K_h)}{\text{slope}} \times \text{Intercept} = K_1 [H^+] + K_2K_h \qquad (46)$$

When the values of experimental slopes and intercepts obtained from data shown in Table 10, derived from equation (45), are plotted against $[H^+]$, straight lines should be obtained. Figures (30) and (31) show that plots of left hand side of equation (46) against $[H^+]$, are linear in the range of hydrogen ion concentrations studied. Similar linear plots were also obtained at other temperatures. The equilibrium constants (K_{kin}) derived from such plots are presented in Table 11 and compared with those derived from initial optical density changes equation(39). The agreement of data seems to be satisfactory. The larger errors in the values of K_1 are in fact associated with the assessment of the values of intercepts of plots of k_{obs}^{-1} vs $[HL]^{-1}$.

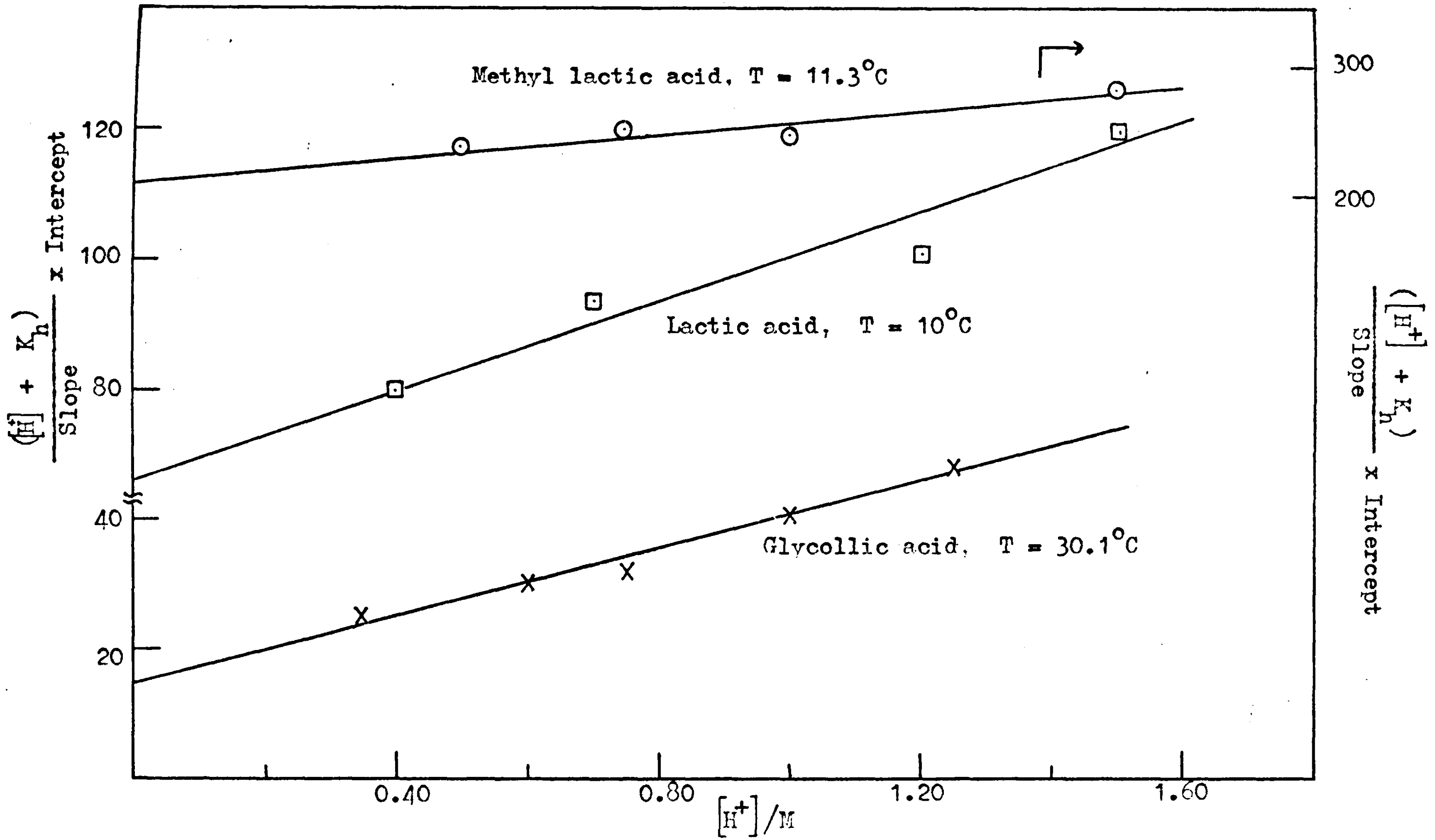


Figure 30 :- Plots of $\frac{([H^+] + K_h)}{\text{Slope}}$ x I versus $[H^+]$ (equation 46) for glycollic, lactic and methyl lactic acids.

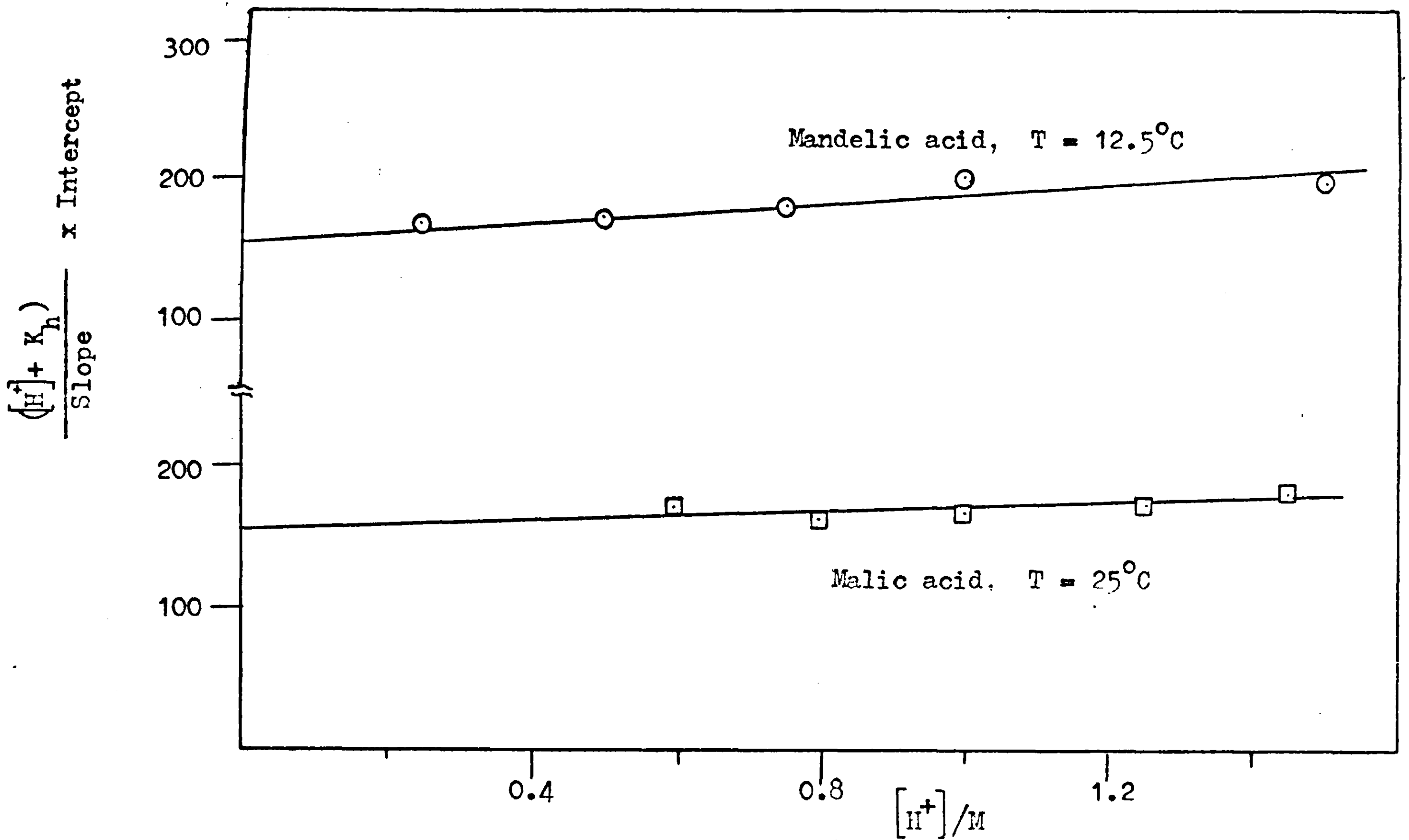


Figure 31 :- Plots of $\frac{([H^+] + K_h)}{\text{Slope}}$ x Intercept versus $[H^+]$ (equation 46) for malic and mandelic acids.

TABLE 11

COMPARISON OF EQUILIBRIUM CONSTANTS DERIVED FROM KINETIC[(a)] AND SPECTROPHOTOMETRIC[(b)] DATA

α-Hydroxy Acid	T/°C	K_1 (c)		K_2K_h		10^{-2} K_2 (c)
		(a)	(b)	(a)	(b)	
Glycollic	11.4	28.4±1.8	33±5	43.9±1.4	40±6	3.43
	17.6	19.7±2.0	25±6	30.8±2.0	30±5	2.00
	25.2	19.8±4.1	22±5	23.7±2.7	25±6	1.15
	30.1	26.4±3.2	23±4	14.4±2.7	18±4	0.65
Lactic	10.0	33 ± 7.4	31±5	67.5±7.7	70±10	5.61
	20.0	17.2±2.7	25±6	41.8±2.8	55±7	2.45
	25.0	15.2±2.9	15±4	38.1±2.8	40±6	1.90
	30.0	18.5±4.9	21±7	27.8±5.3	23±9	1.21
Methyl Lactic	11.3	43 ± 17	52±15	212±17	205±28	17.6
	16.1	84.8±17	90±20	167±18	170±22	12.0
	20.7	77±14	77±21	114±14	145±20	8.55
	25.0	55±10	40±12	74.5±11	110±18	3.72
Mandelic	6.4	66±21	(d)	200±21	(d)	20.0
	12.5	40±13	(d)	151±12	(d)	12.4
	17.5	75±23	(d)	100±19	(d)	7.70
Malic	10.6	30±10	50±30	195±20	175±25	15.5
	16.0	10±4	35±15	205±10	220±15	14.6
	20.0	20±10	25±10	190±10	200±20	11.4
	25.0	10±4	16±10	155±15	145±25	7.80

(a) - calculated using equation (46)

(b) - calculated using equation (39)

(c) - units of M^{-1}

(d) - not calculated due to analytical difficulties

(f) Comparison of Equilibrium and Thermodynamic Data with Oxygen Containing Substrates

The equilibrium constants (K_1) for complexes in Table 12 suggest that the presence of adjacent hydroxyl group in the organic substrate causes a substantial increase in the stability of the complex compared to compounds with only one hydroxyl. Thus the equilibrium constant for cis and trans 1,2-cyclohexanediol[92] are considerably larger than monohydric alcohols cyclohexanol[92] and trans 2-methoxy cyclohexanol[92]. Similarly the greater stability of the complexes with 1,2-glycol[83] as compared to isopropanol[110], sec-butanol[111], methanol[112] and ethanol[113] support the contention that chelates are formed in the former case. On this reasoning one might postulate that chelates are also formed with α-hydroxy acids. This is further substantiated by the fact that monocarboxylic acids i.e. formic[115] and acetic acids[81], form complexes with much smaller equilibrium constants (probably less than unity) which are comparable to monofunctional alcohols. The large errors in the values of K_1 (Table 11) make it difficult to comment of the trend (if any), nevertheless the values are substantially larger than monofunctional substrates.

The trend observed in the values of K_2 (Table 11)

TABLE 12

EQUILIBRIUM CONSTANTS OF INTERMEDIATE COMPLEXES FORMED IN THE COURSE OF THE REDUCTION OF Ce(IV) BY SOME OXYGEN-CONTAINING SUBSTRATES IN AQUEOUS PERCHLORATE MEDIA

SUBSTRATE	T/°C	$K_1^{(a)}$	$K_3^{(b)}$	Remarks	Ref
cis 1,2-cyclohexanediol	15	29.0	(c)	H^+ =1.0M	(92)
trans 1,2-cyclohexanediol	15	18.0	(c)	H^+ =1.0M	(92)
2-methoxy-cyclohexanol	15	2.9	(c)	H^+ =1.0M	(92)
2,3-butanediol	0	17	(c)	H^+ =1.0M	(83)
Ethanol	20	3.0	(c)	H^+ =3.0M	(113)
isopropanol	20	2.2	(c)	H^+ =1.0M	(80)
sec-butanol	15	2.3	(c)	H^+ =1.0M	(80)
cyclohexanol	$15(20)^d$	$4.6(3.9)^d$	(c)	H^+ =1.0M	(80)
α-hydroxy acid	20	20	> 5	I = 1.50M	(e)
Formic acid	49.2	< 1	(c)	I = 2.00M	(115)
Acetic acid	50	< 1	(c)	I = 1.20M	(81)

(a) - units of M^{-1}

(b) - units of M

(c) - not found

(d) - reference (92)

(e) - this work Table (11)

can possibly be explained on the basis of two controlling factors, ionisation constant and the nature of the substituent. From Table 5 the ionisation constants of these acids are in the sequence mandelic $>$ malic $>$ glycollic $>$ lactic $>$ methyl lactic as expected due to inductive effects. Thus, if co-ordination through - OH of the - COOH group is taking place then the relative order in K_2 should be according to the increasing value of the ionisation constant. In fact, the sequence in the values of K_2 (Table 11) is glycollic $<$ lactic $<$ methyl lactic $<$ mandelic $<$ malic. This trend may be understood in terms of the inductive electron releasing effect of alkyl groups in the α-position in the α-hydroxy acids. Unfortunately no comparison of K_2 values can be directly made owing to lack of data on such cerium(IV) complexes.

Plots of $\log K_2$ against I/T show good linearity (Figures 32, 33) and the values of the thermodynamic parameters associated with K_2 are given in Table 13. The greater stability of these chelate complexes as compared to monofunctional alcohols (Table 12) is no doubt supported by more negative values for ΔG_2, but in order to understand the chelate effect properly, one must consider in more detail the significance of these parameters. The two equations used to relate equilibrium constants with thermodynamic

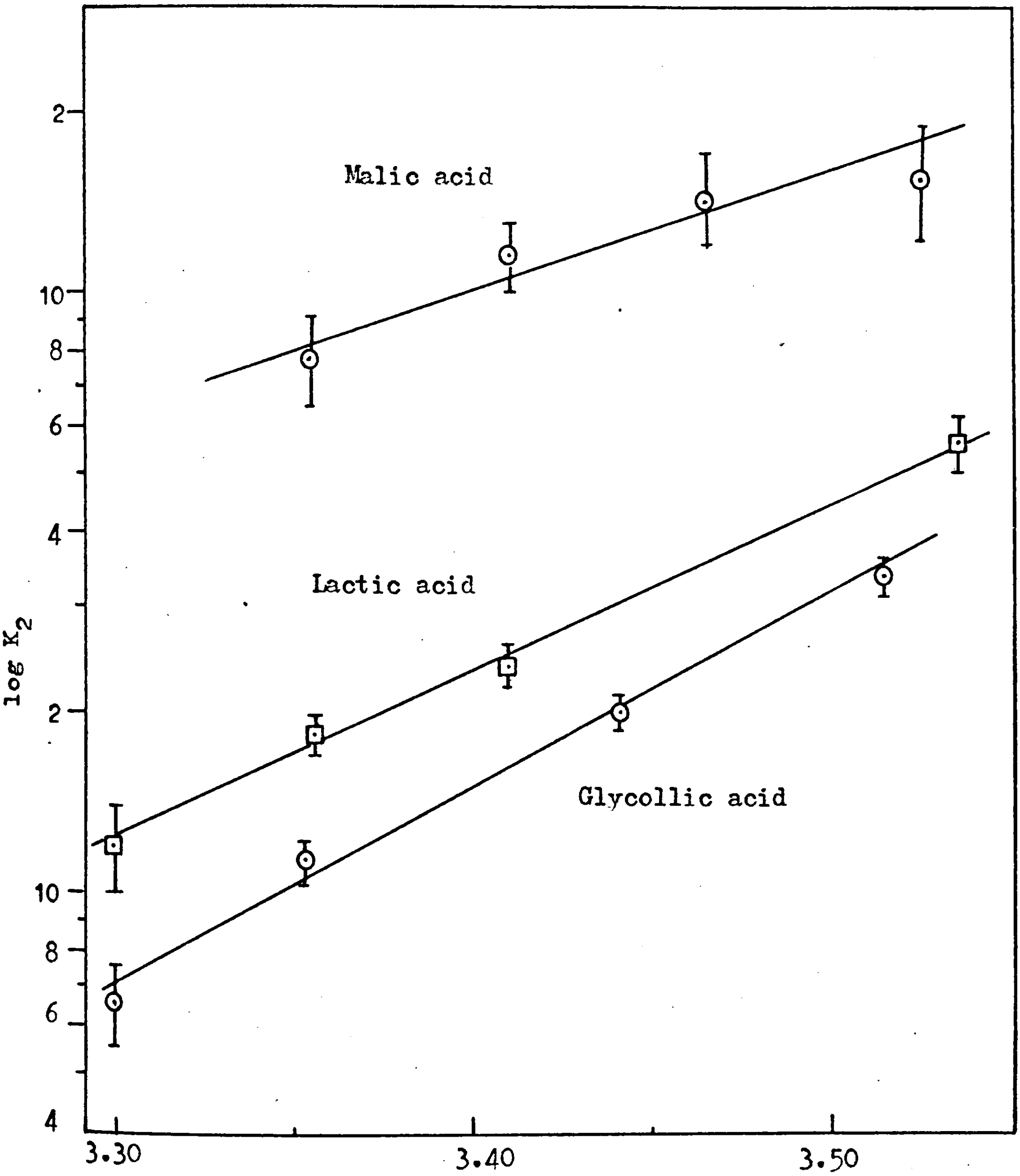


Figure 32 :- Plots of log K_2 against I/T for glycollic, lactic and malic acids(Table 11).

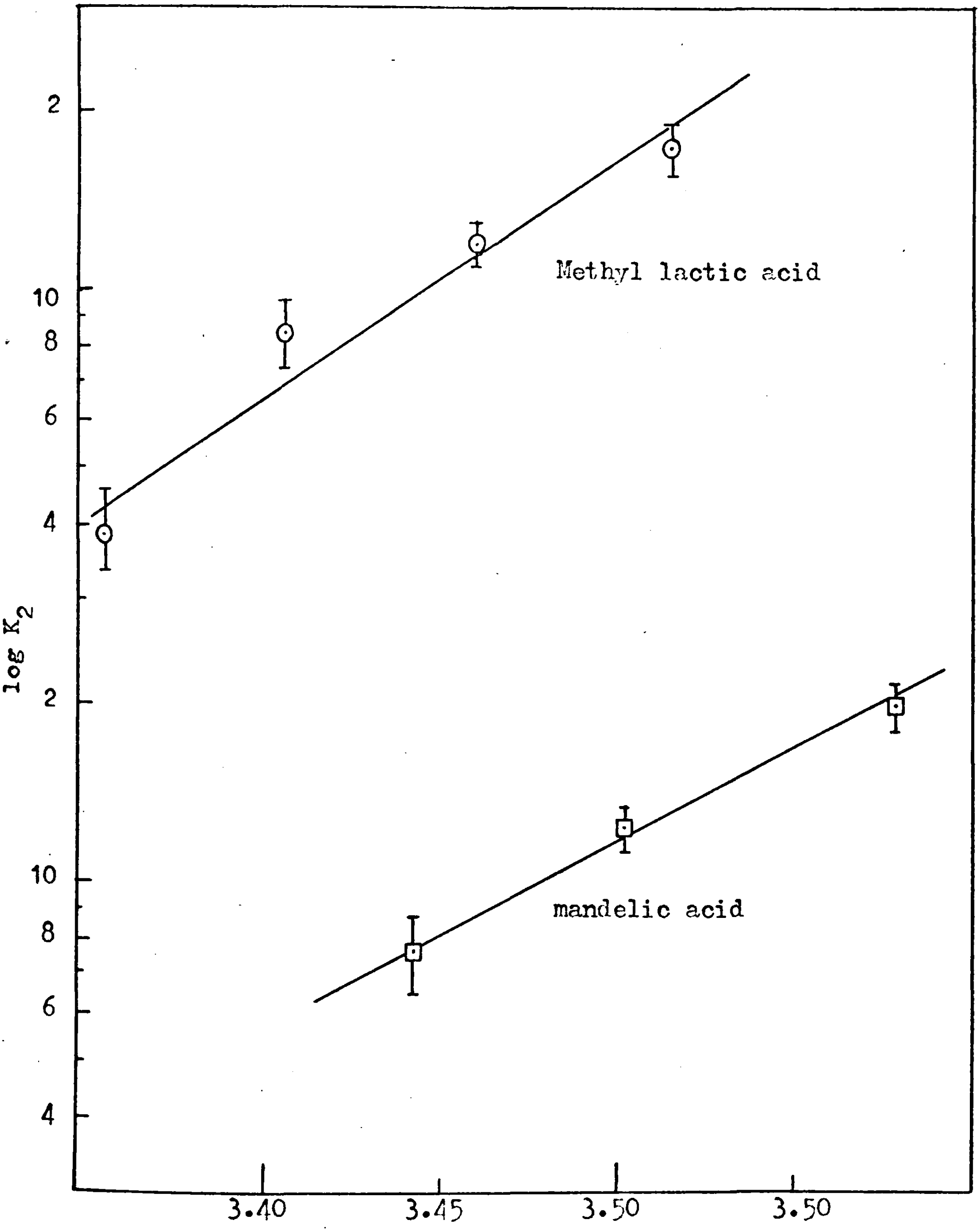


Figure 33 :- Plots of log K_2 against I/T for mandelic and methyl lactic acids (Table 11).

TABLE 13

THERMODYNAMIC PARAMETERS(a) RELATING TO INTERMEDIATE COMPLEXES FORMED IN THE REDUCTION OF CERIUM(IV) BY α-HYDROXY ACIDS AT 25°C IN AQUEOUS PERCHLORIC ACID MEDIA

Substrate	$-\Delta G_2^{(b)}$	$-\Delta H_2^{(b)}$	$-\Delta S_2^{(c)}$
glycollic acid	2.81±0.26	14.7±1.0	39.9±5
lactic acid	3.10±0.17	12.8±0.75	32.5±2
methyl lactic acid	3.51±0.33	18.5±3.3	50.3±4
mandelic acid	3.61±0.46(d)	14.7(d)±1.5	37.2(d)±2
malic acid	3.94±0.40	9.4±2.8	18.5±5

(a) - for K_2

(b) - k cal mole^{-1}

(c) - cal $\text{deg}^{-1}\text{mole}^{-1}$

(d) - extrapolated

parameters are

$$\Delta G^o = - RTInK \qquad (47)$$

and

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (48)$$

Thus an increase in an equilibrium constant may arise because ΔH^o becomes more negative, because ΔS^o becomes more positive, or both.

In the formation of a complex, ΔH^o is attributable mainly to the differences in the bond energies of the metal-oxygen bonds broken and the new metal ligand bonds formed. Experimental studies of the enthalpy changes for a number of reactions have shown that enthalpy differences between chelated and nonchelated systems cannot, in general, account for the chelate effect. Hence the chelate effect must be mainly an entropy effect, and, from the measured values of the equilibrium constants and enthalpies, the ΔS^o values may be calculated.

Although the oxidations of moncfunctional alcohols have been extensively studied, no apparent correlations of either ΔH or ΔS with equilibrium constants have emerged. The same situation seems to be prevailing in α-hydroxy acids. Thus no direct comparison with any related system is possible. One may, however, generalise a rationalisation of these reactions in terms of both ΔH_2 and ΔS_2 terms being operative.

It is acknowledged that more data are required on systems involving chelate and non-chelate complexes in perchlorate media in order to completely understand this interesting part of cerium(IV) chemistry.

Although a transient complex has been characterised in the Co(III) oxidation of malic acid[120] with an equilibrium constant of $34M^{-1}$ at 25^{o}C, whereas with other α-hydroxy acids there are speculations whether or not such complexes exist[121]. A complete study on these systems may be helpful in understanding the role of such intermediates. The larger values for K_2 (and possibly K_1) probably arise from a combination of the higher cationic charge and of the greater size of the hydrated cerium(IV) ion (as evidenced by co-ordination number>6[89]) compared with $Mn(III)_{aq}$ and $Co(III)_{aq}$. Thus with Ce(IV) the ion-dipole forces are stronger and the substrate can penetrate more easily and farther into the sheath of water molecules.

(g) Evaluation of Rate Constants

From equation (45) and the slopes of plots of k_{obs}^{-1} vs $[HL]^{-1}$, equation (49) can be deduced, so that

$$\frac{([H^+] + K_h)}{\text{Slope}} = n\,k_1K_1[H^+] + n\,k_2K_2K_h \qquad (49)$$

a plot of $([H^+] + K_h)$ / slope against $[H^+]$ should be linear and from values of K_1 and K_2K_h computed by equation (46), k_1 and k_2 can be calculated. Values of $([H^+] + K_h)$/slope calculated from the known values of K_h, $[H^+]$ and slope are given in Table 14 and typical plots are shown in Figure 34, where it may be seen that no significant variations with $[H^+]$ were observed over a wide concentration range, indicating that only one complex, namely the species CeL^{3+} undergoes intramolecular decomposition (k_2). The two possible reasons for not observing the decomposition of $CeHL^{4+}$ species are: firstly, the complex $CeHL^{4+}$ is present in too low concentration, secondly, the rate constant, k_1, is markedly smaller than k_2 or both. As shown in Table 11 the values of K_1, calculated for malic acid, is at or near the limits or detection by the methods used in this study. Also if negligible concentrations of this complex are present in solution, the assumptions made earlier for the value of K_h are justified. Thus equation (49) can be rearranged to the following form

$$\frac{[H^+]}{nk_2K_2K_h} + \frac{1}{nk_2K_2} = \text{slope} \qquad (50)$$

so that the plot of slope vs $[H^+]$ should give a straight line with intercept and slope equal to $1/nk_2K_2$ and $1/nk_2K_2K_h$, from which K_h can be evaluated. The data for malic acid (Table 10) when computed in this manner yielded an independent

TABLE 14

DERIVATION OF RATE CONSTANTS FOR THE REDOX REACTION BASED ON EQUATION (49)

α-Hydroxy Acid	T/°C	$[H^+]$/M	$\frac{([H^+] + K_h)/s^{-1}}{S}$
Glycollic	30.1	0.35	27.2 ± 0.63
		0.60	28.1 ± 0.38
		0.75	27.1 ± 0.39
		1.00	31.4 ± 0.48
		1.25	31.8 ± 0.82
	25.2	0.35	16.7 ± 0.40
		0.70	18.1 ± 0.40
		0.85	17.6 ± 0.68
	17.6	0.70	6.75 ± 0.26
		1.00	6.53 ± 0.072
		1.25	6.80 ± 0.20
	11.4	0.30	3.47 ± 0.11
		0.50	3.33 ± 0.11
		0.70	3.48 ± 0.05
		0.90	3.49 ± 0.02
		1.25	3.26 ± 0.05
Lactic	30.0	0.50	262 ± 1.9
		0.75	281 ± 3.2
		1.00	308 ± 7.7
		1.50	296 ± 1.52
	25.0	0.25	169 ± 7.6
		0.50	173 ± 3.0

α-Hydroxy Acid	T/°C	$[H^+]$/M	$\frac{([H^+] + K_h)/s^{-1}}{S}$
Lactic	25.0	0.75	168 ± 2.2
		1.25	171 ± 1.01
		1.50	175 ± 3.4
	20.0	0.30	90.3 ± 2.1
		0.60	93.9 ± 2.3
		1.25	105 ± 1.6
		1.50	96.4 ± 1.1
	10.0	0.40	30.0 ± 1.2
		0.70	32.8 ± 0.39
		1.20	32.3 ± 0.7
		1.50	37.8 ± 1.1
Methyl Lactic	25.0	0.60	832 ± 21
		0.75	840 ± 18
		0.90	874 ± 14
		1.20	841 ± 15
		1.35	838 ± 15
		1.50	812 ± 12
	20.7	0.35	594 ± 23
		0.50	639 ± 15
		0.75	581 ± 10
		1.00	556 ± 11
		1.25	587 ± 16
		1.50	576 ± 11
	16.1	0.50	425 ± 11
		0.75	447 ± 16

α-Hydroxy Acid	T/°C	$[H^+]/M$	$\frac{([H^+] + K_h)/s^{-1}}{S}$
Methyl Lactic	16.1	1.00	406 ± 7
		1.25	426 ± 17
		1.50	382 ± 8
	11.3	0.50	245 ± 9
		0.75	240 ± 5
		1.00	204 ± 3
		1.50	188 ± 3
Malic	25.0	0.60	790 ± 23
		0.80	805 ± 19
		1.00	833 ± 6
		1.25	798 ± 9
		1.45	800 ± 10
	20.0	0.50	504 ± 11
		0.75	495 ± 17
		1.00	475 ± 15
		1.25	504 ± 7
		1.50	489 ± 13
	16.0	0.30	302 ± 13
		0.90	305 ± 6
		1.25	310 ± 2
		1.50	304 ± 5
	10.6	0.25	180 ± 16
		0.50	152 ± 3
		0.75	158 ± 2
		1.00	169 ± 3
		1.45	177 ± 5

α-Hydroxy Acid	T/°C	$[H^+]$/M	$\frac{([H^+] + K_h)/s^{-1}}{S}$
Mandelic	17.5	0.75	7210 ± 331
		1.00	6690 ± 198
		1.25	6830 ± 125
	12.5	0.50	4460 ± 192
		0.75	4260 ± 125
		1.00	4340 ± 101
		1.25	4160 ± 50
	6.4	0.25	2430 ± 253
		0.50	2930 ± 129
		0.75	2620 ± 154
		1.00	2530 ± 82
		1.35	2290 ± 20
		1.50	2450 ± 120

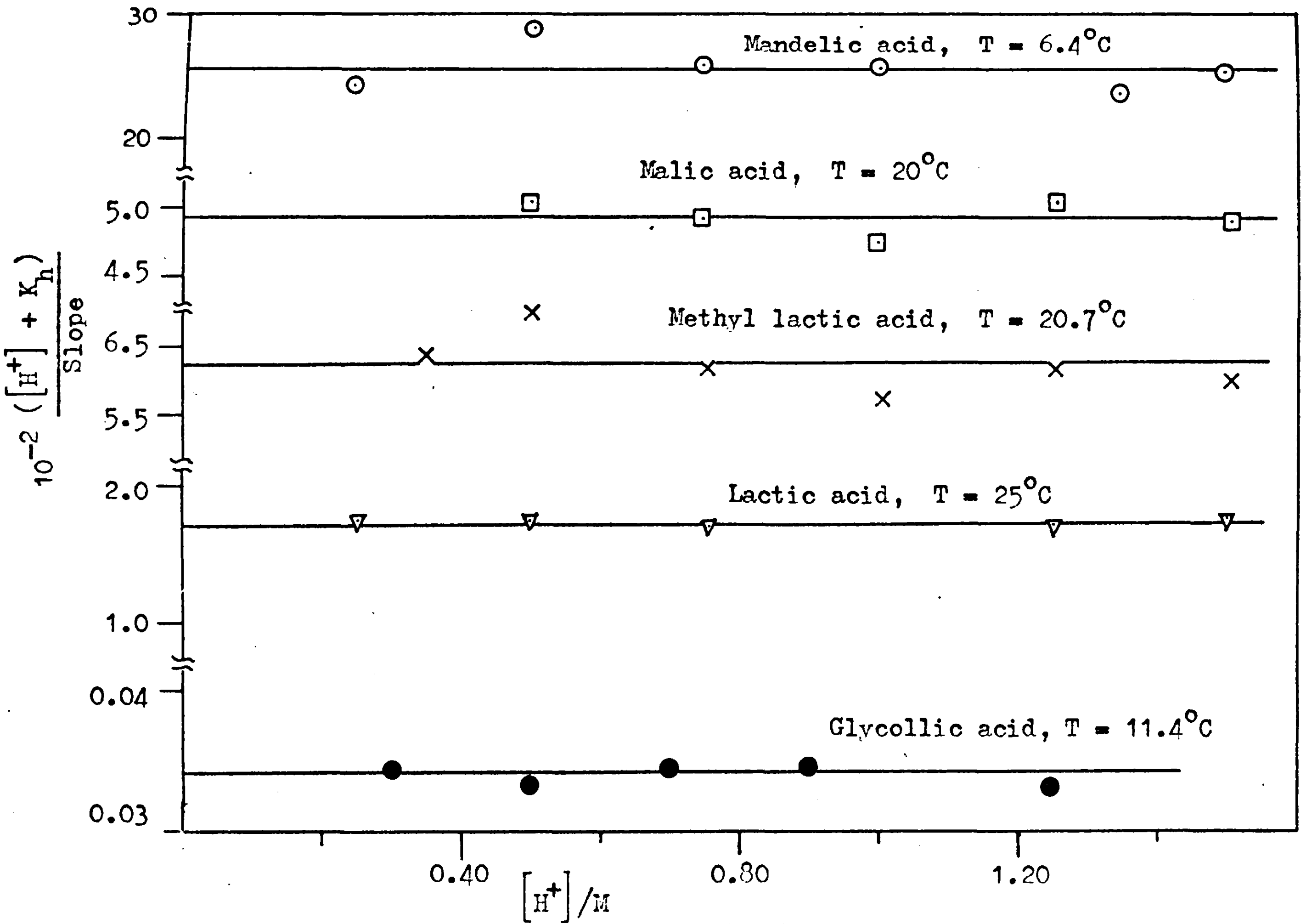


Figure 34 :- Plots of $\frac{([H^+] + K_h)}{\text{Slope}}$ against $[H^+]$ (equation 49) for α-hydroxy acids.

measurement of K_h (Table 15) by kinetic methods and further substantiates the finding of a value for the hydrolysis constant which is considerably lower than that quoted previously[77,80,81,121].

The situation regarding the estimation of K_h by the above method in other α-hydroxy acids is somewhat different in that the values of K_1 and K_2K_h are comparable in some cases, especially at high temperatures. It may be added here that intercepts of plots of k_{obs}^{-1} vs $[HL]^{-1}$, unlike malic acid, show a greater dependence on $[H^+]$. This then leads to the conclusion that k_1 is considerably lower than k_2. This result is surprising, since protonation would not be expected to alter radically the redox potential of the cerium(IV) complex.

The only systems studied so far in which paths corresponding to k_1 and k_2 have been observed, are that of oxidation of isopropanol[110], sec-butanol[111], and cyclohexanol[111]. The rate constants for the oxidation of $CeRR_1OH^{4+}$ (k_1) and CeR_1RO^{3+} (k_2) have been measured and k_1 is upto 5 times larger than k_2. It may be pointed out that in other investigations on a large number of mono[80,92,112,113], and polyfunctional alcohols[91,114], the path corresponding to k_2 has not been detected.

The existence of transient complexes in the reactions

TABLE 15

HYDROLYSIS CONSTANT (K_h) FROM KINETIC DATA[a]

$T/^{o}C$	$K_h^{(b)}/M$	
10.6	0.12	
16.0	0.14	
20.0	0.17	$0.17^{(c),(d)}$
25.0	0.20	

(a) - from equation (50)

(b) - $\Delta H = 5.2 \pm 0.7$ k cal $mole^{-1}$

(b) - $\Delta S = 14.3 \pm 4$ cal $K^{-1}mol^{-1}$

(c) - chapter (3)

(d) - reference (79)

of these oxygen containing substrates in perchlorate media has been well documented. Two types of mechanism have been described to explain the kinetic data. Firstly, in which the rate of decomposition of these complexes increases with increasing $[H^+]$ and secondly, where an inverse $[H^+]$ dependence is observed. In this, the α-hydroxy acids are observed to follow the second pattern of behaviour. The malonic acid, however, (see later) is representative of the first class.

The oxidations of ethanol[113], 2,3-butanediol[83] and glycerol were the first examples in which the increase in the rate of decomposition of the transient complexes with increasing $[H^+]$ was observed. The authors have chosen to consider Ce^{4+} as an oxidant to explain the observed $[H^+]$ dependence. This suggestion was later confirmed in a number of other kinetic studies. For example, Mohamad and Rao[112] reported the oxidation of methanol by cerium(IV) perchlorate and based on their kinetic data the value of K_h was found to be 3.6M at 20°C and a common intercept of plots of k_{obs}^{-1} vs $[CH_3OH]^{-1}$ at all acidities was observed. In a more extensive study on the oxidation of a large number of a variety of alcohols viz. aliphatic - primary, secondary and tertiary and also aromatic primary alcohols, Santappa and Rangaswamy[80] also observed no $[H^+]$ dependence on intercepts of plots of k_{obs}^{-1} vs $[\text{Alcohol}]^{-1}$, thus suggesting only one species, namely $CeROH^{4+}$, undergoing decomposition. Surprisingly enough the value of ΔH for K_h was found to be $\simeq$ 16 k cal mole^{-1} for thirteen different alcohols, as compared to $\Delta H = 5.2$ k cal mole^{-1}, obtained in this study as well as by Skoog and Offner[79]. Moreover, the value of K_h (5.2M) obtained by Santappa and Rangaswamy[80], in fact contradicts the previous reported value of 0.13 ± 0.003M at 25°C by Santappa and Venkatakrishnan[119] in the kinetic study of the oxidation of acetone by cerium(IV) in perchloric acid media. This value of K_h was reported to be in good agreement with another value obtained at the same cerium(IV) concentration ($\backsim$ 0.01M) in a study[122] on the polymerisation of methylacrylate initiated by cerium(IV) ion in aqueous solution.

Recently Wells and Husain have re-investigated the kinetics of the oxidation of isopropanol[110], sec-butanol[111] and cyclohexanol[111] and suggested that in fact both forms of cerium(IV), i.e. Ce^{4+} and $CeOH^{3+}$, form complexes of the type $CeROH^{4+}$ and $CeRO^{3+}$. In addition they also postulated that alcohols are present as protonated species, although no kinetic evidence was observed for the oxidation of these species. It may be added that no such species was considered to be present in earlier studies on these alcohols[80,83,92,112-114]. Furthermore, in the oxidation of isopropanol[110] k_{obs} was found to be independent of isopropanol when the latter was present in the range of two thousand to six thousand times excess of Ce(IV). The observed $[H^+]$ dependence of the intercepts of k_{obs}^{-1} vs $[\text{isopropanol}]^{-1}$ at different temperatures was suggested to be due to the proton equilibria of the type

$$CeROH^{4+} \rightleftharpoons CeRO^{3+} + H^+ \qquad (51)$$

and reported the rate constants $k_1 = 2.2 \times 10^{-3}S^{-1}$ and $k_2 = 1.02 \times 10^{-3}S^{-1}$ at 25°C, corresponding to the decomposition of $CeROH^{4+}$ and $CeRO^{3+}$ respectively. It must be pointed out that the values of equilibrium and rate constants quoted in that studies[110,111] were obtained by using a high K_h value (5.2 as compared to 0.2) and also incorporating K_e (protonation constant for alcohols) in their rate laws. However, on carefully re-examining the published kinetics data for sec-butanol and cyclohexanol[111], the author has found no acid dependence, as compared to α-hydroxy and malonic acids reactions (Figures 25-29,45), on the intercepts of plots of k_{obs}^{-1} vs $[ROH]^{-1}$ at 25°C and 35°C for sec-butanol (Figure 35) and from 15° to 44.7°C for cyclohexanol (Figure 36). The data at 15° for

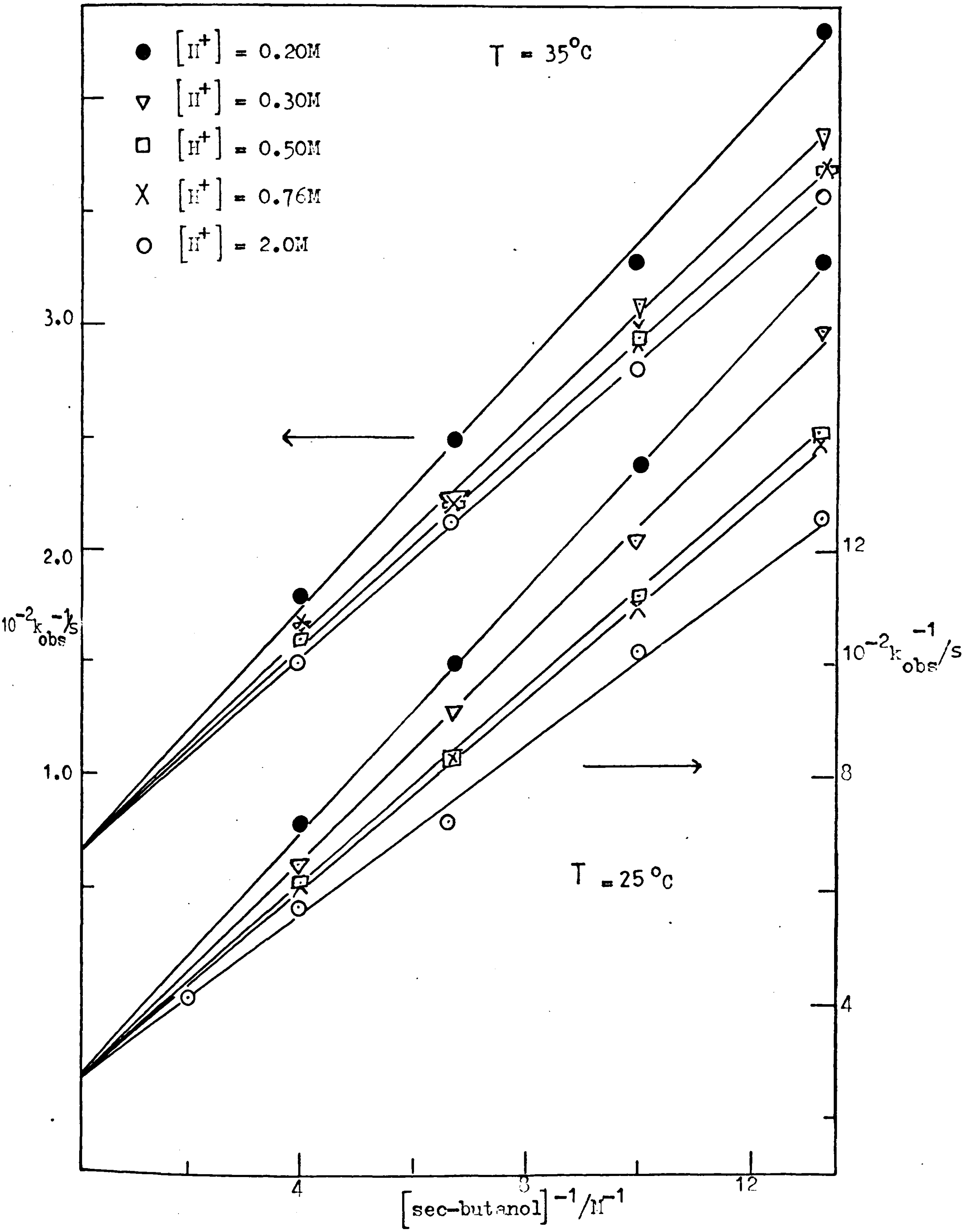


Figure 35 :- Plots of k_{obs}^{-1} versus $[\text{sec-butanol}]^{-1}$ (data from ref. 111).

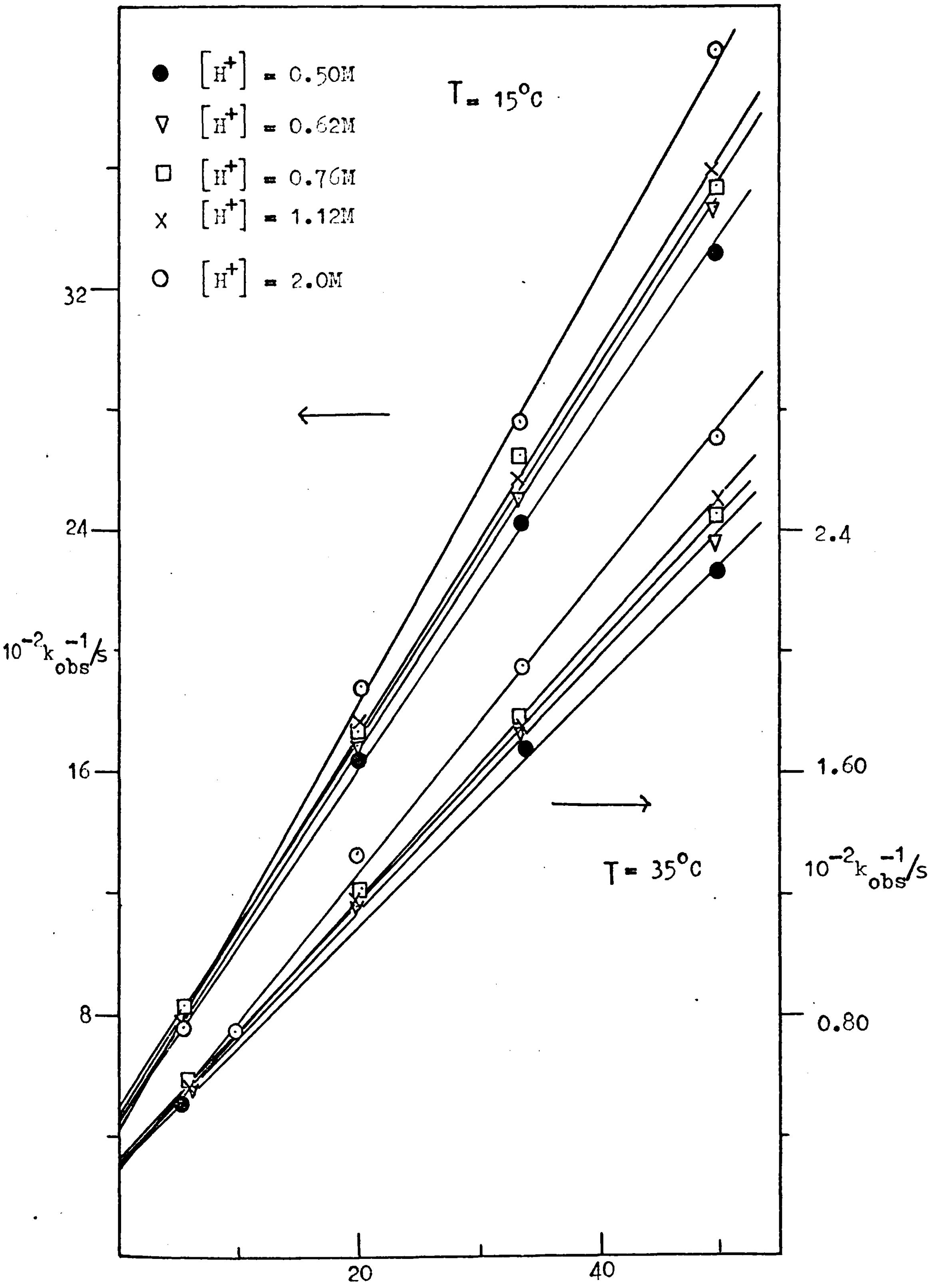


Figure 36 :- Plots of k_{obs}^{-1} versus $[\text{cyclohexanol}]^{-1}$ (data from ref. 111)

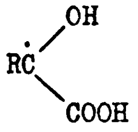
sec-butanol[111] are not consistent with the experimental observations, thus showing some deviation from the common intercept of plots of k_{obs}^{-1} vs $[ROH]^{-1}$. Another observation worth mentioning about their data is that an inverse dependence of k_{obs} on $[H^+]$ was found in the oxidation of cyclohexanol[111]. This observation is not in keeping with results from other laboratories[80,92]. The fact that since there is only a slight acid dependence on the rate of these reactions suggests that both complexes decompose at the same rate. Treatment of their kinetic data according to the scheme (45) proposed in the present study yielded almost identical rate constants, ie. $k_1 \simeq k_2$, with an activation energy of 23k cal mole^{-1} and 25k cal mole^{-1} for sec-butanol and cyclohexanol respectively. These values are no doubt in good agreement with those reported by Santappa and Rangaswamy[80], but differ markedly from 18.3 and 29.7 k cal mole^{-1} for sec-butanol[111] and 31 and 24 k cal mole^{-1} [111]for cyclohexanol, as reported by Wells and Husain, for reaction paths corresponding to k_1 and k_2 respectively. Similarly the discrepency observed in the values of equilibrium constants (K_1) for these substrates can be explained on the same reasoning discussed above. Using the scheme (45) the values of K_1 obtained, based on Well's data, are from 3 to 6 M^{-1} as compared to 19 and 21 M^{-1} at

$25^\circ C$ for both sec-butanol and cyclohexanol. It may be pointed out that if Santappa's data[80] is treated according to scheme (46), equilibrium constants (K_1) lower than those reported in Table 12 would be obtained and thus the comparison made previously (Table 12) is justified.

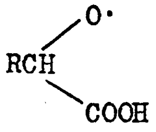
Comparison of Rate Constants and Thermodynamic Parameters in Related Systems

Transient intermediates formed as precursors to the oxidation step have now been well documented in many cases, both kinetically and in a few cases direct formation has been observed. The findings in the present study further support an inner-sphere mechanism as the one operating and a comparison can thus be made between an inner- and outer-sphere or apparent bimolecular mechanism.

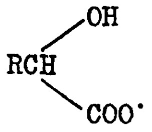
The oxidation of α-hydroxy acids by cerium(IV) sulphate has been extensively studied and unfortunately different conclusions have been derived[100–102,104,105,118]. Although the stoicheiometry of mandelic[102] and methyl lactic acids[102,105,118] has been established as two equivalents of cerium(IV) per mole of organic substrate to yield benzaldehyde and acetone respectively; with other α-hydroxy acids differing stoicheiometry and mechanisms have been reported in support of their data. The main difference lies in the site of initial oxidation of the substrate yielding the following possible radicals



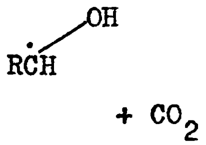
I



II



III



IV

Radical I can be ruled out because it would be oxidised to a α-keto acid which would be rapidly further oxidised to R COOH; in fact the stoicheiometry as determined in the present study is 2 Ce(IV) : 1 molecule of α-hydroxy acid (except malic acid) and the major product is aldehyde or ketone. These data are, however, compatible with the production of radicals II - IV and discrimination can be made only with the aid of kinetics.

Krishna and Tewari[101] have favoured II to account for the mixture of products. In the oxidation of deuterated mandelic acid by cerium(IV), Kemp and Waters [123] found no kinetic isotopic effect and suggested C - C fission to be important. This was later confirmed by Grover and Gupta[118] in the oxidation of glycollic and substituted glycollic acids. Radical IV is thus seen as being best suited to explain the trend observed in this study, as well as previously[105], in the rates of oxidation of these α-hydroxy acids, if stabilisation of the radical R CHOH is important. The same radical has been also postulated to be formed in the Mn(III) oxidation[123], but the trend in the oxidation rates is altered for V(V)[123]. It is interesting to note that although the same sequence in the oxidation rates is observed in both acid media, the larger values of rate constants in perchlorate media reflect the enhanced oxidative power of cerium(IV) as compared to that of cerium(IV) sulphate complexes. Figure 37 illustrates the comparison in rates of oxidation of α-hydroxy acids by Ce(IV) in sulphate and perchlorate media and by Mn(III) and V(V).

The reaction stoicheiometry in the malic acid oxidation may be understood if the ligand is oxidised in a one electron step to yield cerium(III) and a radical which would be further oxidised by another mole of Ce(IV) yielding oxaloacetic acid. Independent studies on the cerium(IV) oxidation of this substrate show it to be extremely reactive and undergo further oxidation to malonic acid. The oxidation product is not considered to be malonic acid since this reaction is slower than for malic acid, and it may be that, in this case, further decarboxylation of the radical occurs with

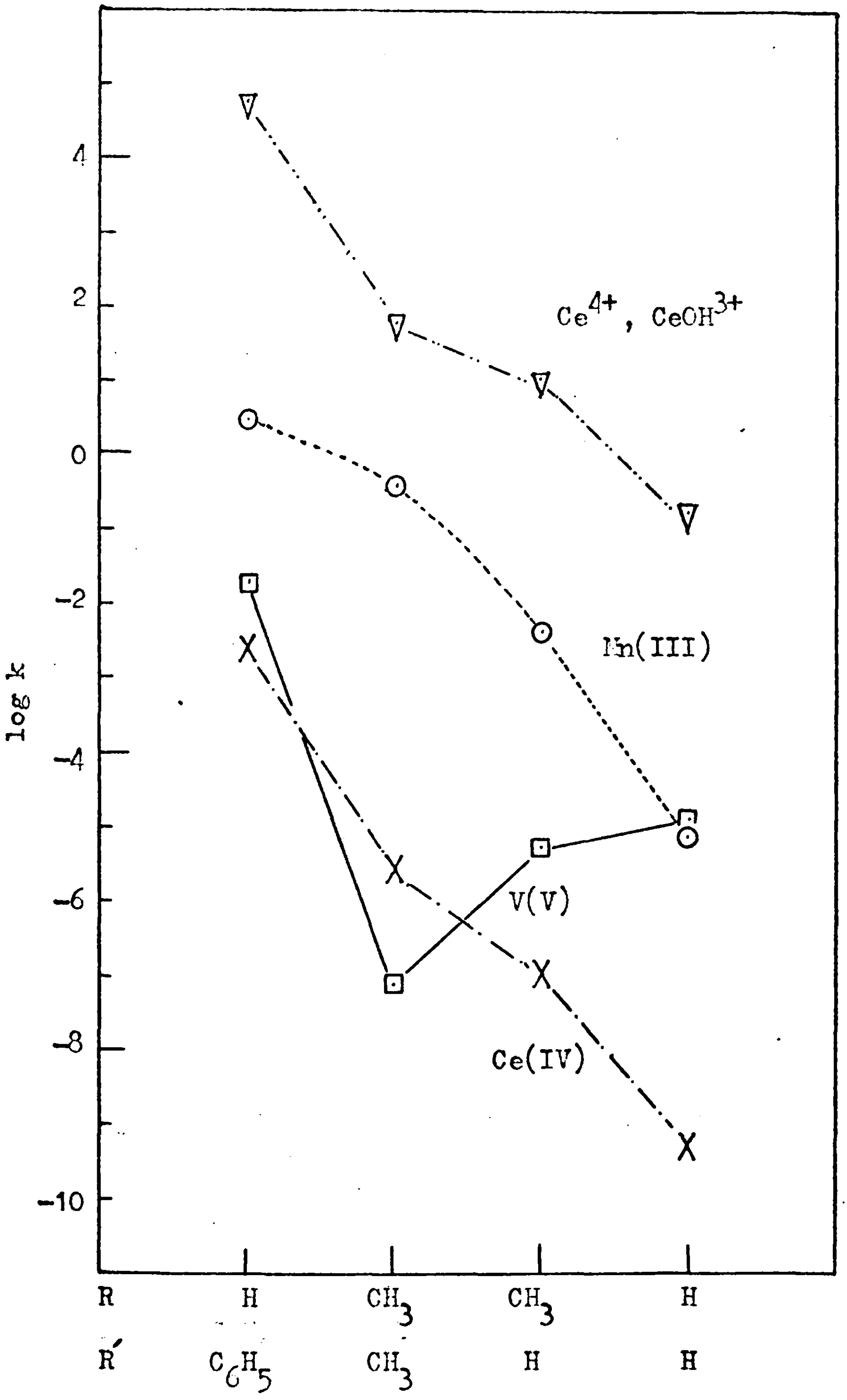


Figure 37 :- Relative rates of oxidation of α-hydroxy acid (R R′ C(OH)COOH) by Mn(III), Ce(IV) and V(V) in dilute H_2SO_4 medium. Temperature=24.4°C (Mn(III)),26.6°C (V(V) and Ce(IV)) (data taken from ref. 123) and Ce(IV) in perchlorate media T = 25°C (this work - Table 16).

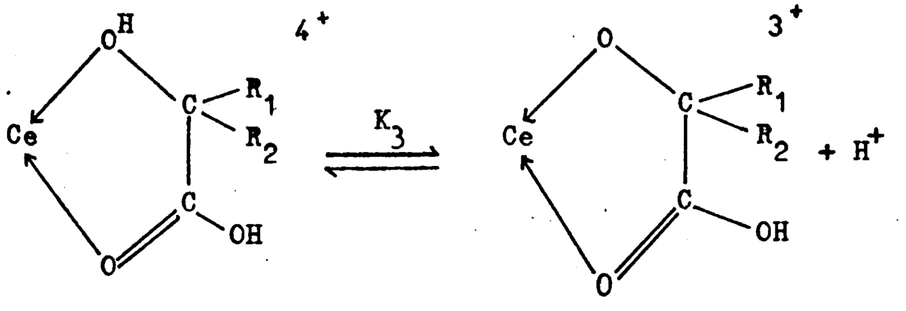
accompanying increase in the number of moles of oxidant required.

The oxidation of the free radical intermediate produced in the oxidation of organic substrates by cerium(IV) depends on a number of factors. The problem of whether the radical will undergo further oxidation or whether dimerisation and disproportionation products will occur, seems to be determined by the reactivity of both the oxidant and the substrate. The only recorded cases of dimer formation in the presence of cerium(IV) seem to be observed by Schaafsma[124] in the oxidation of cyclopropanol in sulphuric acid and by Rocek[125] in the oxidation of cyclobutanol in perchloric acid media. This can be explained on the basis that the radicals are less reactive than the substrates and so allow accumulation of radicals to undergo polymerisation. The fact that analysis of the oxidation products of α-hydroxy acids in both acid media shows them to be similar, strongly suggests that the intermediate radicals formed are far more reactive than the original substrates.

Wells and Husain have shown that rate of oxidation of isopropanol[110] (ROH) approaches a limiting value, ie. k_{obs} becomes zero order in ROH, under a very large excess of alcohol and only at high $[H^+]$ and low temperatures.

They suggested[110] that the formation of $CeRO^{3+}$ occurs via proton dissociation from $CeROH^{4+}$ and not via $CeOH^{3+}$ and ROH. No limiting rate was observed in the Mn(III) oxidation of primary alcohols[126,127], but on the comparative basis it was postulated that the same mechanism also operates in Mn(III) oxidations. Since this limiting rate was not observed, at least under the experimental conditions employed, it is difficult to distinguish kinetically the paths (36) and (37) for the formation of CeL^{3+} species.

It should be noted that $K_2K_h = K_1K_3$ equations (21),(35) - (37) and that, whilst an approach has been adopted which yields confirmation of K_2, K_1 and K_h values, an alternative path for complex formation is via dissociation of the protonated complex, $CeHL^{4+}$. A value of $K_3 \sim 5$-$15M^{-1}$ in the case of malic acid, and ~ 2-$5M^{-1}$ for other α -hydrpxy acids may be calculated from the present data, the inaccuracy resulting from uncertainties in K_1. There are certain attractions in this approach in that it is difficult to envisage from electrostatic considerations



(52)

why the tripositive $CeOH^{3+}$ should complex more strongly than Ce^{4+}_{aq} ion, and it may be that, although thermodynamically the overall reaction (36) is favoured ($\Delta G > 2.8$), in fact K_2 represents a composite equilibrium constant in which one of the formation steps is kinetically slow. If this were the case, then reaction (52) would represent the rate by which the reactive species in the redox system is formed.

Arrhenius plots of the temperature dependence of rate constants, k_2 (Table 16), show good linearity (Figures 38, 39) indicating that the enthalpy of activation is constant over the temperature range studied. Although the values of k_2 (Table 15) decrease in the order (allowing the same stoicheiometry and initial step in the malic acid reaction) mandelic > methyl lactic > malic > lactic > glycollic acids, as expected due to greater stabilisation of radical, the enthalpy of activation, ΔH_2^* (Table 16), does not decrease in the order glycollic > lactic > malic > methyl lactic > mandelic acids. This however, contrasts with the apparent bimolecular (or an outer-sphere) oxidation of α-hydroxy acids by cerium(IV) in sulphate media[105], where the rate constant decreases in the sequence methyl lactic > lactic > glycollic acids, but the enthalpy of activation is approximately the same ($\sim$ 20 k cal $mole^{-1}$) in all cases. It may be added that comparison with other

TABLE 16

DEPENDENCE OF k_2 ON TEMPERATURE

Substrate	T/°C	k_2/s^{-1}	$\Delta H_2^{*(a,b)}$	$\Delta S_2^{*\,(a,c)}$
Glycollic Acid	11.4	0.0388 ± 0.006		
	17.6	0.109 ± 0.005		
	25.2	0.374 ± 0.02	28.8 ± 1.2	36.2 ± 5
	30.1	1.01 ± 0.05		
Lactic Acid	10.0	0.246 ± 0.02		
	20.0	1.18 ± 0.04		
	25.0	2.25 ± 0.05	25.0 ± 0.8	26.9 ± 4
	30.0	5.20 ± 0.1		
Methyl Lactic Acid	11.3	0.516 ± 0.08		
	16.1	1.24 ± 0.06		
	20.7	2.57 ± 0.06		
	25.0	5.60 ± 0.08	28.5 ± 0.4	40.5 ± 6
Mandelic Acid	6.4	6.35 ± 0.06		
	12.5	14.2 ± 0.04		
	17.5	34.4 ± 0.1	23.4 ± 1.3	$28.8 \pm 3^{(c)}$
Malic Acid	10.6	0.085 ± 0.010		
	16.0	0.149 ± 0.001		
	20.0	0.259 ± 0.007		
	25.0	0.52 ± 0.06	20.6 ± 1.5	9.5 ± 5

(a) - T = 25°C

(b) - units of k cal mole^{-1}

(c) - units of cal $\text{deg}^{-1}\text{mole}^{-1}$

(d) - extrapolated

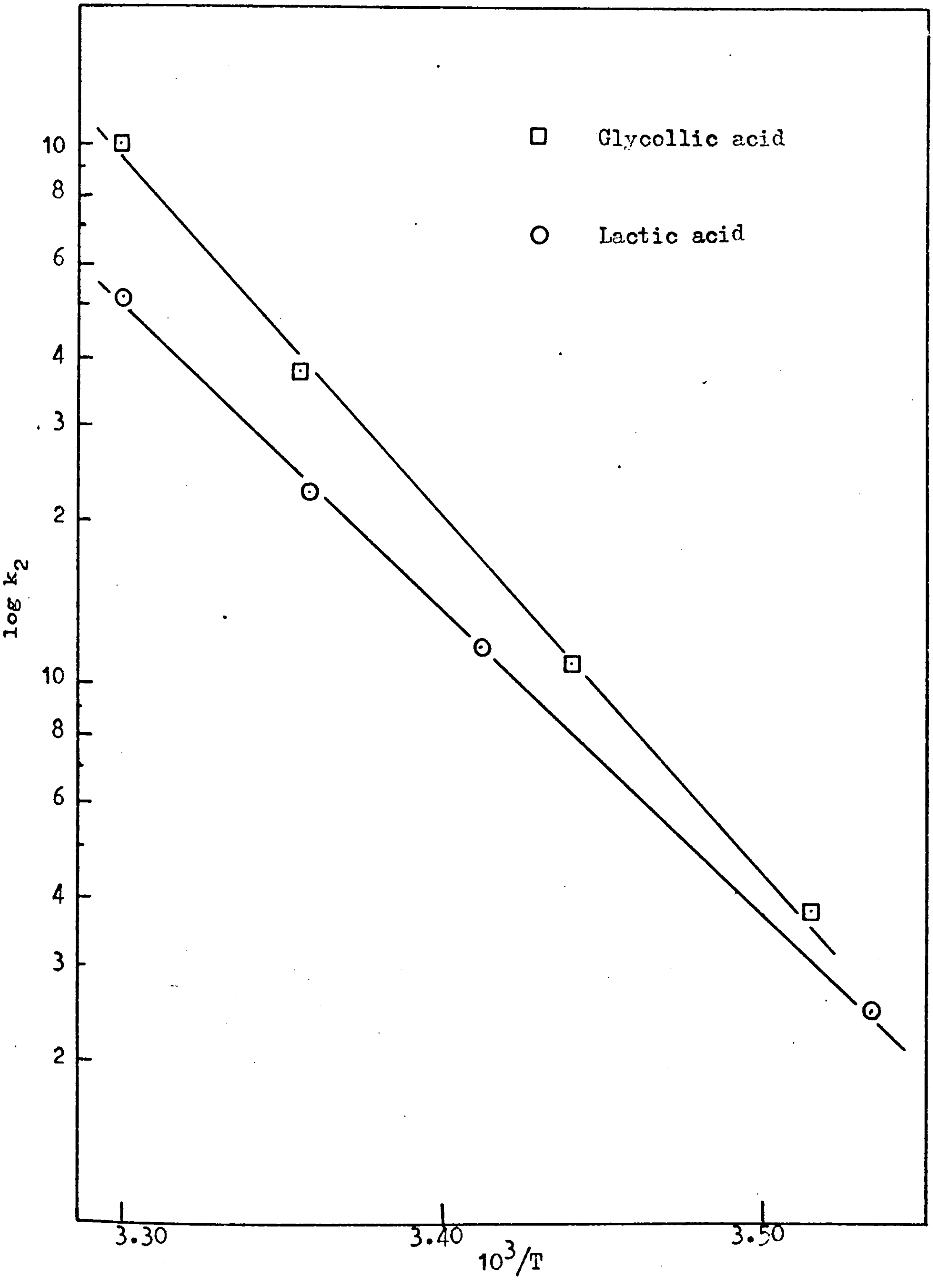


Figure 38 :- Plots of log k_2 versus $^{I}/_{T}$

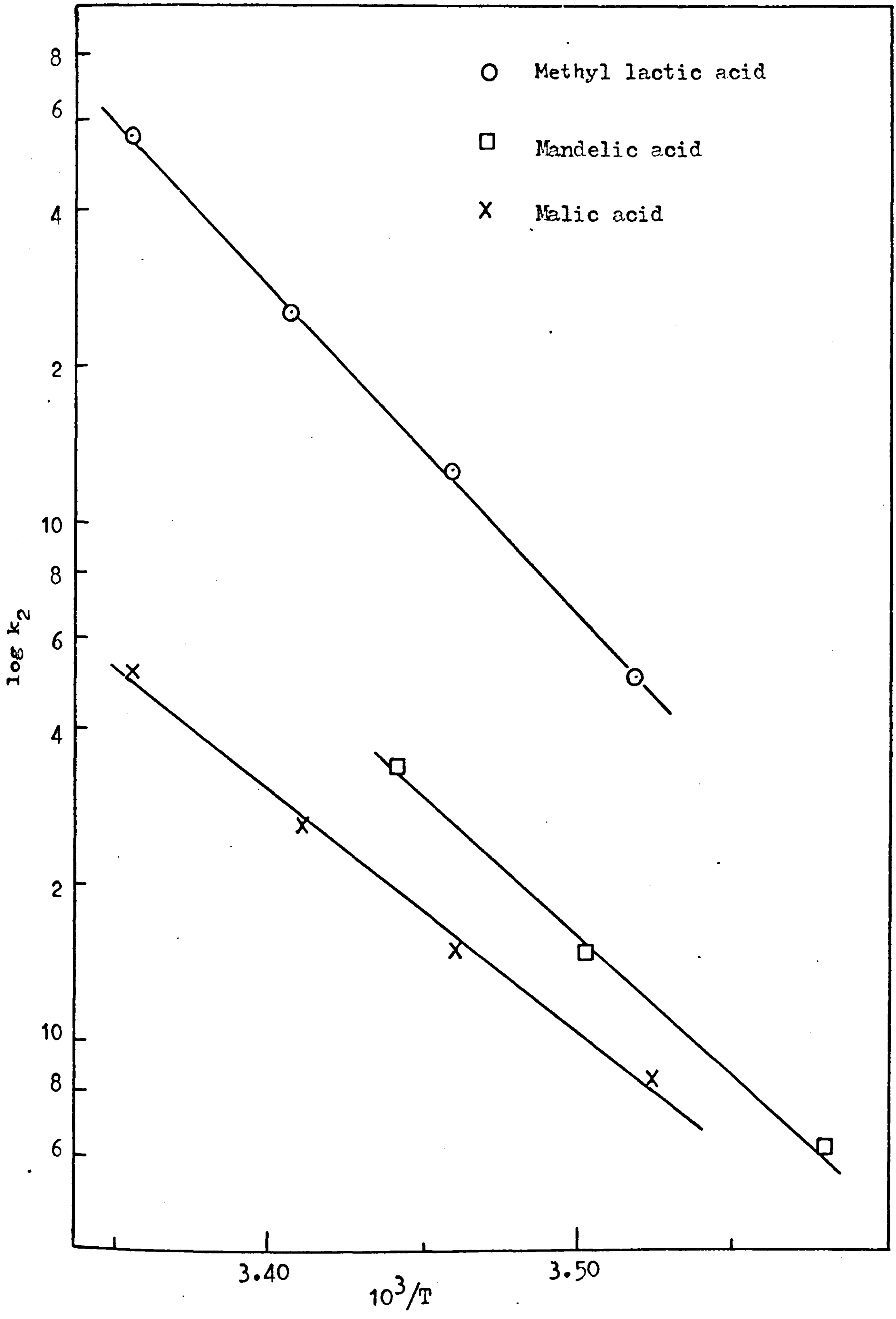


Figure 39 :- Plots of log k_2 versus $^I/_T$

α-hydroxy acids, i.e. malic and mandelic acids, is not possible because of different experimental conditions employed in sulphate media. However, it is interesting to note that the overall enthalpy of reaction for the formation and decomposition of CeL^{3+} species ($\Delta H_2 + \Delta H_2^*$), does decrease in the expected sequence. This is not surprising as such a correlation has previously been noted in Mn(III)[126,127] oxidations of primary alcohals via the route corresponding to k_1. Another interesting feature to note in the oxidation of CeL^{3+} is that the enthalpy of activation for the redox reactions of these complexes is about the same, i.e. 27 - 31 K cal mole^{-1}, but certainly higher than observed in reactions of these substrates in sulphate media. This change may be related to the differences in the oxidation-reduction potentials of strong vs weak cerium(IV) complexes.

The change in entropy can be explained by similar reasoning. The overall change in entropy (Table 16) for the formation and decomposition of CeL^{3+} species follows the same sequence as discussed above, with the exception of mandelic acid.

(h) Medium Effects

The use of sodium perchlorate as a background electrolyte in reactions involving metal ions and organic substrates has been the subject of much recent interest and comment. Very often a mixture of sodium perchlorate and perchloric acid is used to keep the ionic strength (~3M) constant at varying hydrogen ion concentrations. Since the activity coefficients of lithium and hydrogen ions are much more similar than those of sodium and hydrogen ions, the use of a latter mixture should be preferred, if possible in eliminating salt effects. Recent studies[128,129] have shown that different hydrogen ion dependences are observed by replacing sodium with lithium perchlorate. Thus in order to confirm the $[H^+]$ dependences on observed rate in the present studies, some kinetic measurements were made where lithium perchlorate was used in place of sodium perchlorate. Results on such measurements are given in Table 17, thus suggesting no medium effect. It may be added that similar behaviour was also observed in the oxidation of thiourea[130], and thiols[131] by Cr(IV) which have been shown to occur via well characterised Cr(VI)–S bonded transient complexes. On the other hand, in another study on the Fe(III) oxidation of α-mercapto carboxylic

TABLE 17

EFFECT OF LITHIUM/SODIUM PERCHLORATE ON THE REACTION OF Ce(IV) WITH MANDELIC ACID

$[Ce(IV)] = 2.50 \times 10^{-4}M$, $\lambda = 357nm$, Ionic strength = 1.50M,

T = 6.4°C.

$[H^+]/M$	10^2[Mandelic Acid] /M	a k_{obs}/S^{-1}	b k_{obs}/S^{-1}
0.25	0.50	9.65	9.70
0.50	0.50	7.60	7.45
0.75	0.50	5.96	5.98
1.00	0.50	5.25	5.18
1.25	0.50	4.08	4.13

a - in lithium perchlorate   b - in sodium perchlorate acids[132] in these laboratories, the rate of formation of the transient complexes has been shown to be dependent on the medium employed, but the overall $\left[H^+\right]$ dependence was approximately the same.

II

THE CERIUM(IV) OXIDATION OF MALONIC ACID IN ACID PERCHLORATE MEDIA

Chelate complexes are formed in the oxidation of malonic acid. Complex compounds of malonic acid with Mn^{3+} ion have been identified by many workers[133–135]. Drummond and Waters[135] investigated the oxidation of this acid with manganic pyrophosphate and found that this is a free radical reaction. The first step consists in formation of chelate complex which breaks up forming a free radical. Then, this radical reacts with Mn^{3+} ion and water to form tartronic acid. Further oxidation gives glyoxalic acid which is oxidised to the end products - carbon dioxide and formic acid.

A similar interpretation was given by Huebner, Amos and Bubl[136] for oxidation of malonic acid with periodic acid. In each case from one malonic acid molecule, two molecules of carbon dioxide and one of formic acid are formed.

The kinetics and mechanism of the oxidation of malonic acid by cerium(IV) under different experimental conditions have been the subject of a number of studies. Yadar and Bhagwat[137] applied for malonic acid oxidation cerium(IV) solution in sulphuric acid. Based on their kinetic studies the authors proposed a reaction mechanism similar to that of manganic pyrophosphate oxidation.

Although Sengupta and Aditya[138] observed the usual sequence for cerium(IV) salts viz. $ClO_4^- > NO_3^- \gg SO_4^{2-}$, the kinetic data indicate that linear plots are obtained by plotting log Ce(IV) vs time, when equal molar concentration of Ce(IV) are taken. This implies a first order dependence on Ce(IV) and zero order dependence on malonic acid concentration. Kemp[139], however, found a clear first order dependence on malonic acid concentration for the cerium(IV) sulphate oxidation, using an excess of reductant.

In a separate investigation[140] in perchlorate media, spectrophotometric evidence indicated the presence of an intermediate complex. However, the rate law was consistent with an apparent bimolecular mechanism operating. A chelate complex, $CeOH^{3+}$ - malonic acid, was postulated to be a kinetically important species.

Since many of the present data on cerium(IV) oxidation of organic substrates occurring via a transient complex refer to monofunctional carboxylic acids, ie. formic[115], acetic and substituted acetic[81], and α-hydroxy acids, the present study was undertaken to investigate the mechanism of reaction of a dicarboxylic, malonic acid. Comparison of this study may then be made with other work on the oxidation of analogous substrates.

EXPERIMENTAL

Malonic acid (B.D.H., Poole, Reagent Grade) was twice recrystallised from methanol : H_2O (1 : 1) mixture and the purity confirmed by the elemental analysis:

	found (%)	literature (%)	M.Pt(°C)
C	34.6	34.6	136(lit.136)
H	3.92	3.84	

The methods of preparation and standardisation of stock solutions of all the reagents used in this study are as described in Chapter 3.

RESULTS AND DISCUSSION

(a) Stoicheiometry

Attempts to determine volumetrically the amount of formic acid produced as the final product by the method described in section I were made, but due to strong interference by malonic acid, no accurate measurements were possible. Similarly, a stoicheiometry of greater than six equivalents of Ce(IV) per mole of reductant was obtained in an attempt to estimate formic acid collected after distilling the reacted solution (Ce(IV) $\ll$ reductant). A stoicheiometry of 6.1 ± 0.1 (four determinations) was finally achieved, consistent with previous measurements[138,140], by estimating the excess of Ce(IV) within a few minutes after the reaction was over. Thus the overall reaction may be written as

$$6Ce(IV) + CH_2(COOH)_2 \xrightarrow{H_2O} 6Ce(III) + 6H^+ + 2CO_2 + HCOOH \quad (53)$$

(b) Spectrum of the Intermediate Species

The deepening of the yellow colour of Ce(IV) solution when malonic acid solution was added to the former is indicative of complex formation. It was thus possible to construct a spectrum of this intermediate complex and is shown in Figure 40. For comparison, acetic and formic acids were mixed with solutions of Ce(IV) and spectra similar to that of cerium(IV) malonic acid were obtained, suggesting a lack of chelation in the latter case. These spectra, however, differ substantially from those shown in Figure 15.

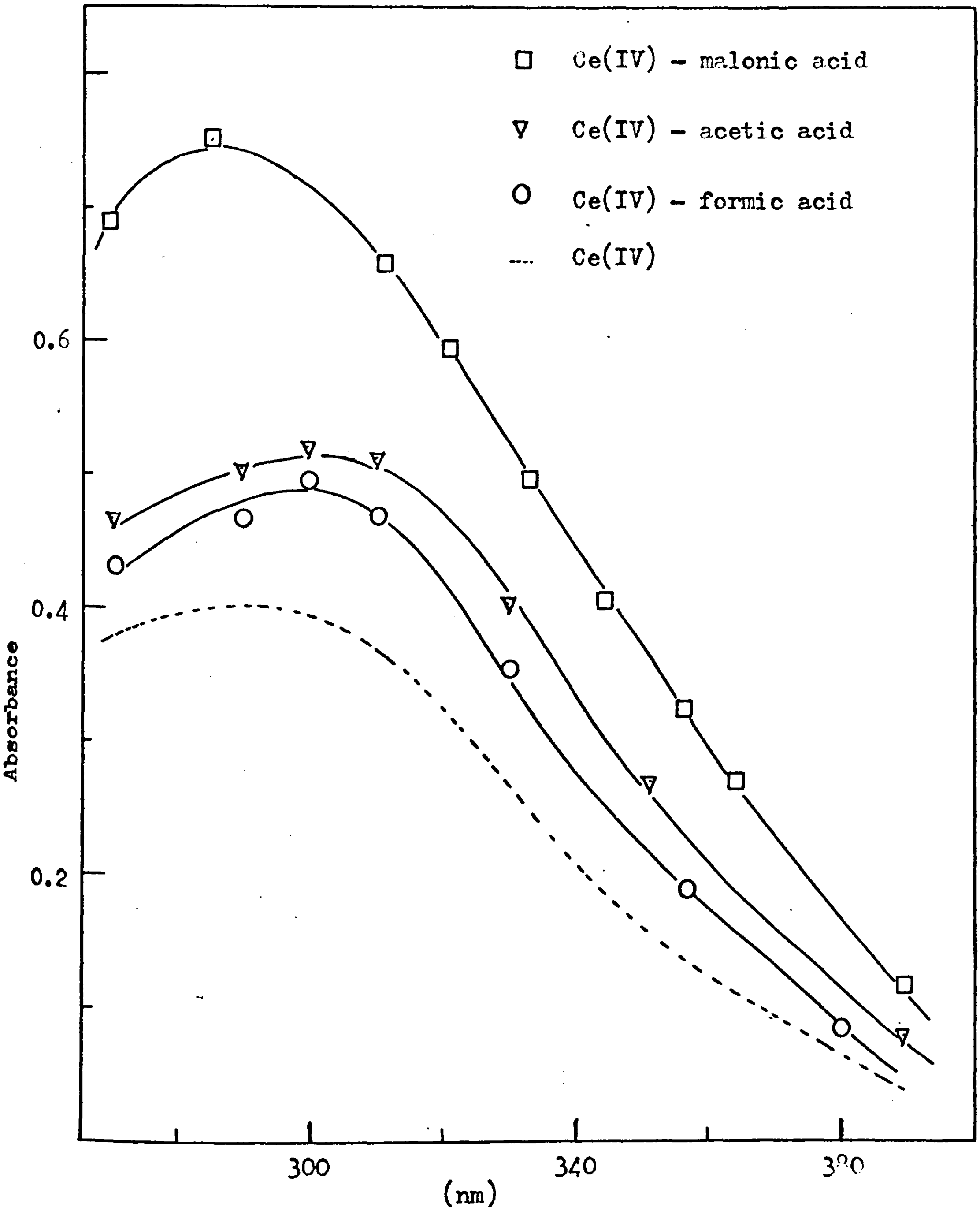


Figure 40 :- Spectra of Cerium(IV) intermediate complexes with malonic acid (□ 2.5×10^{-2}M, $[H^+]$=0.3M, T=7.4°C), acetic acid (∇ 3.25×10^{-2}M, $[H^+]$ = 1.0M) and formic acid (O 2.8×10^{-2}M, $[H^+]$ = 1.0M,) at room temperatures and $[Ce(IV)]$ = 2.5×10^{-4}M.

(c) Kinetics and Mechanism

The first order dependence of rate on Ce(IV) was observed in the linear plots of $\ln(A_t - A_\infty)$ against time under the large excess of malonic acid. Typical plots are shown in Figure 41 and were linear up to at least 85–90% reaction. Addition of Ce(III) ions (fifty fold excess) had no effect (Table 18) on the rate of reaction, thus establishing the absence of any back reaction. Similar results (Table 18) were also obtained by adding fifty fold excess of nitrate to that of Ce(IV). In addition, no differences in k_{obs} (Table 19) were found by using either cerium(IV) perchlorate or ceric ammonium nitrate in perchloric acid. Any cerium(IV) nitrato complexes[69], if present, are considered kinetically unimportant[81]. The values of observed rate constants, k_{obs}, at various $[H^+]$ and temperatures are collected in Table 19.

Although the acid dissociation constants of α-hydroxy carboxylic acids (Table 5) are ∽ 3–10 times lower than for malonic acid ($K_1 = 1.4 \times 10^{-3}$M), the amount of monoprotonated malonate ion ($CH_2(COOH)COO^-$) present under the experimental conditions employed in this study, is ∽ 0.1 – 0.4%. Similarly, the $[H^+]$ produced due to malonic acid dissociation as compared to $[H^+]$ used is also

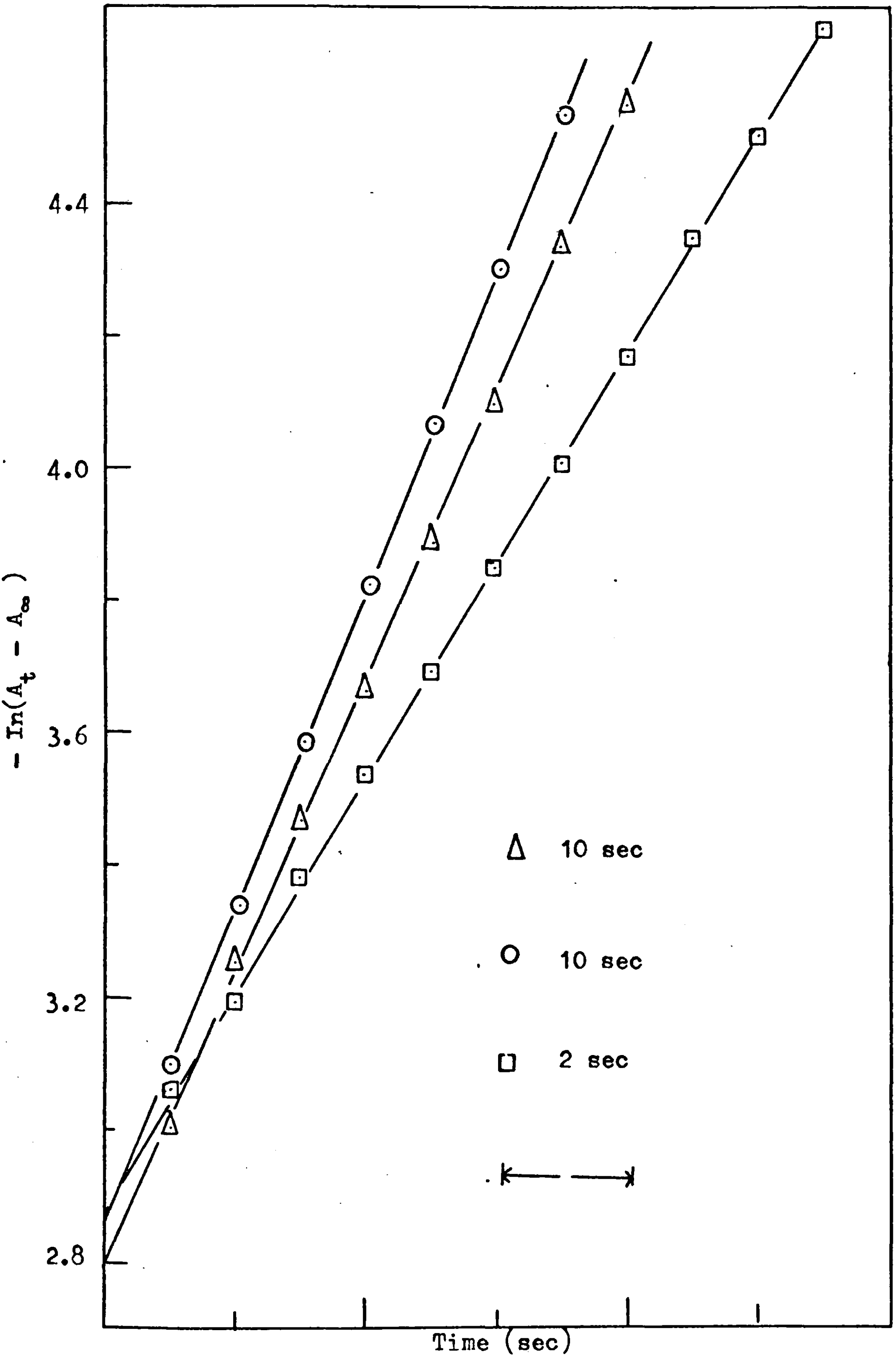


Figure 41 :- First order decay of Ce(IV) with malonic acid at various temperatures.
(Δ)[Malonic acid]=2 x 10^{-2}M, [H^+] =0.30M,T=10.4°C
(O)[Malonic acid]=6.43 x 10^{-2}M, [H^+]=0.50M,T=30.1°C
(□)[Malonic acid]=1.36 x 10^{-2}M, [H^+]=0.70M,T=35.4°C

TABLE 18

EFFECT OF Ce(III) AND NITRATE IONS ON THE REACTION RATE

at $T = 25^{o}C$, $\lambda = 357nm$, $[H^{+}] = 0.60M$,
$[\text{Malonic Acid}] = 2.5 \times 10^{-2}M$, $[Ce(IV)] = 2.50^{-4}M$,
Ionic Strength = 1.50M.

$10^{3}[Ce(III)]/M$	$10k_{obs}/s^{-1}$	$10^{3}[NO_3^-]/M$	$10k_{obs}/s^{-1}$
0.0	1.32^{a}	0.0	1.32^{a}
0.25	1.33^{b}	0.25	1.34^{b}
1.00	1.32^{b}	1.00	1.32^{b}
2.50	1.33^{b}	2.52	1.33^{b}
12.50	1.28^{b}	12.50	1.30^{b}

a - the perchlorate salt of Ce(IV) was used

b - the nitrate salt of Ce(IV) was used

TABLE 19

OBSERVED RATE CONSTANTS AT VARYING MALONIC ACID AND HYDROGEN ION CONCENTRATIONS

I = 1.50M, λ = 357nm, and $[\mathrm{Ce(IV)}]_T = 2.5 \times 10^{-4}$M
Slope (S) and intercepts (I) were derived from plots
according to equation (62)

T/°C	$[H^+]$/M	10^2[Malonic Acid]/M	$10^2 k_{obs}/s^{-1}$
35.4	0.30	0.682	5.61
	0.50	0.682	7.15
	0.70	1.363	15.9
	0.90	0.682	8.45
		1.363	16.9
		2.726	34.4
	1.10	0.682	9.25
		1.363	18.2
	1.50	0.682	9.97
30.1	0.30	0.643	4.02
		1.286	8.10
	0.50	0.643	5.01
		1.286	10.2
	0.80	0.643	5.81

T/°C	$[H^+]$/M	10^2[Malonic Acid]/M	$10^2 k_{obs}/s^{-1}$
30.1	1.00	0.643	6.13
		1.286	12.5
		1.929	18.8
		2.573	24.2
		3.859	36.9
25.0	0.50(a)	1.00	5.09
		2.00	9.92
		2.50	12.6
		3.00	15.4
		3.50	18.4
	S = 0.196 ± 0.003	I = 0.098 ± 0.298	
	0.60	1.50	7.98
		2.00	10.6
		2.50	13.5
		5.00	26.4
	S = 0.182 ± 0.003	I = 0.458 ± 0.16	
	1.00(a)	1.00	6.05
		2.50	15.5
		3.50	21.5
		5.00	30.6
	S = 0.156 ± 0.015	I = 0.095 ± 0.075	

T/°C	$[H^+]$/M	10^2[Malonic Acid]/M	$10^2 k_{obs}/s^{-1}$
25.0	1.25[a]	1.00	7.06
		1.50	10.8
		2.00	14.4
		2.50	17.4
		3.00	20.9
		3.50	25.4
		5.00	35.5
	S = 0.140 ± 0.001	I = 0.0019 ± 0.006	
18.0	0.60	1.03	3.64
		1.50	5.34
		2.00	7.06
		2.50	8.58
		3.50	11.8
		5.00	16.8
	S = 0.274 ± 0.002	I = 0.507 ± 0.09	
	0.70	1.00	4.00
		1.50	5.66
		2.50	9.45
		3.00	11.2
		3.50	13.2
		5.00	18.1
	S = 0.248 ± 0.006	I = 0.594 ± 0.13	
	0.90	1.00	4.32
		1.50	6.18
		2.00	8.25

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Malonic Acid}]/M$	$10^2k_{obs}/s^{-1}$
18.0	0.90	2.50	10.1
		3.00	12.5
		3.50	14.2
		5.00	20.1

S = 0.228 ± 0.004 I = 0.581 ± 0.22

	1.10	1.00	4.91
		1.50	7.06
		2.00	9.35
		2.50	12.0
		3.00	14.4
		3.50	16.0
		5.00	22.6

S = 0.202 ± 0.003 I = 0.419 ± 0.18

10.4	0.30	1.00	2.16
		1.50	2.98
		2.00	4.06
		2.50	5.03
		3.00	6.06
		3.50	6.81
		5.00	8.99

S = 0.450 ± 0.012 I = 2.03 ± 0.63

	0.50	1.00	2.54
		1.50	3.51
		2.00	4.76
		2.50	5.86

$T/^{o}C$	$[H^{+}]/M$	$10^{2}[\text{Malonic Acid}]/M$	$10^{2}k_{obs}/s^{-1}$
10.4	0.50	3.00	7.18
		3.50	8.05
		5.00	10.5
	S = 0.383 ± 0.11	I = 1.70 ± 0.14	
	0.70	1.00	2.86
		1.50	4.22
		2.00	5.38
		2.50	6.83
		3.00	7.72
		3.50	9.12
		5.00	12.2
	S = 0.335 ± 0.004	I = 1.53 ± 0.20	
	0.90	1.00	3.29
		1.25	4.85
		2.00	6.12
		2.50	7.66
		3.50	10.4
		5.00	13.9
	S = 0.289 ± 0.004	I = 1.51 ± 0.27	
	1.25	1.50	6.01
		2.00	7.60
		2.50	9.35
		3.00	11.0
		3.50	13.5
		5.00	17.3
	S = 0.237 ± 0.01	I = 1.03 ± 0.36	

$T/^{o}C$	$[H^+]/M$	$10^2[\text{Malonic Acid}]/M$	$10^2k_{obs}/s^{-1}$
7.8	0.288	1.00	1.70
		1.53	2.57
		2.00	3.19
		2.50	4.02
		3.50	5.23
		5.00	6.93
	S = 0.554 ± 0.007	I = 3.14 ± 0.40	
	0.50	1.50	3.08
		2.00	3.96
		2.50	4.78
		3.50	6.48
		5.00	8.66
	S = 0.450 ± 0.005	I = 2.60 ± 0.24	
	0.75	1.00	2.46
		1.50	3.55
		2.00	4.62
		2.50	5.60
		3.50	7.49
		5.00	9.90
	S = 0.383 ± 0.002	I = 2.50 ± 0.098	
	1.00	2.04	5.48
		2.50	6.79
		3.50	8.77
		5.00	11.6
	S = 0.327 ± 0.001	I = 1.99 ± 0.53	

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Malonic Acid}]/M$	$10^2 k_{obs}/s^{-1}$
7.8	1.25	1.00	3.35
		1.50	4.90
		2.00	6.28
		2.50	7.70
		3.50	10.7

S = 0.285 ± 0.003 I = 1.44 ± 0.23

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Malonic Acid}]/M$	$10^2 k_{obs}/s^{-1}$
3.4	0.30	1.00	1.45
		1.50	1.97
		2.00	2.74
		2.50	3.13
		3.00	3.56
		3.50	4.11
		5.00	5.30

S = 0.635 ± 0.021 I = 6.25 ± 1.2

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Malonic Acid}]/M$	$10^2 k_{obs}/s^{-1}$
	0.45	1.00	1.63
		1.50	2.39
		2.00	2.99
		2.50	3.56
		3.00	4.18
		3.50	4.77
		5.00	6.47

S = 0.564 ± 0.018 I = 4.83 ± 0.51

$T/^{\circ}C$	$[H^+]/M$	$10^2[\text{Malonic Acid}]/M$	$10^2 k_{obs}/s^{-1}$
	0.60	1.00	1.90
		1.50	2.79
		2.00	3.47

T/°C	$[H^+]$/M	10^2[Malonic Acid]/M	$10^2k_{obs}/s^{-1}$
3.4	0.60	2.50	4.23
		3.00	4.88
		3.50	5.56
	S = 0.481 ± 0.006	I = 4.38 ± 0.40	
	0.70	1.00	2.02
		1.50	2.88
		2.00	3.86
		2.50	4.48
		3.00	5.21
		3.50	5.85
		5.00	7.78
	S = 0.456 ± 0.006	I = 3.85 ± 0.32	
	1.00	1.00	2.45
		1.50	3.69
		2.50	5.58
		3.50	7.16
		5.00	9.61
	S = 0.374 ± 0.008	I = 2.91 ± 0.51	

(a) - the perchlorate salt of Ce(IV) was used.

considered negligible.

The following scheme is consistent with the experimental observations:

$$Ce^{4+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} CeOH^{3+} + H^+ \qquad (21)$$

$$Ce^{4+} + H_2L \overset{K_4}{\rightleftharpoons} Ce\,H_2L^{4+} \qquad (54)$$

$$CeOH^{3+} + H_2L \overset{K_5}{\rightleftharpoons} CeHL^{3+} + H_2O \qquad (55)$$

$$CeH_2L^{4+} \overset{K_6}{\rightleftharpoons} CeHL^{3+} + H^+ \qquad (56)$$

$$CeH_2L^{4+} \xrightarrow{k_3} Ce^{3+} + H^+ + \text{Radical} \qquad (57)$$

$$CeH_2L^{4+} + H^+ \xrightarrow{k_4} Ce^{3+} + 2H^+ + \text{Radical} \qquad (58)$$

$$CeHL^{3+} \xrightarrow{k_5} Ce^{3+} + \text{Radical} \qquad (59)$$

$$Ce(IV) + \text{Radical} \xrightarrow{k_6} Ce(III) + \text{Product} \qquad (60)$$

In the above scheme H_2L represents malonic acid, CeH_2L^{4+} and $CeHL^{3+}$ are the two possible intermediate complexes, the latter being formed either via reactions (54) and (56) or via (55) (which are kinetically indistinguishable). Although in a similar reaction of formic acid oxidation, a protonated complex, $CeHCOOH_2^{5+}$, was postulated[115], there is little evidence to believe that such a species would have formed from Ce^{4+} and $HCOOH_2^+$. Since no such species of malonic acid is known to be present in solutions in this range of (0.2 - 1.5M) $[H^+]$, reaction (58) is consistent with the observations and data. The electron transfer within the complexes results in the formation of a radical and this is assumed to be the rate determining step. The oxidation of this radical by Ce(IV) then continues rapidly until formic acid is produced. If it is assumed that the pre-equilibria (reactions 21, 54-56) are rapidly established as compared to rate determining steps (57) - (59) and also $k_6 \gg k_3, k_4, k_5$, then the rate of decrease of $[Ce(IV)]_T$ may be expressed as

$$\frac{-d[Ce(IV)]_T}{d} = 6\,k_3[CeH_2L^{4+}] + 6\,k_4[CeH_2L^{3+}][H^+] + 6k_5[CeHL^{3+}] \qquad (61)$$

and k_{obs} as

$$k_{obs} = \frac{6(k_3K_4[H^+] + k_4K_4[H^+]^2 + k_5K_5K_h[H_2L])}{([H^+] + K_h) + K_4[H^+] + K_5K_h[H_2L]} \qquad (62)$$

Two limiting cases of this equation are of interest as they have also been observed in other reactions of cerium(IV) :

(a) if $\left(\left[H^+\right] + K_h \right) \ll \left[K_4 \left[H^+\right] + K_5 K_h \right] \left[H_2L\right]$

then equation (61) reduces to

$$k_{obs} = \frac{6(k_3K_4 \left[H^+\right] + k_4K_4 \left[H^+\right]^2 + k_5K_5K_h)}{(K_4 \left[H^+\right] + K_5K_h)} \qquad (62a)$$

(b) if $\left(\left[H^+\right] + K_h \right) \gg \left[K_5 \left[H^+\right] + K_5K_h \left[H_2L\right] \right]$ in equation (61), then

$$k_{obs} = \frac{6(k_3K_4 \left[H^+\right] + k_4K_4 \left[H^+\right]^2 + k_5K_5K_h) \left[H_2L\right]}{(\left[H^+\right] + K_h)} \qquad (62b)$$

According to equation (62a) k_{obs} should be independent of $\left[H_2L\right]$ and although this equation has been shown to hold in the oxidation of isopropanol[110], cyclohexanol[111], and formic acid[115] by Ce(IV) under a very large excess of reductant , no evidence for this limiting rate law was found under the most extreme experimental conditions, i.e. malonic acid $\sim$ 200 times greater than $\left[\text{Ce(IV)}\right]_T$, at low temperature (3.4°C).

At higher temperature, i.e. $\geqslant 25^\circ$C, there is no kinetic evidence for complex formation, suggesting that the equilibrium constants for these complexes are negligibly small, confirmed by very small optical density changes under these conditions. If such is the case, then equation (62b) should hold. Typical plots of k_{obs} against $\left[H_2L\right]$ at $\left[H^+\right]$ = 0.90M and 1.00M, at T = 30°C and 35°C yielded good straight lines passing through the origin (Figure 42). Similar plots at other $\left[H^+\right]$ were obtained. It must be pointed out that similar reactions in sulphate media no doubt show identical kinetic behaviour, and thus the existence of weak complexes (with small equilibrium constants) comparable to those determined in the present study, cannot be completely excluded.

After establishing that the overall reaction is first order with respect to both reactants, the next step is to show which path(s) is responsible for the redox reaction. From the Slope of the plot of k_{obs} vs $\left[H_2L\right]$ the following expression can be derived from equation (62b)

$$\left(\left[H^+\right] + K_h\right) \times \text{Slope} = 6\left(k_3K_4\left[H^+\right] + k_4K_4\left[H^+\right]^2 + k_5K_5K_h\right) \quad (63)$$

Using the values of Slope and K_h, the plot of left hand side of equation (63) against $\left[H^+\right]$ at 30°C and 35°C yielded straight lines passing through the origin (Figure 43), thus suggesting that reaction (57), the decomposition of the complex, CeH_2L^{4+}, is the rate determining step.
If only this pathway predominates, then equation (63)

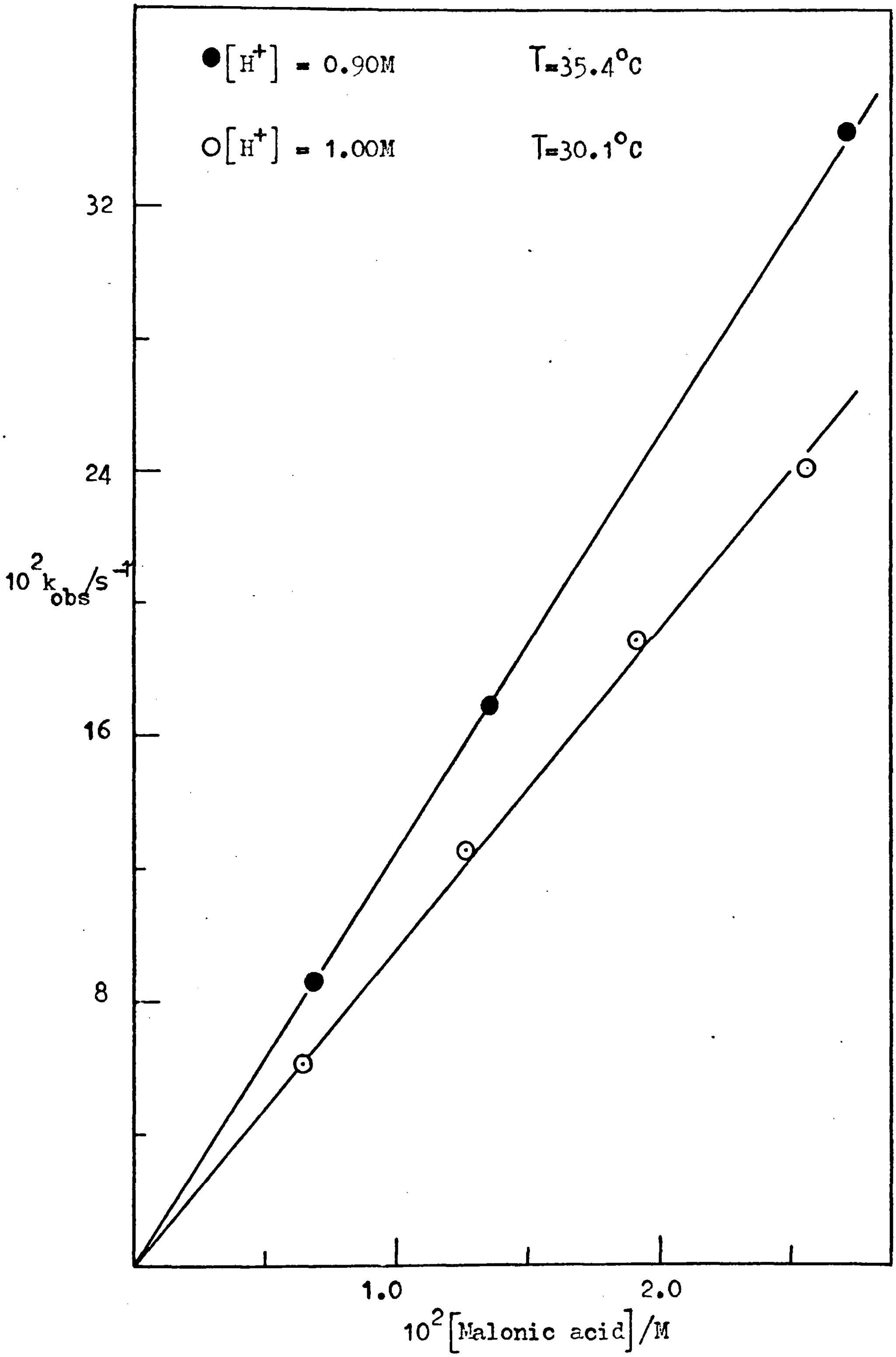


Figure 42 :- Plots of k_{obs} against [Malonic acid] at T = 30.1°C, 35.4°C, λ = 357nm, I = 1.50M and [Ce(IV)] = 2.5×10^{-4}M

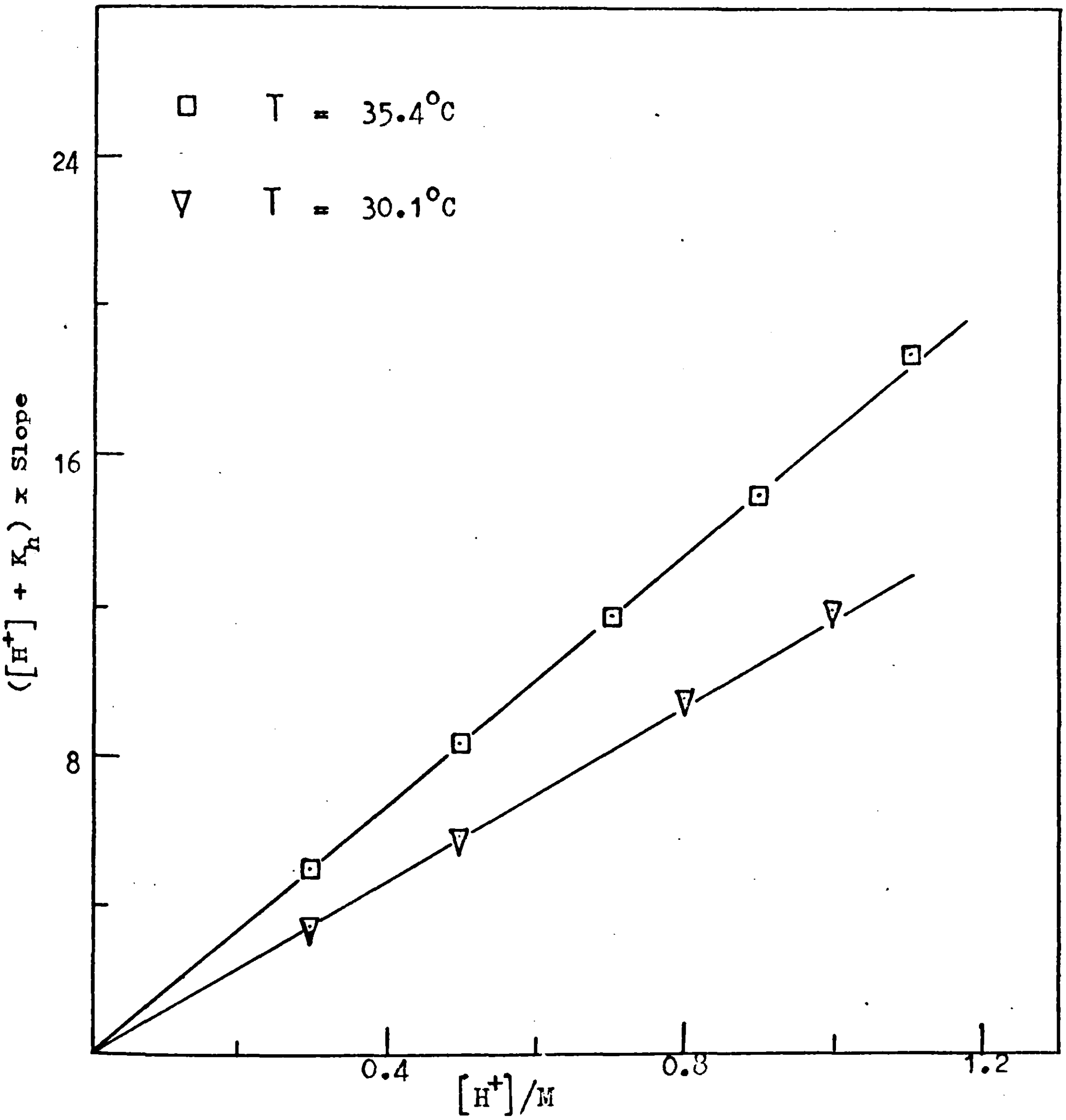


Figure 43 :- Plots of($([H^+] + K_h)$ x Slope against $[H^+]$ (equation 63), using K_h = 0.24M and 0.29M at 30.1° and 35.4°C respectively.

reduces to the form

$$\text{Slope}^{-1} = \frac{1}{6[H^+]\ k_3K_4} + \frac{1}{6\ k_3K_4K_h} \qquad (64)$$

so that a plot of Slope^{-1} against $[H^+]^{-1}$ should be linear with slope and intercept equal to $1/_6\ k_4K_4$ and $1/_6k_3K_4K_h$. Data from Table 19, when treated in this manner, not only support the suggested mechanism, but also yielded K_h values (0.34 ± 0.016, 0.29 ± 0.013 at 35.4° and 30.1°C respectively), by yet another independent method, which are in very good agreement with the previously derived values.

At low temperatures, i.e. $\lesssim 25^\circ$C, the situation is somewhat different from that described above in that both kinetic and spectrophotometric evidence is indicative of the presence of intermediate complexes in appreciable concentrations. This suggests that $([H^+] + K_h)$ is now comparable to $(K_4\ [H^+] + K_5K_h)\ [H_2L]$, so that equation (62) should hold. This is supported by the linear plots of $k_{obs}{}^{-1}$ vs $[H_2L]^{-1}$. Typical plots of $k_{obs}{}^{-1}$ against $[H_2L]^{-1}$ at 18°, 7.8°, 3.4°C and at 10.4°C and various $[H^+]$ are shown in Figures 44 and 45 respectively. The marked dependence of intercept of such a reciprocal plot (Figure 45), similar to that observed in α-hydroxy oxidation, suggests that equilibrium (56) is operating

$$CeH_2L^{4+} \underset{}{\overset{K_6}{\rightleftharpoons}} CeHL^{3+} + H^+ \qquad (56)$$

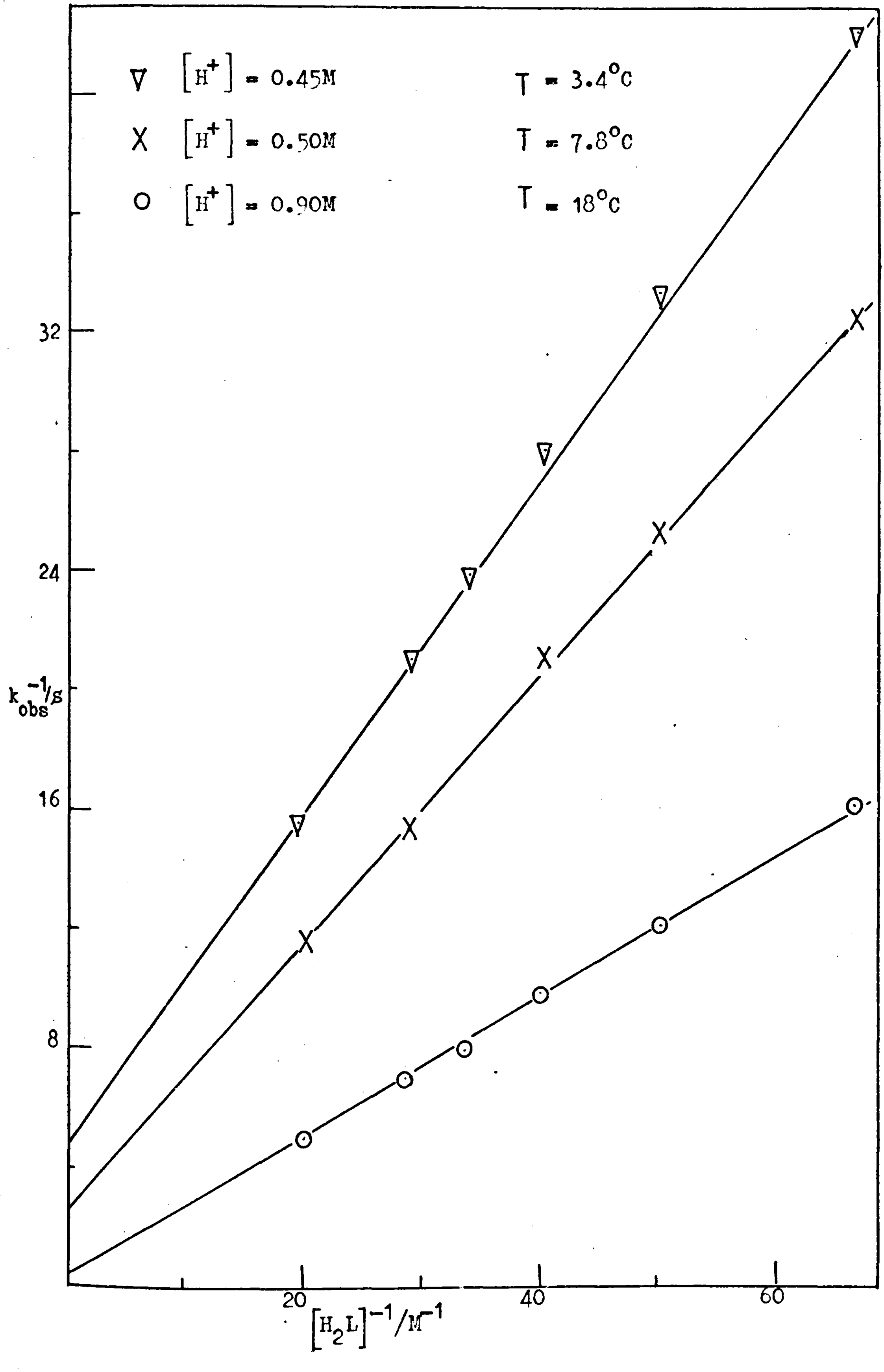


Figure 44 :- Plots of k_{obs}^{-1} versus $[\text{Malonic acid}]^{-1}$ at various $[H^+]$ and temperatures.

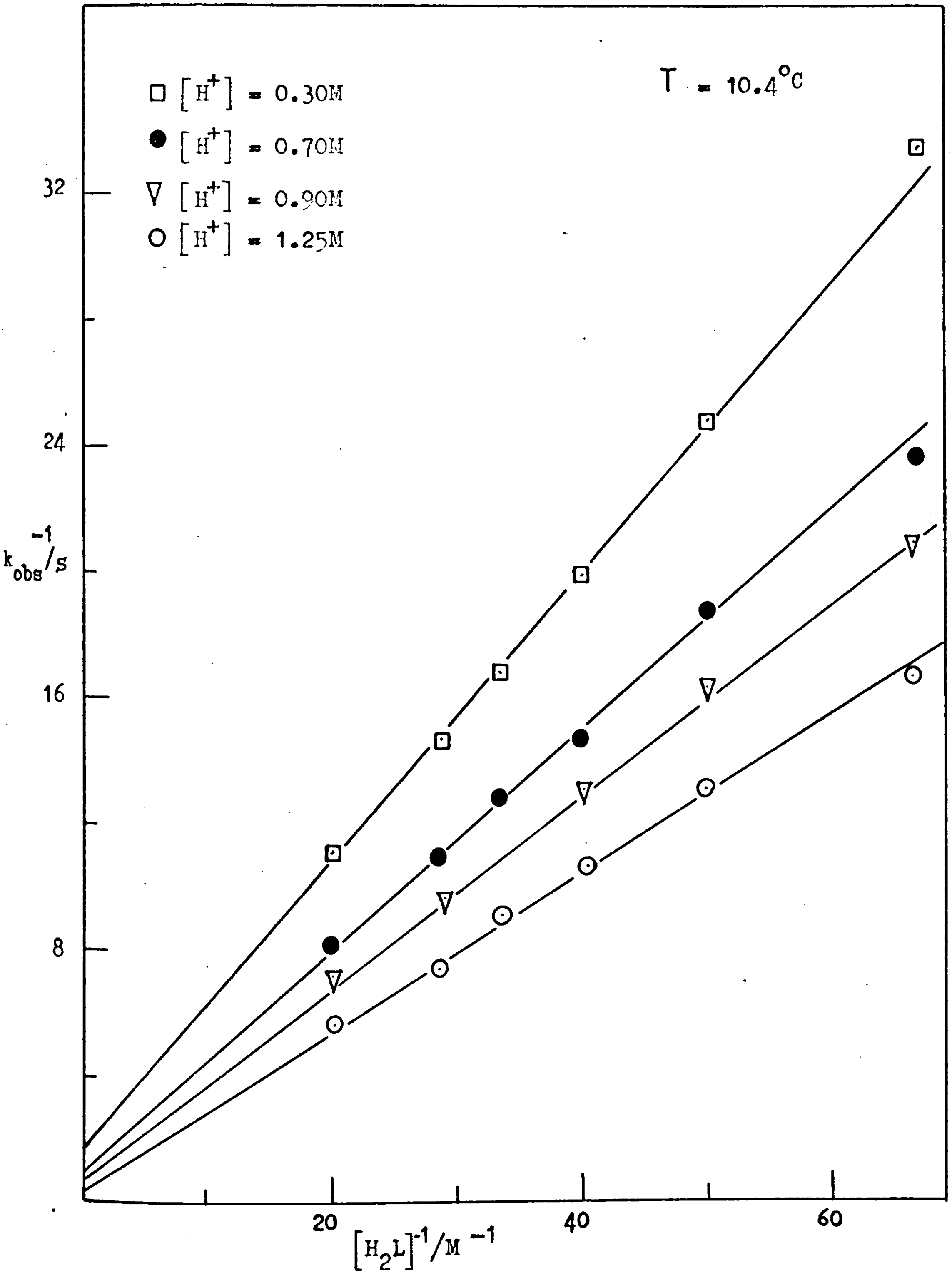


Figure 45 :- Plots of k_{obs}^{-1} against $[\text{Malonic acid}]^{-1}$ at $[H^+]$ = 0.30, 0.70, 0.90, 12.5M, T = 10.4°C, I = 1.50M and $[Ce(IV)] = 2.5 \times 10^{-4}$M.

Evaluation of Equilibrium and Rate Constants

Equation (65) follows from equation (62) and the slopes and intercepts of the plots of k_{obs}^{-1} vs $[H_2L]^{-1}$

$$\frac{([H^+] + K_h)}{\text{Slope}} \times \text{Intercept} = K_4[H^+] + K_5K_h \qquad (65)$$

Using values of experimental Slopes and Intercepts of a reciprocal plot of data from Table 19, and the value of K_h, plots were made against $[H^+]$ and straight lines obtained (Figure 46). The values of K_4 and K_5K_h are given in Table 20. It must be pointed out that since, at 25°C the overall reaction order is nearly two, the errors associated with intercepts are somewhat large for estimates of K_4 and K_5K_h to be derived by this method.

Rate parameters were obtained using equation (62) where the plots of $([H^+] + K_h) / [H^+]$ x Slope against $[H^+]$ yielded good straight lines (Figure 47) at all temperatures. Using the values of K_4 (Table 20) at four temperatures between 3.4 and 18.0°C, rate constants k_3 and k_4 were calculated and are shown in Table 21. Arrhenius plots showed good linearity (Figure 48) and enthalpies and entropies of activation have been obtained for both rate constants, k_3 and k_4. These results are given in Table 21.

TABLE 20

DEPENDENCE OF K_4, K_5K_h, k_3K_4, and k_4K_4 ON TEMPERATURE

T/°C	K_4 (a)	K_5K_h	$6\ k_3K_4$ (b)	$6\ k_4K_4$ (c)
3.4	6.76 ± 0.54	2.04 ± 0.35	1.73 ± 0.07	1.19 ± 0.11
7.8	4.78 ± 0.59	1.39 ± 0.57	2.05 ± 0.18	1.42 ± 0.17
10.4	4.53 ± 0.58	0.67 ± 0.46	2.55 ± 0.16	1.60 ± 0.19
18.0	2.24 ± 0.98	0.32 ± 0.83	3.65 ± 0.19	1.71 ± 0.22
25.0	> 1	> 0.1	6.43 ± 0.19	1.40 ± 0.2
30.1			11.2 ± 0.3	
35.4			16.5 ± 0.5	

at 18°C

$\Delta G_4 = -0.466 \pm 0.4$ k cal mole^{-1}

$\Delta H_4 = -11.9 \pm 1.32$ k cal mole^{-1}

$\Delta S_4 = 39.3 \pm 10$ cal deg^{-1}mole^{-1}

(a) - units of M^{-1}

(b) - units of $M^{-1}s^{-1}$

(c) - units of $M^{-1}s^{-1}$

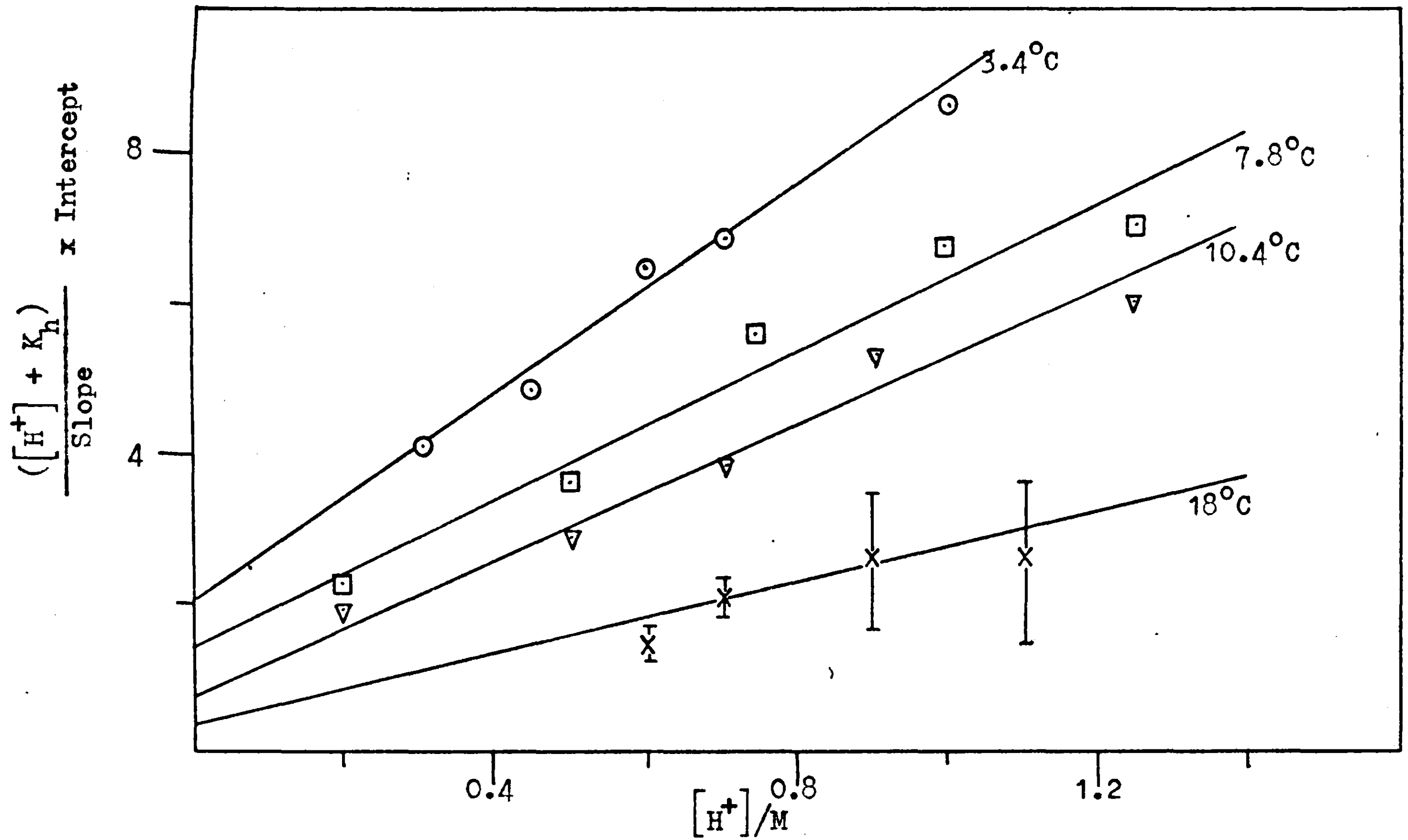


Figure 46 :- Plots of $\frac{([H^+] + K_h)}{\text{slope}}$ x Intercept versus $[H^+]$ (equation 65) at T = 3.4°, 7.8°, 10.4°, 18°C, λ = 357nm and I = 1.50M.

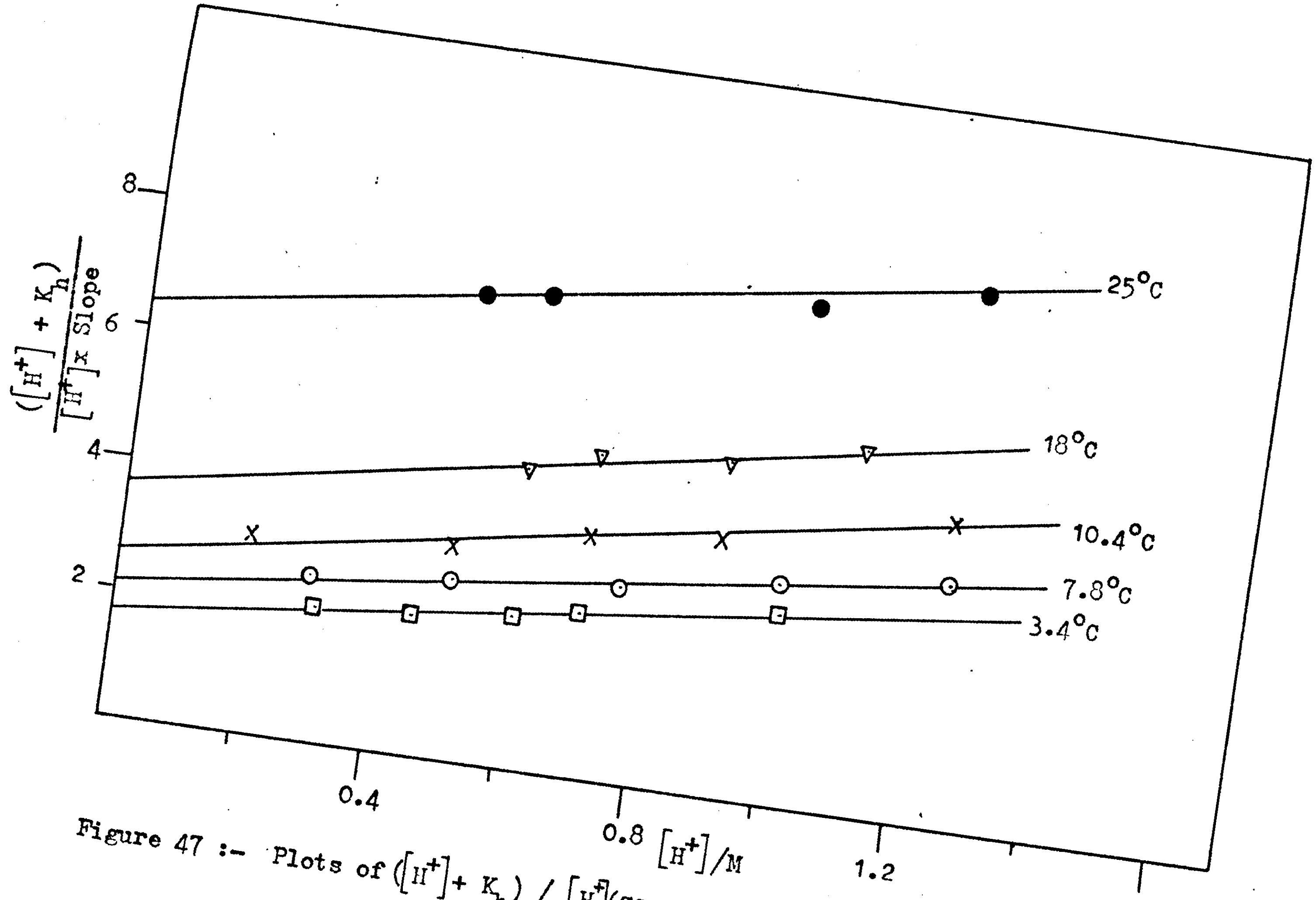


Figure 47 :- Plots of $([H^+] + K_h) / [H^+](\text{Slope})$ versus $[H^+]$ (equation 62) at T = 3.4°, 7.8°, 10.4°, 18°, 25°C, λ = 357nm and I = 1.50M.

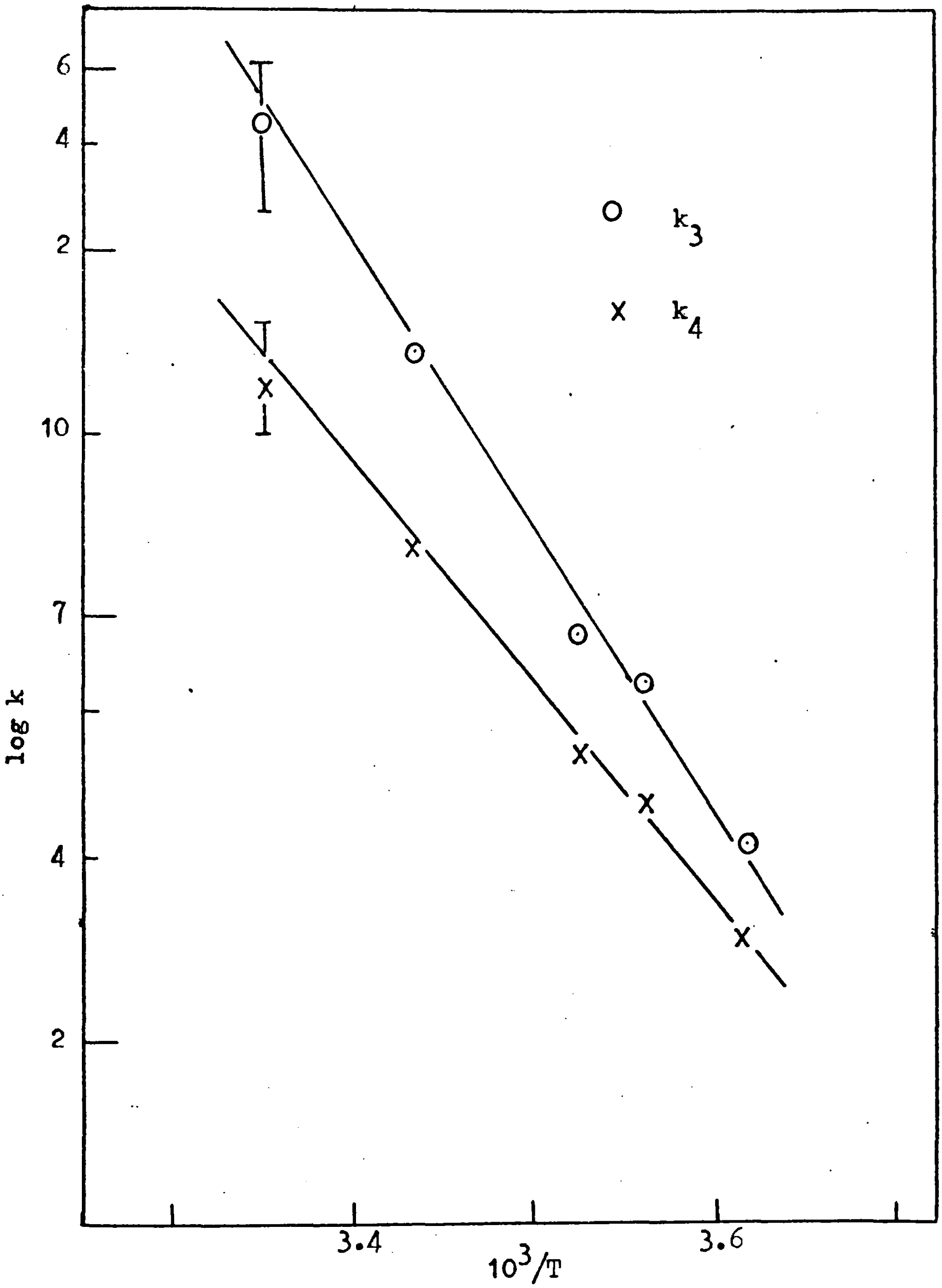


Figure 48 :- Plots of log k_3 and log k_4 against $^I/_T$

TABLE 21

DEPENDENCE OF k_3 AND k_4 ON TEMPERATURE

T/°C	$10^2 k_3/s^{-1}$	$10^2 k_4/s^{-1}$
3.4	4.28 ± 0.8	2.94 ± 0.6
7.8	7.15 ± 1.2	4.95 ± 1.4
10.4	9.38 ± 3	5.88 ± 2
18.0	27.1 ± 10	12.7 ± 5

$\Delta H_3^* = 19.7 \pm 1.0$ k cal mole^{-1} $\Delta S_3^{*\,(a)} = 6.64 \pm 4$ cal deg^{-1}mole^{-1}

$\Delta H_4^* = 15.2 \pm 0.5$ k cal mole^{-1} $\Delta S_4^{*\,(a)} = -10.2 \pm 6$ cal deg^{-1}mole^{-1}

(a) - extrapolated

(d) Comparison of Equilibrium and Rate Constants with Related Systems

The equilibrium constants for oxygen containing substrates are given in Table 22. Two interesting features are worth mentioning. First, the equilibrium constants for alcohols are generally larger than those for either carboxylic acids or ketone. Second, the ΔH_4 for these complexes is comparatively more positive for alcohols than for others.

The oxidation of malonic acid follows the same overall kinetic pattern (k_{obs} increases with increasing $[H^+]$) as observed in most cases of cerium(IV) oxidation of organic substrates. This increase in rate has previously been interpreted in terms of Ce^{4+}, being more reactive than its hydrolysed form, whereas a more recent explanation is based on the relative magnitude of the protonation equilibria (56). From Table 20 the value of K_6 = 0.1–0.3M ($K_6K_4 = K_5K_h$) which can be compared with the previous values of $K_6 > 3 - 30$, obtained in the oxidation of α-hydroxy acids.

The observed rate constants for the oxidation of mono carboxylic and malonic acids are given in Table 23. These studies were made under different experimental conditions and rate constants reported in Table 23 are those

TABLE 22

ACTIVATION PARAMETERS FOR CERIUM(IV) OXIDATION PATHS INVOLVING DECOMPOSITION OF CeS^{4+} COMPLEX AT 25°C

Substrate	ΔH_3^* (a)	K_4 (b)	ΔH_4 (a)	Ref.
methanol	13.8	6.6	-2.0	112
n-propanol	20.3	7.6	-2.2	80
iso-propanol	25.4	15	-1.8	80
sec-butanol	17.4	19.3	-2.1	80
sec-amyl alcohal	19.6	11	-4.6	80
benzyl alcohal	18.3 (c)	$\ll 1$		80
acetone	15.6	4.0	-9.2	119
methyl ethyl ketone	18.8	1.6	-40.0	119
formic acid	12.3 (d)	<1 (c)		115
malonic acid	19.7	~ 1	-11.9	this work
cyclohexanol	24.6	10 (e)	-1.4	80

(a) - units of k cal $mole^{-1}$

(b) - units of M^{-1}

(c) - for composite term, k_3K_4

(d) - for composite term, $k_3K_4^{-1}$

(e) - at 20°C

TABLE 23

OBSERVED RATE CONSTANTS FOR THE OXIDATION OD ACETIC, FROMIC AND MALONIC ACIDS BY Ce(IV) IN AQUEOUS PERCHLORIC ACID MEDIA

SUBSTRATE(S)	$10^2[S]/M$	$10^4[Ce(IV)]/M$	$[H^+]/M$	$T/^oC$	$10^3k_{obs}/s^{-1}$	Ref
chloroacetic	43.35	41.44	1.00	50	0.0308	81
acetic acid	43.35	40.99	1.00	50	0.0545	81
propionic acid	43.35	40.68	1.00	50	0.141	81
formic acid	5.00	5.00	2.00	49.2	0.163	115
malonic acid	2.57	2.5	1.00	30.1	242	this work

where experimental conditions are as close as possible to those used in the present study. The rate of reaction decreases in the sequence propionic > acetic > chloroacetic as expected, due to an increase in the electron density at the reaction centre which facilitates the electron transfer. Although on this basis one would have expected the rate of formic acid oxidation to be less than acetic acid, the reverse order found, however, may be due to different experimental conditions. Another point to note is the large difference in the rates of oxidation going from monocarboxylic acids to malonic acid. This may be due to greater stability of the radical formed in the decomposition of the Ce(IV) - malonic acid complex, as compared to those produced in monocarboxylic acid oxidation.

Wells and Husain[115], in a study on the oxidation of formic acid, postulated the formation of a protonated complex, ie. $CeHCOOH_2^{5+}$, in order to explain the increase in the rate of oxidation with $[H^+]$. It may be added that the kinetics of this reaction are more complicated in that the order of reaction, with respect to substrate changes at constant $[H^+]$ and temperature. These authors[115] have preferred to work under the very large excess of reductant ($\sim$400 times that of Ce(IV)) to achieve the limiting rate law, thus simplifying the kinetics and their interpretation.

Although their suggested rate law includes terms equivalent to k_3, k_4, and k_5, the mechanism is, however, consistent with the decomposition of only one species, ie. $CeHCOOH^{4+}$ which may be compared with CeH_2L^{4+}.

The order of reaction with respect to reductant in the oxidation of acetic acid[81] has been found to be nearly unity, which may be compared with the malonic acid oxidation at 25°C. Moreover, the decomposition of the deprotonated species, ie. $CeCH_3COO^{3+}$, in contrast to CeH_2L^{4+} and $CeHCOOH^{4+}$, was considered kinetically important in the oxidation of acetic acid. However, the value of K_h, based on the data, is 23.5M at 50°C, which is considerably different from the values obtained in this study. Since it has been shown by Wiberg and Ford[71] that cerium(IV) in acetic acid solutions forms various polymeris species, and these species must therefore be accounted for in the interpretation of mechanism proposed by Mathai and Vasudevan[81]. More work on this system is needed to solve this anomalous behaviour.

The enthalpies of activation (ΔH_3^*) for a number of oxygen containing substrates are given in Table 22. It is interesting to note that ΔH_3^* for malonic acid is 19.2k cal mole^{-1} which is closely similar to the corresponding values found in a variety of alcohols and ketones. The oxidation of these substrates is believed to occur via the pathway analogous to the decomposition of the CeH_2L^{4+} complex.

The stoicheiometry of the reaction (53) may be understood if malonic acid is oxidised in a one-electron step to yield cerium(III) and a radical which further reacts rapidly with cerium(IV) in a series of steps to give formic acid. The stages through which the reaction proceeds may be explained by the following scheme

$$\mathrm{Ce(IV)} + \underset{\mathrm{V}}{\mathrm{CH_2(COOH)_2}} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{Complex} \xrightarrow{\text{slow}} \mathrm{CH(COOH)_2} + \mathrm{Ce(III)} + \mathrm{H^+} \qquad (66)$$

$$\mathrm{HC(COOH)_2} + \mathrm{Ce(IV)} + \mathrm{H_2O} \longrightarrow \mathrm{HC(OH)(COOH)_2} + \mathrm{Ce(III)} + \mathrm{H^+} \qquad (67)$$

$$\underset{\mathrm{VI}}{\mathrm{HC(OH)(COOH)_2}} + \mathrm{Ce(IV)} \longrightarrow \mathrm{COOH} + \mathrm{OHC(COOH)} + \mathrm{Ce(III)} + \mathrm{H^+} \qquad (68)$$

$$\mathrm{COOH} + \mathrm{Ce(IV)} \longrightarrow \mathrm{Ce(III)} + \mathrm{CO_2} + \mathrm{H^+} \qquad (69)$$

$$\underset{\mathrm{VII}}{\mathrm{OHC(COOH)}} + \mathrm{Ce(IV)} \longrightarrow \mathrm{Ce(III)} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{HC=O} \qquad (70)$$

$$\mathrm{HC=O} + \mathrm{Ce(IV)} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{VIII}}{\mathrm{HCOOH}} + \mathrm{Ce(III)} + \mathrm{H^+} \qquad (71)$$

where V, VI, VII, VIII represent malonic, tartronic, glyoxalic and formic acid respectively.

General equation (72) similar to (53) for oxidation of malonic acid with cerium(IV) perchlorate was obtained by summation of the above reactions (66) to (71).

$$\mathrm{CH_2(COOH)_2} + 6\,\mathrm{Ce(IV)} + 2\mathrm{H_2O} \longrightarrow \mathrm{HCOOH} + 2\mathrm{CO_2} + 6(\mathrm{CeIII}) + 6\mathrm{H^+} \qquad (72)$$

III

THE CERIUM(IV) OXIDATION OF L - CYSTEINE AND DL - PENICILLAMINE IN ACID PERCHLORATE MEDIA

The Chemistry of L-Cysteine and DL-Penicillamine

(a) Co-ordination to Metal Ions

Much of the current interest in complex formation between transition metal ions and organic compounds containing functional units such as sulphydryl or amino groups is that they may be treated as 'model' compounds for the study of biochemical reactions. Although both L-cysteine and DL-penicillamine are of considerable biological importance, their chief attraction to the co-ordination chemist is in providing three different co-ordination sites, S, N and O, for co-ordination to metal ions.

Potentiometric evidence has been obtained for an O,N-bonded chelate cysteinate complex of Ca(II)[141]. An infra-red study[142] of alkaline solutions of the 1 : 2 complexes formed by cysteine with Pb(II), Cd(II), Hg(II) and Zn(II) indicated that both amino and sulphydryl groups are bonded to the metal ion. It had previously been proposed[143] that cysteine behaves as a tridentate chelate with the first of these ions. A novel complex was reported[142] to form at low pH with Cd(II) and Zn(II), the formula being $[M_3L_4][MX_4^{2-}]$, where L = cysteine and X^- = halide. Bonding was postulated as taking place through only – CO_2H and – SH.

For the reaction of both Zn(II) and Ni(II) with cysteine, Perrin and Sayee[144] found a variety of complexes having a wide range of stoicheiometries and differing degrees of protonation. It has been suggested[143,145] that Ni(II) is chelated by cysteine via N, S, co-ordination.

The reactions of Co(III) with cysteine have been studied extensively. Co(III) forms a monocomplex in which the ligand is attached by all three of its available binding sites[143]. In alkaline media the blue-green Co(III) bis-cysteinate complex is believed to involve nitrogen and sulphur linkages[146], as is the blue-violet tris-cysteinate[147].

Platinum (II) and palladium (II) both form bis-chelate complexes with cysteine[148] in which carboxyl and sulphydryl groups provide the co-ordination sites. In acidic solution Hg^{2+} and Ag^+ both form cysteine complexes in which the metal ion is exclusively sulphur-bonded[149,150]. A sulphur-bonded complex is also formed between copper (I) and cysteine[151].

A rhodium cysteine complex which has been isolated is believed[152] to be dimeric with both amino and sulphydryl groups being co-ordinated.

Tanaka and his co-workers[153] reported that penicillamine forms chelate complexes with Zn(II), Co(II) and Ni(II) and co-ordination occurs through S and N while -COOH remains free. However, in chelates produced from penicillamine with Hg(II), Pb(II), Cd(II), the atoms S, N, and O contribute to co-ordination.

In another investigation[154] the formation of new mixed ligand chelates consisting of penicillamine, bivalent metal, Cd(II), Hg(II) and Pb(II)and some of the secondary ligands like mercaptoethylamine and glutathione, have been reported. Penicillamine has also been shown to form co-ordination complexes with Cu(II)[155], Fe(III)[156], and Cr(III)[157].

(b) Reduction of Metal Ions by L-Cysteine and DL-Penicillamine

The most reactive redox functional groups present in biological systems are thiols. These can be oxidised readily to disulphides which are resistant, under mild conditions, to further oxidation. The RSH/RSSR redox couple plays an important role in electron transport in enzymes which very often incorporate metal ions associated with readily oxidisable sulphydryl groups.

In perchloric acid solution, Co(III) oxidises cysteine to its disulphide, cystine, by way of a spectrophotometrically identifiable transient intermediate which is believed to incorporate a metal-sulphur bond[158].

Iron(II) ions catalyse the oxidation by molecular oxygen of cysteine to cystine. In acidic media oxidation by Fe(III), in excess metal ions, is accomplished by the participation of a blue bidentate monocomplex which contains oxygen and sulphur linkages[159]. In alkaline media a violet tris-cysteinate complex, in which the ligand is similarly bonded, appears to perform the same function[159].

Copper ions, like those of iron, are very important biologically. Although the catalysis of the aerial oxidation of cysteine has been widely reported, no copper(II) complex of this ligand has been characterised and the overall reaction is still far from being understood[152].

Of the large number of systems involving cysteine with metal ions, that which is currently attracting interest is its reaction with molybdenum(V) and (VI). This interest is largely the result of a desire to find satisfactory models for the molybdenum-containing enzymes, xanthine oxidase and nitrogen reductase, in which interaction of a cysteine residue with the metal has been proposed to exist[160,161]. Both oxidation states of this ion form complexes with cysteine. That of Mo(V) is a binuclear doubly-oxygen-bridged diamagnetic species[162] which, in alkaline medium is in equilibrium with a small proportion of paramagnetic monomer[163]. This complex, in which cysteine is terdentate, has been stated[163] to be a fairly good model for xanthine oxidase[164]. The corresponding entity with sulphur bridges has also been proposed as a model. The reduction of Mo(VI) by cysteine yields cystine and Mo(V). The redox rate is second order in ligand and a 1 : 2 metal to ligand stoicheiometry has been measured[165] for the final solution. The only solid complex which could be isolated for such mixtures, however, was the 1 : 1 oxygen-bridged species described above.

Recently oxidation of cysteine[166] and penicillamine[167] by Cr(VI) has been studied using fast reaction techniques. The existence of transient Cr(VI) - S bonded intermediate complexes has been confirmed spectrophotometrically. Product analyses indicate that some of the disulphide is bonded to the Cr(III) product.

The stoicheiometric study on the reactions involving Ce(IV) and Np(VI) in sulphate media with a large number of thiols has recently been reported by Sullivan and his co-workers[168]. Their measurements clearly indicate that for an α-mercapto acid, the variable stoicheiometry observed depends on the nature of the substituent. The effect of oxygen has also been reported in the Np(VI) oxidation of thiomalic acid. For the oxidation of cysteine by Ce(IV) 1 : 1 stoicheiometry was obtained.

In view of the current chemical interest on the redox reactions of sulphur containing organic substrates with various metal ions in these laboratories, the kinetic study of the oxidation of cysteine and penicillamine was thus undertaken.

EXPERIMENTAL

The preparation and standardisation of stock solutions of perchloric acid, sodium perchlorate, and Ce(IV) are as described in Chapter 3. L - cysteine and DL - penicillamine (Koch - Light, pure) were used without further purification. Solutions of L-cysteine, DL-penicillamine, and Ce(IV) were prepared immediately before use to avoid complications due to the slow decomposition which may occur in the presence of perchloric acid.

Stoicheiometry Measurements

The stoicheiometry of the reaction was determined under conditions related directly to the kinetic data, by the acidimetric titration of the sulphydryl group[169]. This involved mixing ~20ml of a solution of ~0.1M thiol, of known concentration, with 50ml of approximately 5×10^{-3}M Ce(IV) in ~ 0.2M $[H^+]$ and the requisite volumes of stock sodium perchlorate and perchloric acid to give $[H^+]$ = 0.2M and I = 1.50M when the mixture was diluted to 100ml. When reaction was complete, a 25ml sample of this mixture was used to charge a Dowex 50W x 8 100/200 mesh cation-exchange resin. The column was rinsed first with water and then with a solution having $[H^+]$ = 0.2M and I = 1.50M. Successive column fractions were titrated until no thiol could be detected.

Kinetic Measurements

The disappearance of Ce(IV) in the presence of a large excess of reductant to ensure pseudo first order conditions, was monitored at $\lambda = 357$nm using the 'fast' stopped-flow apparatus, described in Chapter 2. The temperature was varied between 7.85 to 25°C and the acidity range employed was 0.25 - 1.50M at total ionic strength 1.50M. The pseudo first order rate constants were derived from transmission curves, using a Nova 1200 Computer, by the method given in Chapter 2. Each kinetic run was repeated at least three times with replicate measurements usually agreeing to ± 3%.

RESULTS AND DISCUSSION

(a) Stoicheiometry

Results obtained by the acidimetric titration[169] method indicate the values for the cysteine and penicillamine: Ce(IV) ratio of 1.02 ± 0.02 and 1.03 ± 0.02, consistent with previous measurements[168] under the same conditions, suggesting the overall reaction to be given by equation (73)

$$2Ce(IV) + 2\ HS-RH_2^{+} \longrightarrow 2\ Ce(III) + H_2R^{+}-S-S-R^{+}H_2 \qquad (73)$$

(b) Kinetics and Mechanism

The decay in optical density due to the oxidation of thiols was always of the first order in [Ce(IV)] with [thiol] in excess. Typical plots of $\ln(A_t - A_\infty)$ vs time for reactions of L-cysteine and DL - penicillamine are shown in Figure 49. Values for the pseudo first order rate constant k_{obs} at various [thiol] with varying acidity are given in Table 24. Figures 50 and 51 show that the plots of k_{obs} against [cysteine] and [penicillamine] are linear passing through the origin at all acidities studied, thus establishing first order dependence of the rate on thiol. This observation does not necessarily negate the possibility of the existence of transitional Ce(IV) - thiol complexes; it rather indicates that the formation constant of such a complex is extremely small. The data may be represented by a rate law of the form

$$-\frac{d\,[Ce(IV)]}{dt} = k_{obs}\,[Ce(IV)] \qquad (74)$$

The second order rate constant, k_H ($M^{-1}sec^{-1}$) is defined by the equation

$$k_H = k_{obs}/[thiol] \qquad (75)$$

and was found to be independent of wavelength of measurement

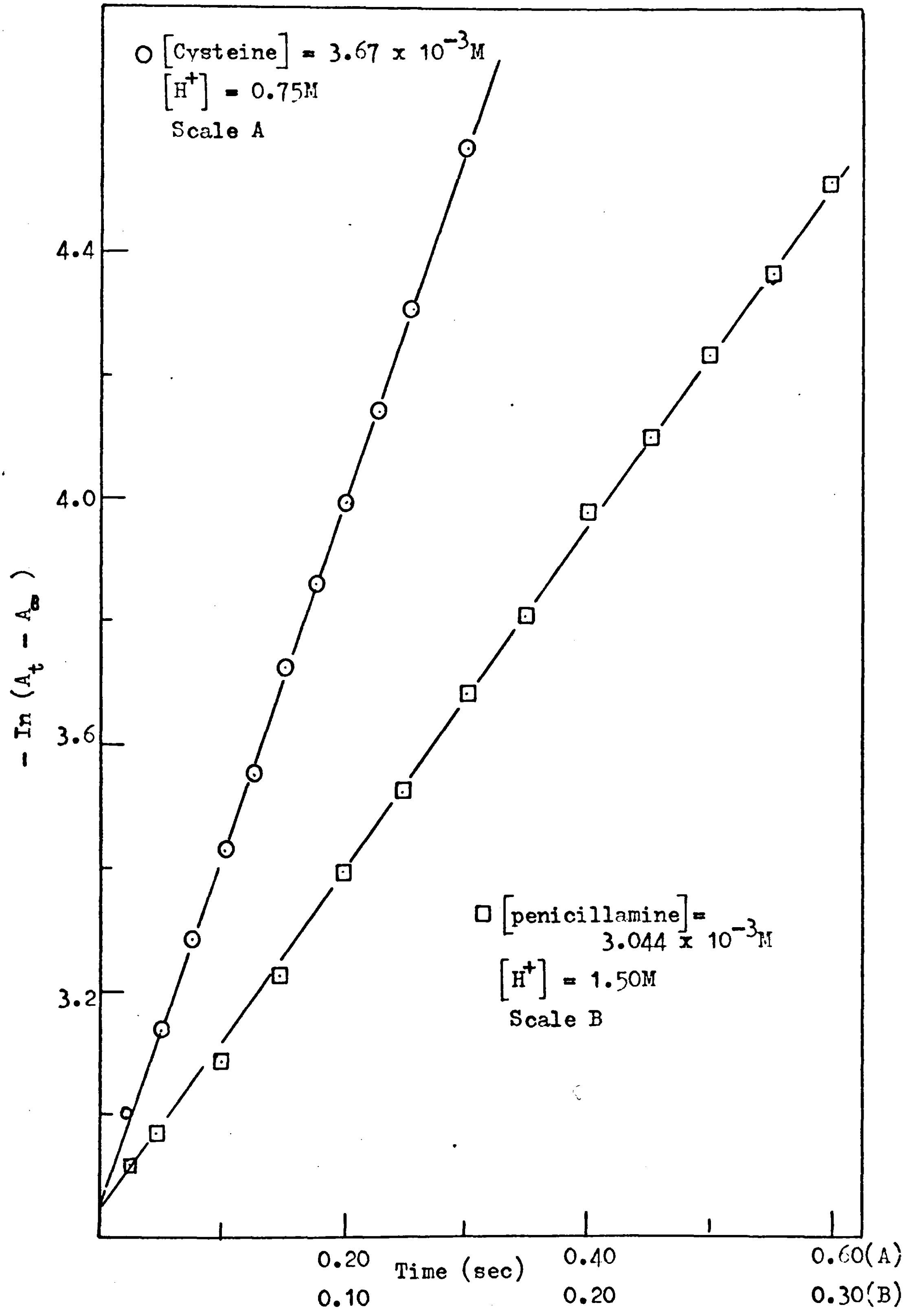


Figure 49 :- First order decay of Cerium(IV) with thiols, at T = 25°C, λ = 357nm and I = 1.50M.

TABLE 24

OBSERVED RATE CONSTANTS AT VARYING THIOL AND HYDROGEN ION CONCENTRATIONS

$[Ce(IV)]_T = 2.5 \times 10^{-4}M$, $I = 1.50M$, and $\lambda = 357nm$

$T/^{o}C$	$[H^+]/M$	$10^3[\text{Cysteine}]/M$	k_{obs}/s^{-1}	$10^{-3}k_H/M^{-1}s^{-1}$
25.0	0.75	3.671	5.60	1.49±0.03
		7.342	10.7	
		11.013	16.4	
	1.25	3.671	4.85	1.32
	1.50	3.671	4.66	1.26±0.03
		7.342	9.48	
		11.013	13.3	
17.9	0.70	5.056	6.73	1.32±0.01
		6.742	8.90	
	0.90	5.056	6.51	1.28±0.01
		6.742	8.58	
	1.10	3.371	4.15	1.21±0.05
		5.056	6.35	
		6.742	7.73	
	1.25	3.371	3.97	1.15±0.03
		6.742	7.55	

$T/^{o}C$	$[H^{+}]/M$	$10^{3}[\text{Cysteine}]/M$	k_{obs}/s^{-1}	$10^{-3}k_{H}/M^{-1}s^{-1}$
12.7	0.40	3.154	4.13	1.39±0.06
		4.731	6.84	
		6.308	9.15	
		9.462	12.5	
		15.77	22.5	
	0.70	3.154	3.82	1.19±0.03
		4.731	5.50	
		6.308	7.73	
		7.885	9.65	
		9.462	10.8	
		15.77	19.0	
	0.85	3.154	3.62	1.16±0.03
		4.732	5.40	
		6.318	7.58	
	1.00	3.154	3.37	1.10±0.03
		4.731	5.15	
		6.308	7.08	
		9.462	11.0	
		12.616	13.9	
		15.717	16.4	
	1.25	3.155	3.13	1.02±0.01
		6.310	6.65	
		9.465	9.73	
7.90	0.25	6.542	8.61	1.32

T/°C	$[H^+]$/M	10^3[Cysteine]/M	k_{obs}/s^{-1}	$10^{-3}k_H/M^{-1}s^{-1}$
7.90	0.50	3.271	3.70	1.14±0.01
		4.906	5.65	
		6.542	7.49	
	0.75	3.271	3.56	1.04±0.03
		4.906	5.00	
		6.542	6.66	
	1.00	4.906	4.57	0.93±0.0
		6.542	6.09	
	1.25	3.271	2.95	0.894±0.01
		6.542	5.80	
		10^3[Penicillamine]/M		
25.0	0.50	3.044	9.98	3.28
	0.75	6.087	16.4	2.68±0.01
		9.131	24.4	
	1.25	3.044	6.33	2.08
	1.50	3.044	5.86	1.93±0.01
		6.087	11.8	
18.0	0.25	3.197	10.6	3.32
	0.40	3.197	8.90	2.76±0.02
		6.394	17.6	

$T/^{o}C$	$[H^{+}]/M$	$10^{3}[\text{Penicillamine}]/M$	k_{obs}/s^{-1}	$10^{-3}k_{H}/M^{-1}s^{-1}$
18.0	0.80	4.795	9.38	1.94±0.01
		6.394	12.3	
	1.00	3.197	5.75	1.79±0.01
		6.394	11.4	
12.7	0.25	3.028	7.92	2,62±0.10
		4.543	12.6	
		6.056	15.5	
		9.084	22.8	
	0.40	4.327	9.38	2.14±0.04
		6.490	14.0	
		8.654	17.9	
		12.981	28.3	
	0.55	3.028	5.55	1.82±0.03
		4.543	8.30	
		6.056	10.6	
		9.084	16.8	
	0.75	3.028	5.12	1.66±0.04
		4.543	7.40	
		6.056	9.80	
		9.084	15.5	
	0.95	3.028	4.58	1.54±0.03
		6.056	9.32	
		9.084	14.2	

$T/^\circ C$	$[H^+]/M$	$10^3[\text{Penicillamine}]/M$	k_{obs}/s^{-1}	$10^{-3}k_H/M^{-1}s^{-1}$
12.7	1.25	3.028	3.93	1.30±0.05
		6.056	7.55	
		9.084	12.3	
7.85	0.25	3.205	6.10	1.94±0.04
		6.410	12.7	
	0.50	3.205	4.78	1.55±0.03
		4.808	7.55	
		6.410	9.95	
	0.75	3.205	4.15	1.32±0.03
		4.808	6.25	
		6.410	8.72	
	1.00	3.205	3.72	1.16±0.01
		4.808	5.62	
		6.410	7.36	

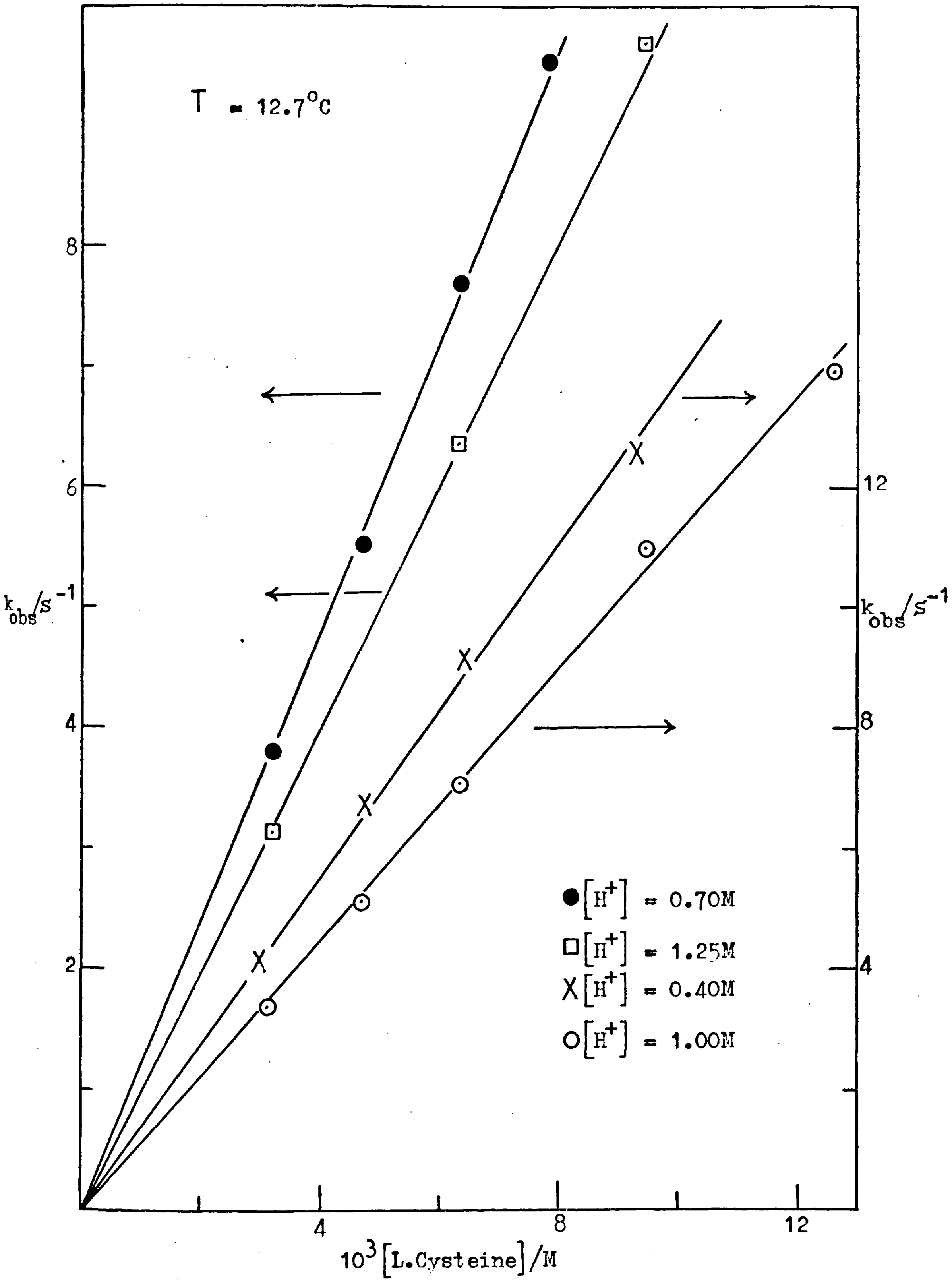


Figure 50 :- Plots of k_{obs} versus L.Cysteine at λ = 357nm, $[H^+]$ = 0.40, 0.70, 1.00, 1.25M, I = 1.50M, T = 12.7°C

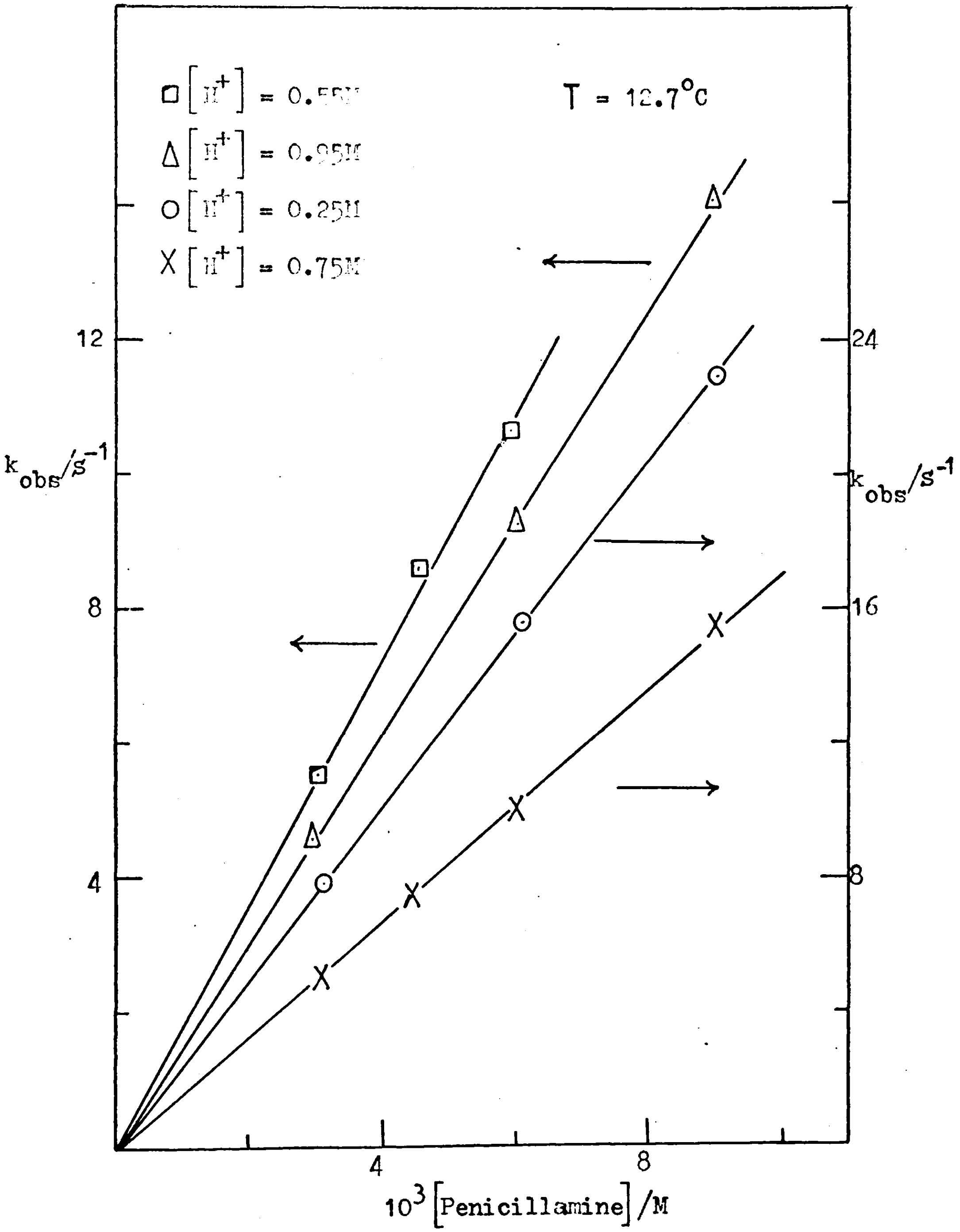


Figure 51 :- Plots of k_{obs} against Penicillamine at $[H^+]$ = 0.25, 0.55, 0.75, 0.95M, λ = 357nm, I = 1.50M, T = 12.7°C.

and oxygen at constant temperature and acidity at ionic strength 1.50M. Extinction coefficients of Ce(IV) obtained by extrapolation of plots to t = 0 were similar to those obtained in the absence of reductant. No effects on the rate were observed by initial addition of Ce(III) and nitrate ions (Table 25), thus suggesting neither reaction (40)[75]

$$Ce^{4+} + H_2O \rightleftharpoons Ce^{3+} + H^+ + OH \qquad (40)$$

nor any nitrato cerium(IV) complexes[66,69] are of any kinetic importance.

Reactions (21), (76) - (81) are consistent with the experimental observations

$$Ce^{4+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} CeOH^{3+} + H^+ \qquad (21)$$

$$TH^+ \overset{K_a}{\rightleftharpoons} T + H^+ \qquad (76)$$

$$Ce^{4+} + TH^+ \xrightarrow{k_6} Ce^{3+} + 2H^+ + X \qquad (77)$$

$$CeOH^{3+} + TH^+ \xrightarrow{k_7} Ce^{3+} + H^+ + X \qquad (78)$$

$$Ce^{4+} + T \xrightarrow{k_8} Ce^{3+} + H^+ + X \qquad (79)$$

$$CeOH^{3+} + T \xrightarrow{k_9} Ce^{3+} + X \qquad (80)$$

$$2X \xrightarrow{fast} X_2 \qquad (81)$$

TABLE 25

EFFECT OF Ce(III) AND NITRATE IONS ON THE REACTION RATE OF Ce(IV) WITH THIOLS

λ = 357nm, T = 25.0°C, Ionic Strength = 1.50M,
$[Ce(IV)]$ = 2.50 x 10^{-4}M, $[H^+]$ = 1.25M.

$10^3[\text{Cysteine}]/M$	$10^3[NO_3^-]/M$	k_{obs}/s^{-1}	$10^3[Ce(III)]/M$	k_{obs}/s^{-1}
3.671	0.0	4.85	0.0	4.85
	0.257	4.88	0.229	4.89
	1.028	4.82	0.918	4.88
	3.084	4.92	1.832	4.93
$10^3[\text{Penicillamine}]/M$				
3.044	0.0	6.33	0.0	6.33
	0.257	6.28	0.229	6.23
	1.028	6.25	0.918	6.31
	3.085	6.35	1.832	6.27

In these equations T and TH^+ are unprotonated and monoprotonated thiol (cysteine and penicillamine) molecules, X is the radical produced by oxidation (state of protonation not known), and X_2 is the disulphide formed in the rapid dimerisation reaction (81). For this mechanism the empirical rate law (82) obtains, with

$$k_H = \frac{k_6[H^+] + k_7K_h + k_8K_a + k_9K_hK_a/[H^+]}{([H^+] + K_h)\ (1 + K_a/[H^+])} \qquad (82)$$

which can be further simplified

a) if $K_a(k_8 + k_9K_h/[H^+]) \ll k_6[H^+] + k_7K_h$ and

$1 \gg K_a/[H^+]$, then

$$k_4 = (k_6[H^+] + k_7K_h) / ([H^+] + K_h) \qquad (82a)$$

and

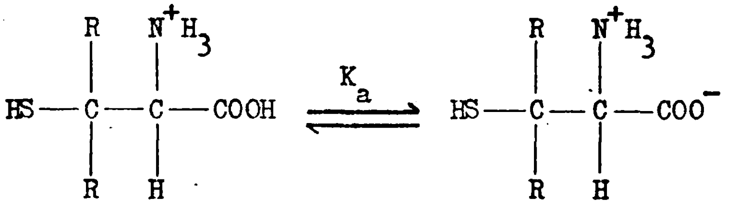
$$k_H ([H^+] + K_h) = k_6 [H^+] + k_7K_h$$

b) if $k_7K_h \gg k_6 [H^+]$ in equation (74a), then

$$k_H = k_7K_h / [H^+] + K_h) \qquad (82b)$$

and $k_H^{-1} = [H^+]/k_7K_h + {}^1/k_7$

For this mechanism the establishment of the limiting forms (82a) and (82b) at any particular temperature is seen to be largely dependent on the magnitude of K_a, defined as



$$\mathrm{HS{-}\underset{R}{\overset{R}{C}}{-}\underset{H}{\overset{\overset{+}{N}H_3}{C}}{-}COOH} \overset{K_a}{\rightleftharpoons} \mathrm{HS{-}\underset{R}{\overset{R}{C}}{-}\underset{H}{\overset{\overset{+}{N}H_3}{C}}{-}COO^-} + \mathrm{H^+} \qquad (83)$$

where R = H, and CH_3 for cysteine and penicillamine, respectively, and K_a has a value of $\sim 10^{-2}$M. pK_a values corresponding to loss of a proton by —SH or $\overset{+}{N}H_3$ of the zwitterion are > 8. Hence under the conditions used in this study the thiols are mostly present as a monoprotonated species. However, with this order of magnitude for K_a, the implicit assumption is obviously that the rate constants k_8 and k_9 are not very much larger than k_6 and k_7, although, of course, they could be of similar magnitude or even smaller (see below).

It is interesting to note that the only known example of Ce(IV) oxidation of organic substrate in perchlorate media in which equation (82b) has been shown to be operating is that of $N_2H_5^+$ [170]. Data from Table 24, when treated in this way, however, showed curvature, thus suggesting $k_6 \not< k_7$.

From the known values of K_h and k_H, a plot of $k_H([H^+] + K_h)$ against $[H^+]$ (equation 82a) should be a straight line with slope and intercept equal to k_6 and k_7K_h respectively. Such a treatment of kinetic data (Table 24) showed excellent linearity for both cysteine and penicillamine as shown in Figures 52 and 53 respectively, and the values of k_6 and k_7 are collected in Table 26.

The neglect of steps (79) and (80) in the mechanism and the corresponding assumptions in deriving equation (82a) may now be critically examined. If one assumes that

$$k_6 [H^+] + k_7K_h \gtrsim 10\ k_9K_aK_h/[H^+] \qquad (84)$$

at the lowest experimental acid concentration ($[H^+] = 0.25M$) in equation (84), then with $K_a \approx 10^{-2}M$, $K_h = 0.20M$, it follows that $k_9 \leqslant 1 \times 10^4\ M^{-1}sec^{-1}$ at 25°C.

Since these are the first kinetic studies on Ce(IV) oxidation of thiols in aqueous perchloric acid, direct comparison or the relative values of k_8 and k_9 cannot be made. However, it has been shown in a number of kinetic studies on the oxidation of organic substrates by Mn(III)[171], which like Ce(IV) is also one electron oxidant, that $k_8 \leqslant k_9$ in steps (79) and (80). Thus it is likely that $k_8 \leqslant 1 \times 10^4 M\ sec^{-1}$ at 25°C, justifying the assumptions that intercepts of plots of equation (82a) for the data for both thiols are essentially k_7K_h.

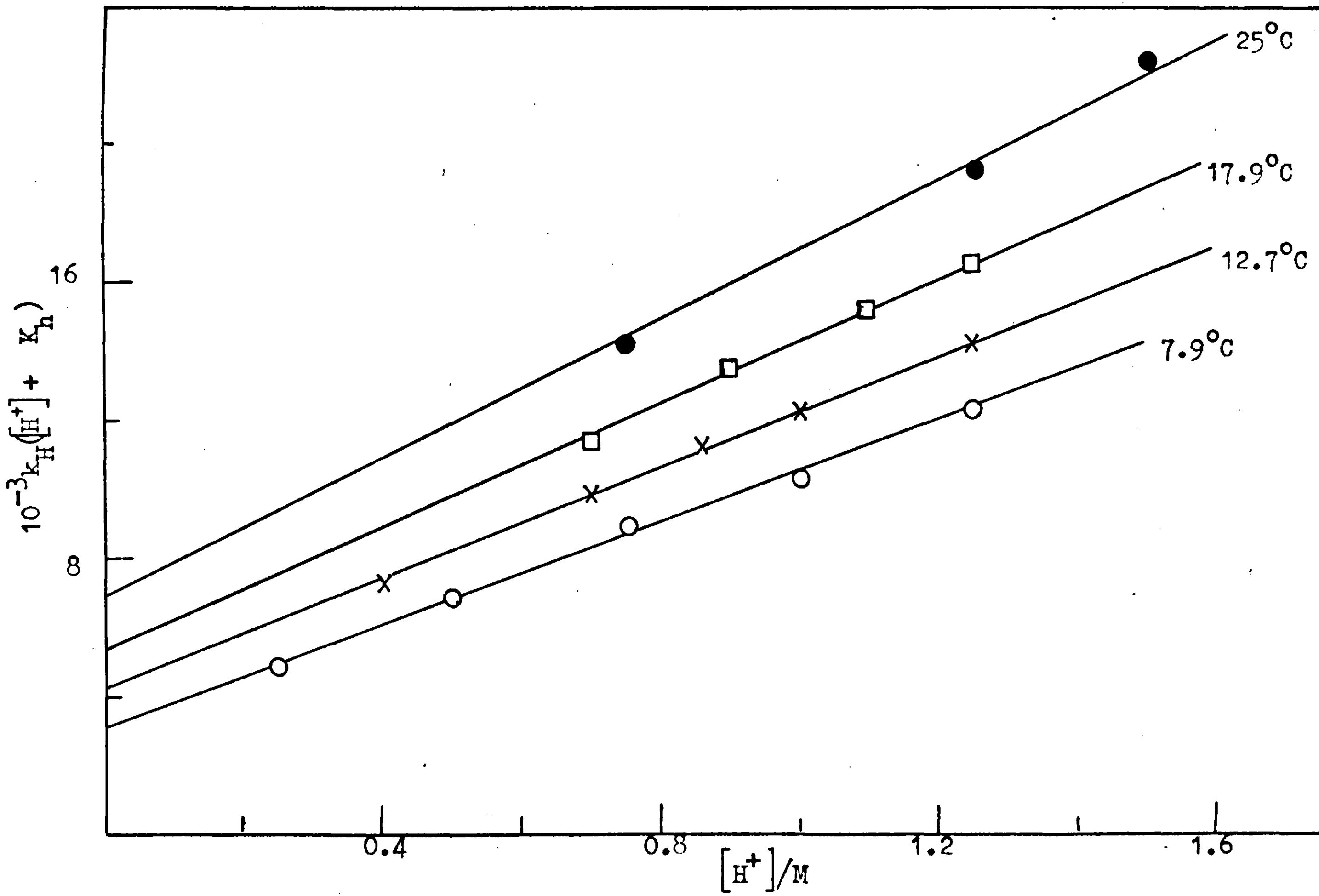


Figure 52 :- Plots of $([H^+] + K_h)k_H$ against $[H^+]$ (equation 82a) for cysteine at $T = 7.9°, 12.7°, 17.9°, 25°C$, $\lambda = 357nm$, and $I = 1.50M$.

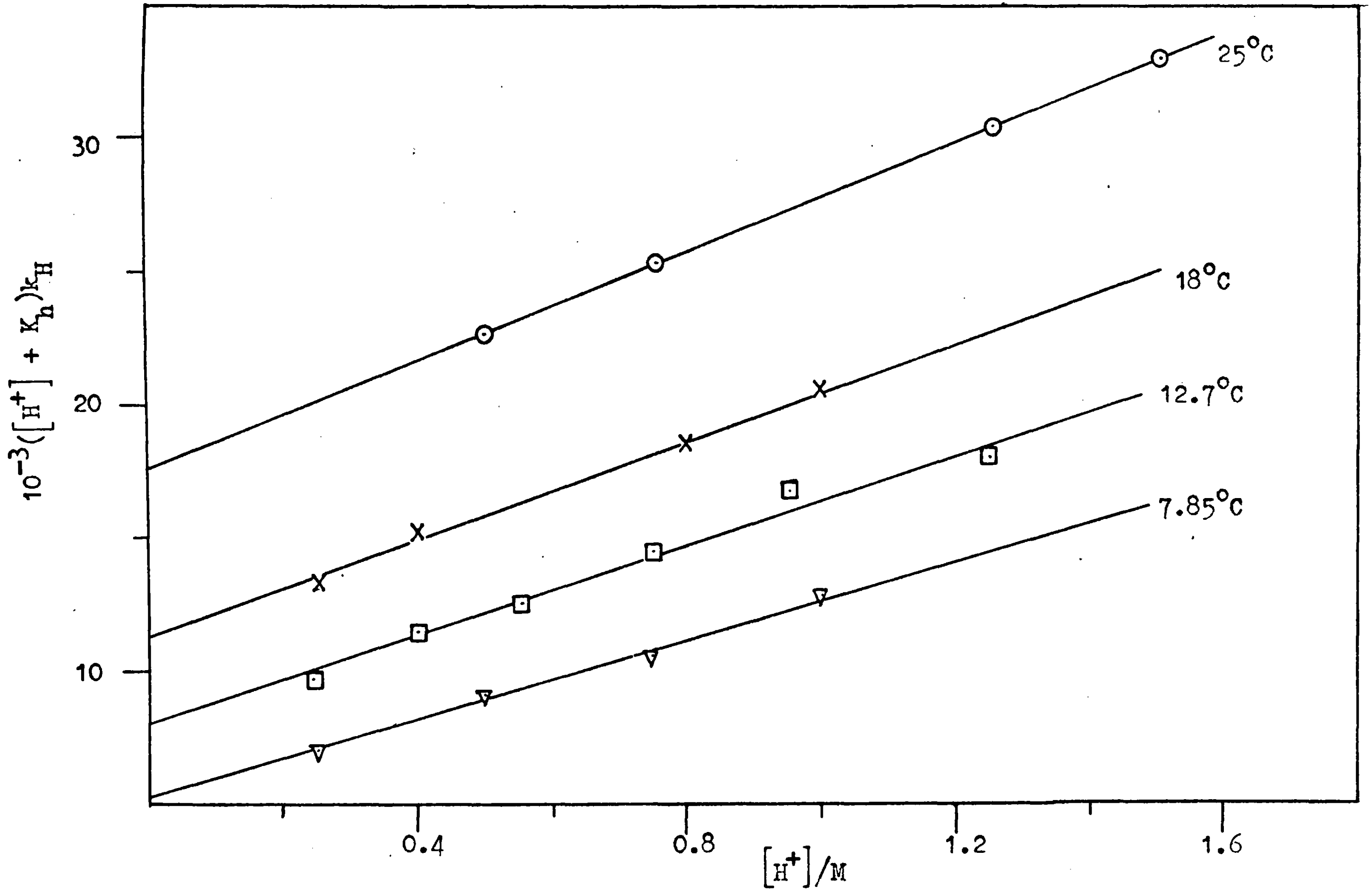


Figure 53 :- Plots of $([H^+] + K_h)k_H$ against $[H^+]$ (equation 82a) for penicillamine at T = 7.85°, 12.7°, 18°, 25°C, λ = 357nm and I = 1.50M.

TABLE 26

KINETIC PARAMETERS FOR REACTIONS OF CERIUM(IV) WITH THIOLS IN PERCHLORATE MEDIA

Thiol	T/°C	$10^3k_6/M^{-1}s^{-1}$	$10^3k_7/M^{-1}s^{-1}$
Cysteine	7.90	0.726±0.031	2.90±0.21
	12.7	0.799±0.036	3.31±0.22
	17.9	0.875±0.056	3.39±0.19
	25.0	0.965±0.03	3.51±0.17
Penicillamine	7.85	0.791±0.041	4.74±0.34
	12.7	0.833±0.057	6.17±0.31
	18.0	0.918±0.048	7.18±0.23
	25.0	0.972±0.012	9.06±0.25

Cysteine $\Delta H_6^* = 2.19\pm0.15$ k cal mole^{-1}, $-\Delta S_6^* = 37.5\pm7$cal $\text{deg}^{-1}\text{mole}^{-1}$

$\Delta H_7^* = 1.09\pm0.3$ k cal mole^{-1}, $-\Delta S_7^* = 38.6\pm10$cal $\text{deg}^{-1}\text{mole}^{-1}$

penicillamine $\Delta H_6^*=1.47\pm0.13$k cal mole^{-1}, $-\Delta S_6^*=39.9\pm10$cal $\text{deg}^{-1}\text{mole}^{-1}$

$\Delta H_7^*=5.49\pm0.5$k cal mole^{-1}, $-\Delta S_7^* =21.9\pm8$cal $\text{deg}^{-1}\text{mole}^{-1}$

As far as the site for initial attack of Ce(IV) on a thiol is concerned, previous observations must be considered. For example, it has been shown that for an organic substrate containing a carboxyl group the reaction must proceed via a complex and high enthalpy of activation, and since such a situation does not exist for thiols, the attack at oxygen can be ruled out. Moreover, the attack at nitrogen may be excluded as $k_6 \nless k_7$ as observed in the oxidation of hydrazine[170]. Furthermore, the stability of the radical may be demonstrated by the formation of disulphides. These findings are thus suggestive of attack at the sulphur atom.

The thermodynamic parameters are given in Table 27, which includes data for Ce(IV) oxidation of α-mercapto acids[106] and thioureas[107] in sulphate media and Co(III)[172,173] in perchlorate media. The former reactions are believed to occur via an apparent second order mechanism, whereas transient complexes have been characterised[172] in the oxidation of thiomalic acid with Co(III). The observed high rates of reactions of these sulphur containing systems compared with their oxygen containing analogues are due to favourable enthalpies and entropies of activation. The favourable activation energy may be explained if it is considered that the electron transfer occurs through

TABLE 27

THERMODYNAMIC PARAMETERS FOR THIOLS OXIDATIONS[a]

Oxidant	Thiol	ΔH^{*}(b)	$-\Delta S^{*}$(c)	Ref
Co^{3+}	thiourea	10.0	10	173
$CoOH^{2+}$	thiourea	15.0	10	173
Ce(IV)(d)	thiourea	7.3	32.7	107
	T.G.A.(e)	7.3	27	106
	T.L.A.(e)	6.2	31	106
	T.M.A.(e)	7.0	30	106
Ce^{4+}	L-cysteine	2.2	37	this work
	DL-penicillamine	1.5	39	this work
$CeOH^{3+}$	L-cysteine	1.1	39	this work
	DL-penicillamine	5.5	22	this work
Mn^{3+}	ethylene thiourea	(f)	(f)	175
$MnOH^{2+}$	ethylene thiourea	6.0	11	175

(a) - 25°C, and in perchlorate media

(b) - units of k cal $mole^{-1}$

(c) - units of cal $deg^{-1} mole^{-1}$

(d) - in sulphate media

(e) - thioglycollic, thiolactic and thiomalic acids

(f) - $k_6 \ll k_7$ ref. equation (82b)

the —SH group and that sulphur atoms are involved in the activated complex. If this were the case, then sulphur, with its d - orbitals, is more likely to stabilise the activated complex than oxygen which has no such d - orbitals. The existence of sulphur radicals as intermediates is well known in the oxidation reduction of sulphur systems and values of -20 to -34 eu have been ascribed to the nature of electron pairing and unpairing process in radical reactions[174]. The formation of the disulphides as the products of the reactions of these systems seems to support the fact that the reaction proceeds through the sulphur centre to give free radicals which then dimerise to form the final products. The disulphides have been shown to be the final products in the oxidation of thioureas, α-mercapto carboxylic acids by Ce(IV)[106,107], Co(III)[172,173], Mn(III)[175], V(V)[176], and Cr(VI)[130].

The rate of oxidation of L-cysteine was found to be lower than that of DL-penicillamine by cerium(IV) in perchlorate media. Since the reaction involves the transfer of electrons from the organic substrate to the metal ion, any group which has the tendency to increase the electron density at the point of transfer (and in this case, the sulphur atom) is likely to enhance the reaction. Therefore, the higher rate constants for the DL-penicillamine than for the L-cysteine may be as expected.

More data on other substituted species are, however, required before a full description of the effect of the substituent groups on the rates of reactions of this nature can be made.

Chapter 5

THE REACTION OF THIOMALIC ACID WITH THALLIUM(III)

INTRODUCTION

Although over the last few decades considerable kinetic data have been accumulated on the oxidation-reduction reactions involving metal ions and inorganic and organic compounds, most metal ion systems studied have involved a single electron transfer to attain a lower stable oxidation state. Thallium(III), however, needs two electrons for this purpose. The chemistry of thallium has recently been reviewed by Lee[177].

For oxidation-reduction reactions between metal ions in which a two equivalent change is possible there has been considerable discussion of the factors determining whether such changes might take place in successive one electron steps or by a single step in which two electrons are transferred. Recent reviews[178,179] on this subject reflect the incomplete understanding of these systems due to a lack of kinetic and thermodynamic data for reactions of the frequently highly reactive intermediate oxidation states which participate in two equivalent reactions proceeding by one electron transfer steps.

The electron exchange between Tl(I) and Tl(III) has been extensively studied. For reactions with a number of one electron oxidants and reductants, Tl(II) has been postulated as an intermediate from kinetic evidence. Recently pulse radiolysis and flash photolysis techniques[180–182] have been successfully used to generate Tl(II) in solution and an identical spectrum of this highly reactive species has been obtained by these techniques. A major and more substantial contribution in the chemistry of Tl(II) has recently been made by Lawrence and his co-workers[182]. Using the flash photolysis technique they studied the kinetics of oxidation-reduction reactions of Tl(II) with a large number of transition metal ions and also estimated, based on kinetic data, the electrode potentials of the following reactions

$$Tl^{3+} + e \rightleftharpoons Tl^{2+} \qquad E_1^o = 0.31V \qquad (85)$$

$$Tl^{2+} + e \rightleftharpoons Tl^{+} \qquad E_2^o = 2.22V \qquad (86)$$

Although the agreement between the standard reduction potential for the Tl(III) - Tl(I) couple calculated using these values of E_1^o and E_2^o and the literature value is fairly good, E_1^o and E_2^o values are, however, markedly different from earlier estimates. The very high value of E_2^o is somewhat unexpected, as compared to Higginson's[183] suggested value of $>1.5V$. The estimate of the reduction potentials by Hush[184] was dependent on the assumption that the electron exchange reaction between Tl(I) and Tl(III) ions involves two successive one electron transfer steps, and this assumption is to some extent conditioned by values of the reduction potentials. The reduction potentials provide a more reliable base than was previously available for discussing the oxidation-reduction chemistry of thallium. The high value of E^o_2 suggests that Tl^{2+}_{aq} ions are much stronger oxidising agents than Co^{3+}_{aq}. Furthermore, E^o_2 value being close to that of Cu^{3+}_{aq}, it is possible that in neutral solutions Tl^{2+} ions may exist in equlibrium with OH radicals, as do Cu^{3+}_{aq} ions[185].

(a) Oxidation of Orgainc Substrates by Tl(III)

Thallium(III) has recently been used as a mild oxidant in the oxidation of a variety of organic compounds. Most of these oxidations have been carried out in acetic acid solutions, mainly because organic compounds are generally more soluble in acetic acid than in more polar solvents. Although in many cases H_2SO_4, HNO_3, and HCl have been tried as reaction media, the reaction kinetics become more difficult to interpret. In perchloric acid medium the situation is, however, somewhat simpler in that there is less tendency for complex formation between Tl^{3+} and ClO_4^- to occur.

The first study of the oxidation of olefins by Tl(III) salts was made by Grinstead[186]. In the reaction between 2 - hexene and Tl(III) acetate in acetic acid-water mixtures, the main products were acetate esters of hexene - 2,3 diol. yields of which varied with the water content of the medium. The reaction has been considered to proceed by an oxythallation - dethallation sequence.

Oxidation of ethylene to ethyleneglycol occurs with both thallium(III) nitrate in nitric acid and thallium(III) sulphate in sulphuric acid. Thallium(III) chloride in hydrochloric acid, however, is unreactive. In another study on the oxidation of ethylene by Tl(III) in aqueous sulphuric, nitric, and perchloric acids, the rate law suggests first order dependences on Tl(III) and olefin respectively and the rate increases with increasing salt concentration[187]. The only primary products detected were acetaldehyde and ethyleneglycol and the proposed mechanism involved the initial formation of a π-complex which then rearranged to a σ-complex. Since π-complex formation with metal ions is usually a very fast process, it has been suggested that the rate determining step is rearrangement of π-complex to σ complex, followed by its decomposition to yield the final prducts.

Recently the stopped-flow technique has been used to study the oxidation of catechol by Tl(III) in perchlorate media[188,189]. Under the experimental conditions of excess of oxidant or reductant, the kinetic dependences on the oxidation of catechol with thallium(III) ions suggest that the same mechanism is operating in both cases with no spectrophotometric evidence of complex formation.

Srinvasan[190] reported that the oxidation of oxalic acid by Tl(III) in aqueous sulphuric acid proceeds by a simple bimolecular process and suggested the formation of Tl(II) as an intermediate. However, in perchloric acid the oxidation of this substrate occurs via the formation of a complex which decomposes in a rate determining step involving a two electron transfer to CO_2 and Tl(I)[191].

Spectrophotometric evidence for the intermediate complex formed between Tl(III) and organic species in perchlorate media was first given by Halpern[192] in the Tl(III) oxidation of formic acid. The interesting kinetic features of this reaction are that at low reactant concentrations and high acidities, the rate law conforms to a relatively simple form. However, in the region of higher reactant concentrations, more extensive complexing between Tl^{3+} and $HCOO^-$ leads to a modification of the kinetic scheme[193].

(b) The Chemistry of Thiomalic Acid

Thiomalic acid has been shown by potentiometric studies[194,195] to form chelates with Ag(I), Co(II), Hg(II), Ni(II) and Zn(II). The stability constants of thiomalic complexes are on the whole considerably higher than those of its nitrogen and oxygen analogues, aspartic and malic acids respectively. This would indicate that sulphur has better donating properties for the metal ions investigated than either oxygen or nitrogen. In both of the above papers it was noted that Cu(II) underwent redox reaction and cannot be studied photometrically. A spectrophotometric and polarographic study has been carried out on the intensely violet coloured complex obtained when Cu(II) is mixed with thiomalic acid[196] (RSH). It was concluded that the violet colour was due to the mixed valence complex $Cu(II)(Cu(I)SR)_4$.

Most metal ion oxidation of thiols yields disulphides if the reductant is present in excess[197,198]. Thiomalic acid is no exception, although it has been shown[168] to be over oxidised by both Np(VI) and Ce(IV) in an argon atmosphere to an extent which appears to be governed only by the magnitude of the initial thiol concentration.

A kinetic study[106] of the cerium(IV) sulphate oxidation of thiomalic acid showed, however, that the product is exclusively disulphide under the reaction conditions used therein. No complex formation was reported, the reaction being simple first order in each of the two reactants.

Intermediate complexes have also been identified in the oxidation of thiomalic acid by V(V)[176] and Co(III)[172]. In the former system the kinetic data suggest the involvement of a pathway, in addition to the more usual first order process, where a ligand molecule interacts with the complex. Disulphide was found to be the exclusive organic product of both redox processes[172,176].

The blue intermediate formed in the reduction of Fe(III) by thiomalic acid has also been characterised[199] spectrophotometrically. Disulphide and Fe(II) are the overall reaction products. The difference in reactivity conferred by replacement of oxygen by sulphur is illustrated well by the absence, under normal conditions, of any measurable redox reaction of the Fe(III) malate complex[200].

A recent study[201] on the oxidation of thiomalic acid by Cr(VI) in perchlorate medium has also shown the existence of a transient complex as precursor to the oxidation step. The spectrum of this complex has ${}_{max}$ similar to other Cr(VI) - S bonded complexes[130,131,167].

(c) Interaction of Tl(III) with Thiols and its Biological Importance

Much of the current interest in complex formation between transition metal ions and organic compounds containing functional units such as sulphydryl or amino groups is in anticipation that 'model' compounds for the study of biochemical reactions will result. Thiol containing ligands have received considerable attention[195,202,203] since many enzyme active sites have, or are thought to have, nearby both a sulphur stom and a metal ion which are involved with the catalytic activity.

The types of reaction between sulphydryl groups and metal ions differ considerably depending on the oxidation state of metal. For example, Tl(III) - Thiol complexes are more susceptible[204] to reduction in acid medium, as compared to Tl(I) complexes. Furthermore, it has been shown that the stability of Tl(III) - Thiol complexes can be increased by using chelating thiols[205].

Recently, penicillamine hydrochloride, a thiol, has been successfully used as an antidote for thallium poisoning. The complete mechanism and physiological mode of action of thallium poisoning[206,207] is still unclear, but recently the n.m.r. technique has been used to study the binding of Tl(I) to enzymes[208]. Although only preliminary data have so far been published, this method may well produce much information of fundamental significance for the study of enzyme structure and activity.

The results of preliminary investigations on reactions involving Tl(III) and a large number of thiols in perchlorate media suggest that relatively strong Tl(III) - Thiol complexes are formed which depending upon the experimental conditions, decompose to Tl(I) products. Since very little is known about the Tl - S chemistry, the kinetic study of oxidation of thiomalic acid by Tl(III) was initiated and results are reported in this chapter.

EXPERIMENTAL

Thallium(III) perchlorate solutions were prepared by dissolving Tl_2O_3 (Koch - Light Laboratories, 99.998%) in 5 - 7 M $HClO_4$ at 60 - 70°C for 6 - 8 hours. The thallium concentration was determined as follows: A known volume of Tl(III) in $HClO_4$ was diluted to yield less than 0.5M solution in $HClO_4$ and added to a 2% solution of KI. The liberated iodine was titrated against standard sodium thiosulphate (Hopkin and Williams, AnalaR). The end point was marked by the change from dirty blue to clear yellow of the precipitate of thallous iodide. The dilution of the reacted mixture was necessary as concentrated solution of $HClO_4$ liberates iodine from KI solution.

The thallium(I) content of the solution was determined, following addition of HCl, by titration with standard potassium iodate (Hopkin & Williams, AnalaR) solution using chloroform as an indicator.

The analytical concentration of $[H^+]$ in the $Tl(ClO_4)_3$ solutions was measured in the following way: To a known volume of the solution, a small excess of dilute H_2O_2 (Hopkin and Williams, AnalaR) was added, which immediately reduced the Tl(III) ions quantitatively to Tl(I). The excess of H_2O_2 was destroyed by boiling, and after cooling, the solution was titrated with NaOH. Assuming the reaction (87),

$$Tl^{3+} + H_2O_2 \longrightarrow Tl^{+} + 2H^{+} + O_2 \qquad (87)$$

the difference between the titrated hydrogen ion concentration and twice the molar concentration of Tl(III) ions is equal to the hydrogen ion concentration before the reduction. The acid content of the H_2O_2 was found to be negligible.

Freshly prepared $Tl(ClO_4)_3$ solution (ca. 0.225M Tl^{3+}

in 6.349M $HClO_4$) was found to contain less than 0.1% Tl(I) and since the solution was stored in a dark bottle at ~ $5^{o}C$ and protected from sunlight, the amount of Tl(I) was not greater, even after three months, than 0.3% of the total thallium content.

Thiomalic acid (Koch Light Laboratories, pure) was used as provided. The preparation and standardisation of stock solutions of sodium perchlorate and perchloric acid were as described in Chapter 3.

Kinetic Measurements

Kinetic measurements were made under conditions of excess of thiomalic acid on 'slow' stopped-flow apparatus described in Chapter 2. In a typical kinetic experiment reactant solutions were prepared immediately prior to kinetic measurements being made. Comparison of optical density of blank solutions at $\lambda = 280nm$, in which Tl(III) was rapidly diluted with acid perchlorate solution, with those where thiomalic acid was present, indicated formation of a complex within the time of mixing and the subsequent redox reactions were monitored at $\lambda = 290 - 350nm$. The $[H^+]$ range employed was 0.25 - 1.00M at total ionic strength of 2.00M. The temperature was varied between 20.5^{o} and $30^{o}C$.

In some cases, especially at high acidities and low temperature, the reactions were followed up only one half life. All kinetic studies were conducted in the presence of air which was shown to have no detectable effect on the observed rate constants.

RESULTS AND DISCUSSION

Preliminary Experiments

Spectrophotometric measurements made on Tl(III) complexes formed with a number of organic substrates indicate a marked shift of the UV spectrum of Tl(III) to the visible region. For example, sulphur-containing organic substrates show a much more pronounced effect on the Tl(III) spectrum (Figure 54) than the corresponding oxygen analogues. Figure 54 shows a comparison of the spectra of Tl(III) complexes with malic, thiomalic acid, cysteine and penicillamine and it is concluded that bonding in the Tl(III) - thiomalic acid complex is through the -SH group. Another interesting feature of these preliminary investigations was that the redox reactions of sulphur-containing substrates were very much dependent on the reaction conditions. For example, spectrophotometric measurements of Tl(III) - ethylene thiourea

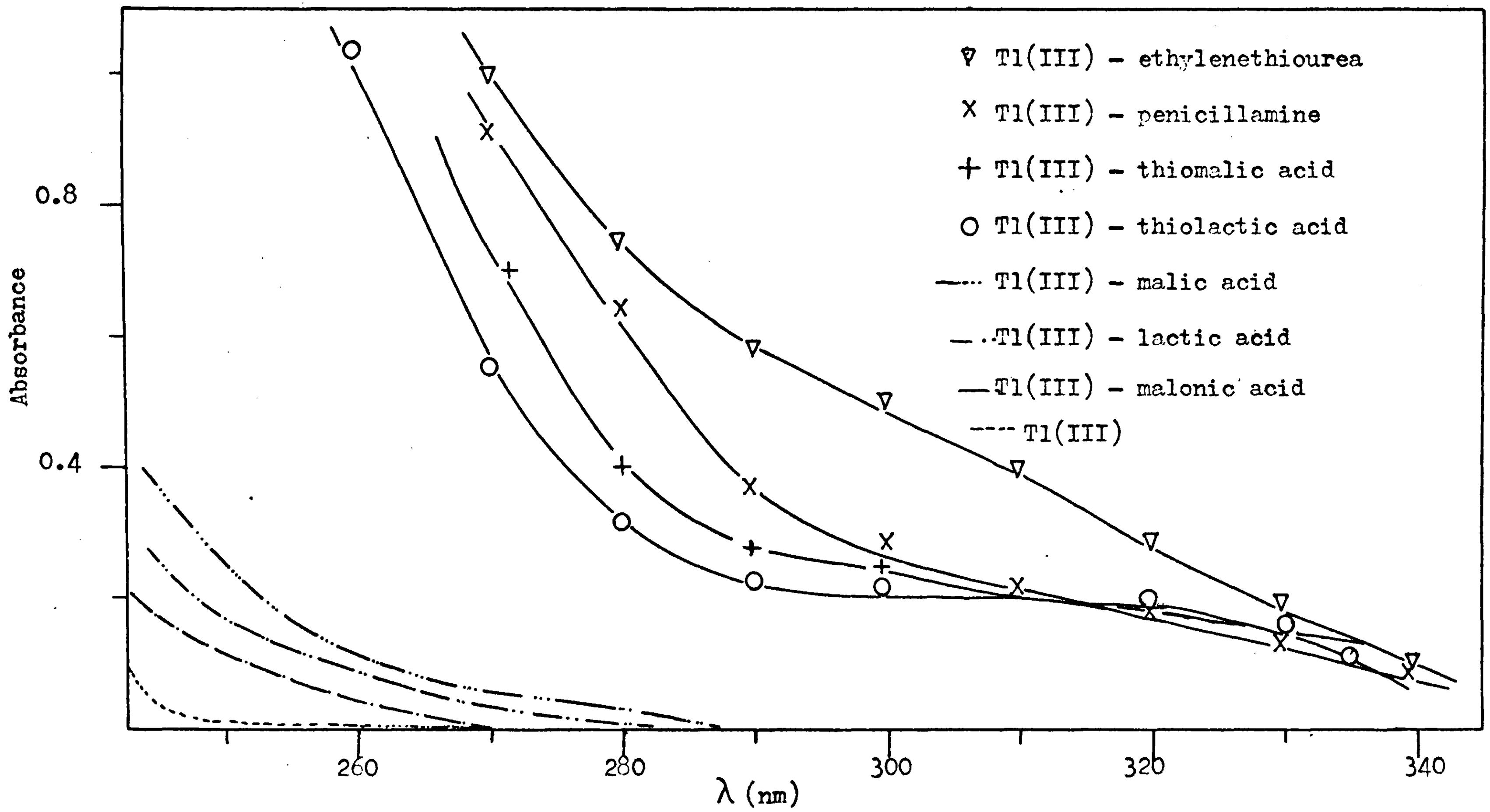


Figure 54 :- Spectra of Tl(III) complexes with sulphur and oxygen containing substrates, $[Tl(III)] = 3 \times 10^{-4}M$, thiomalic, thiolactic, malic, malonic and lactic acids $= 6 \times 10^{-3}M$; $[\text{ethylenethiourea}] = 5 \times 10^{-4}M$, $[Tl(III)] = 5 \times 10^{-3}M$ $[H^+] = 1.0M$

system suggest the formation of a number of complexes of different composition, i.e. 1 : 1, 1 : 2, 1 : 3, 1 : 4, etc. in the presence of an excess of reductant (Figure 55). Moreover, the decomposition of these complex(es) was found to be fast ($t_{\frac{1}{2}} >$ few secs) and to be first order with respect to Tl(III) concentration. However, by working in a large excess of oxidant, the redox reactions were much slower, i.e. $t_{\frac{1}{2}} =$ several minutes (Figure 56). This could be explained in terms of differing oxidation-reduction potentials of these complexes. On the other hand, reactions of Tl(III) with -SH containing substrates, i.e. α- mercaptocarboxylic acids, cysteine and penicillamine, are completely different from those discussed above. Under the conditions of a large excess of Tl(III) over the reductant, although the formation of the transient complexes was very fast ($t_{\frac{1}{2}} =$ few milliseconds), the corresponding redox reactions could be measured, i.e. $t_{\frac{1}{2}}$ few seconds. Such data indicated an unusual inverse dependence on the oxidant concentration. It is interesting to note that spectrophotometric measurements on a reaction mixture containing either a large excess of oxidant or thiomalic acid gave a similar spectrum of the transient intermediate, thus suggesting a 1 : 1 complex (Figure 57). Thus a preliminary kinetic investigation on the reduction of Tl(III)

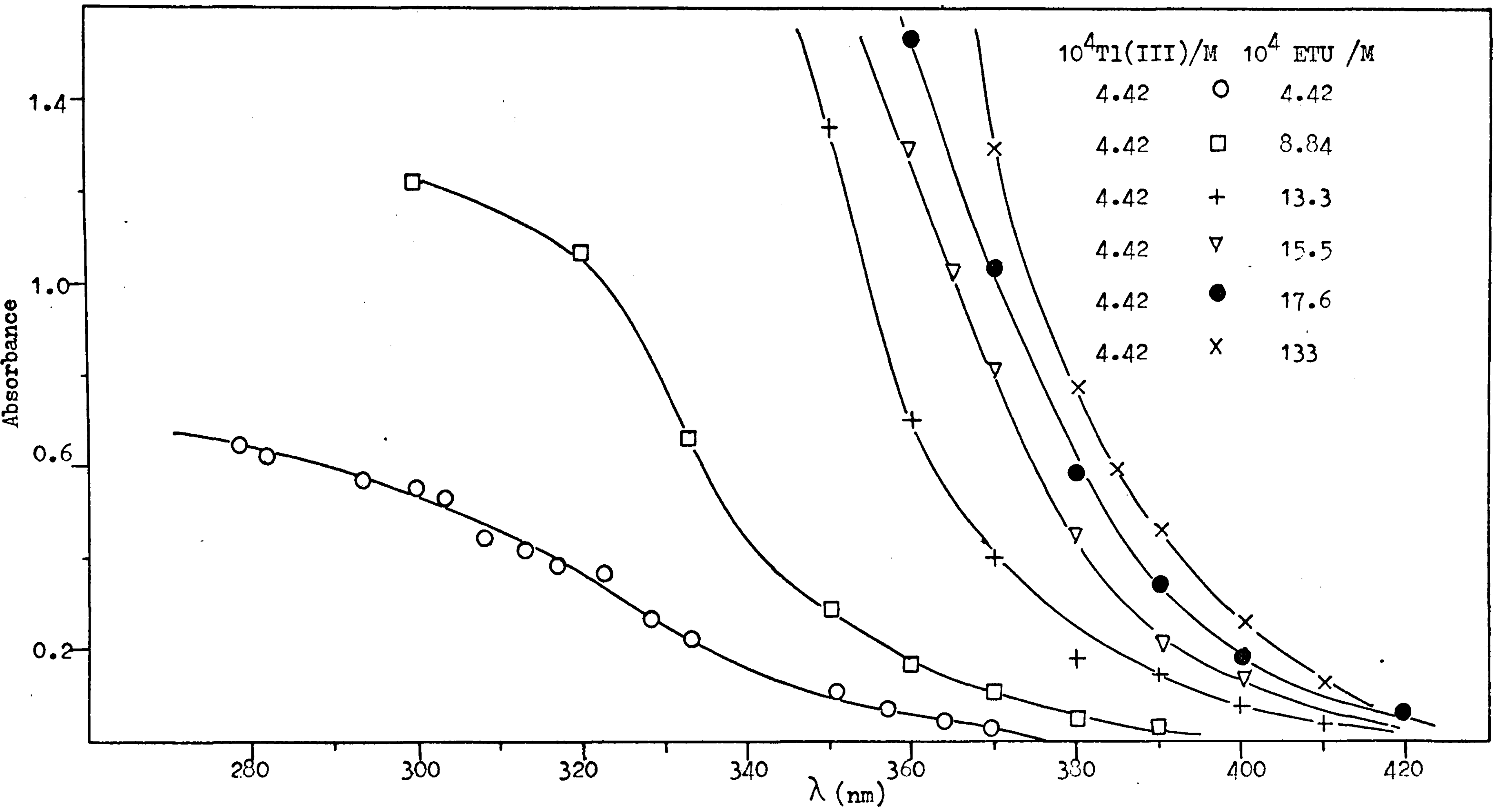


Figure 55 :- Spectra of Tl(III) - ethylenethiourea complexes.

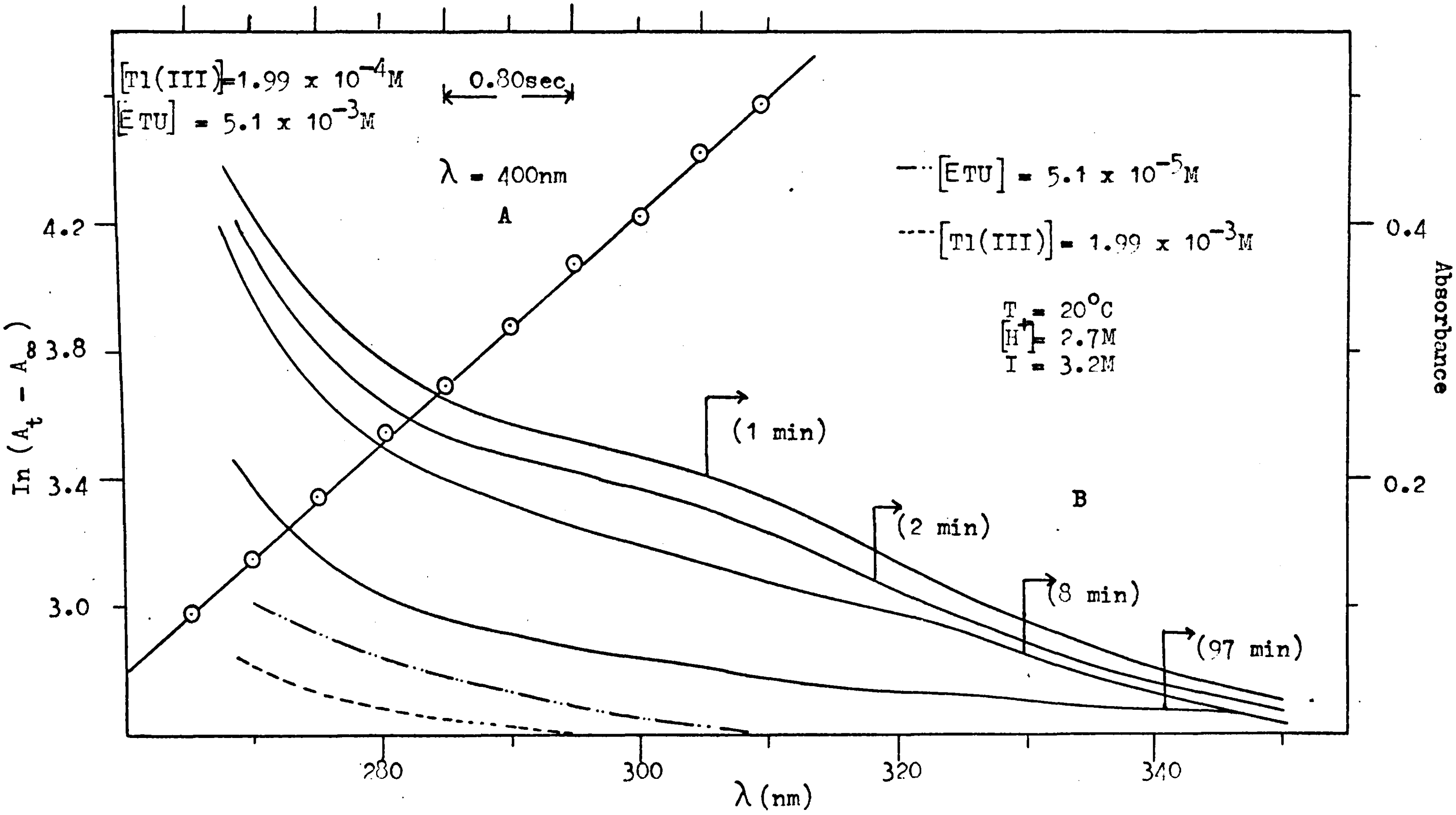


Figure 56:- Comparison of rate of decomposition of intermediate complex (s) of Tl(III) with ethylenethiourea at T = 20°C, (A) Tl≪ETU, (B) Tl≫ETU.

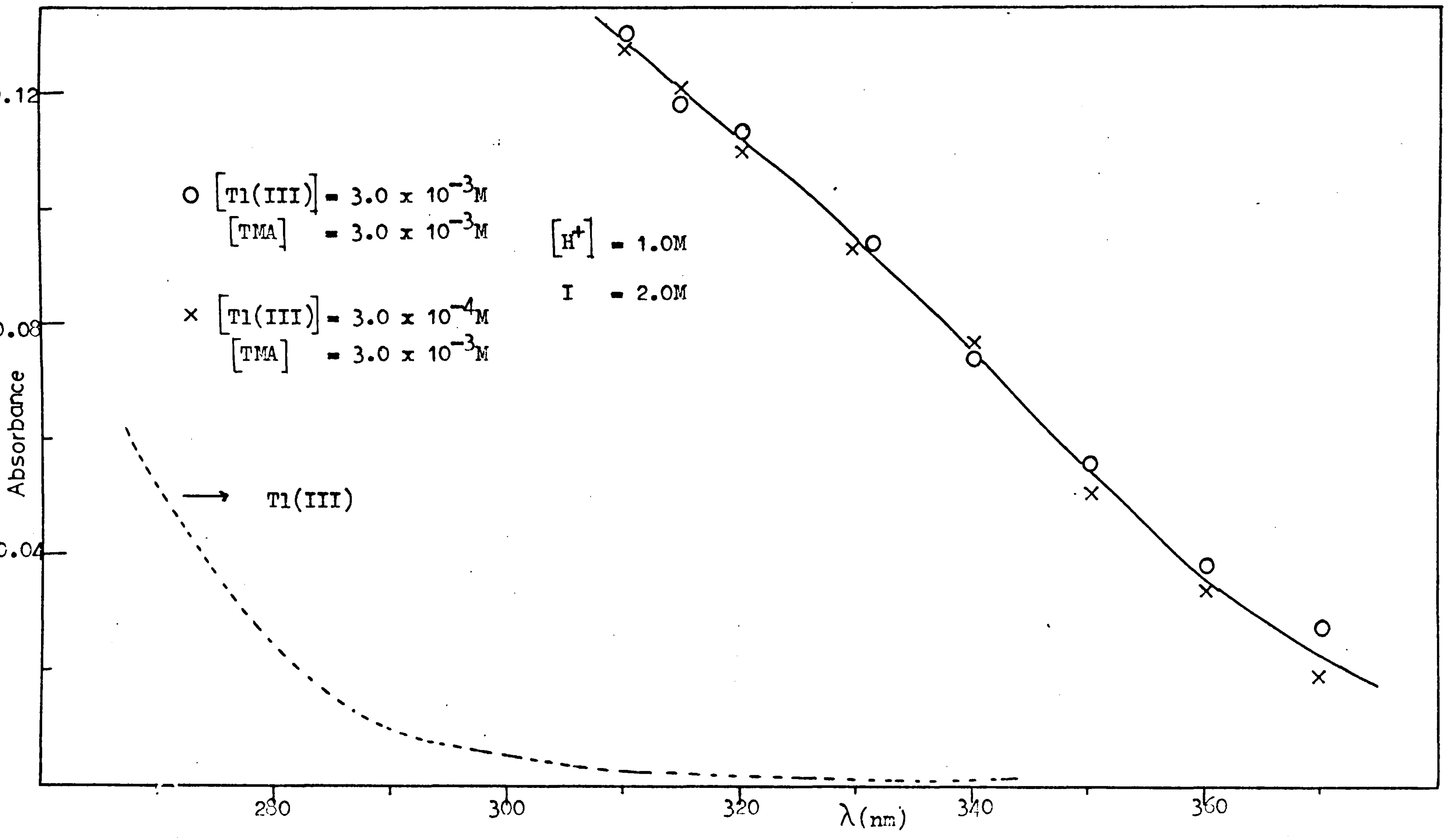


Figure 57 :- Spectra of Tl(III) - thiomalic acid intermediate complex

by thiomalic acid in the presence of a large excess of the latter, was undertaken to obtain some information on this fascinating aspect of Tl - S chemistry.

Stoicheiometry

The stoicheiometry of the reaction was determined by the spectrophotometric estimation of the unreacted thiomalic acid[209] in the reacted mixture. Typical reaction conditions were: Tl(III) = 5 - 12 x 10^{-5} moles, thiomalic acid = 5.2 x 10^{-4} moles, $[H^+]$ = 1.2 M, and three determinations gave a stoicheiometry of 2.1 ± 0.3 moles of thiomalic acid per mole of Tl(III) consistent with (88)

$$\mathrm{Tl(III)} + 2\mathrm{HRSH} \longrightarrow \mathrm{Tl(I)} + \mathrm{HRSSRH} + 2\mathrm{H}^+ \qquad (88)$$

where HRSH = thiomalic acid.

Although the oxidation product was not positively identified in this study, the oxidation of this reductant by a variety of metal ions has been shown to yield only disulphide as the oxidised product in the presence of a large excess of reductant[106,168,172,176].

Kinetics and Mechanism

The overall kinetics may be adequately represented by the following reaction scheme :

$$Tl^{3+} + H_2O \overset{K_h'}{\rightleftharpoons} TlOH^{2+} + H^+ \qquad (89)$$

$$Tl^{3+} + HRSH \overset{K_7}{\rightleftharpoons} TlHRSH^{3+} \qquad (90)$$

$$TlOH^{2+} + HRSH \overset{K_8}{\rightleftharpoons} TlHRS^{2+} + H_2O \qquad (91)$$

$$TlHRSH^{3+} \overset{K_9}{\rightleftharpoons} TlHRS^{2+} + H^+ \qquad (92)$$

$$TlHRSH^{3+} \xrightarrow{k_{10}} Tl(II) + HRS + H^+ \qquad (93)$$

$$TlHRS^{2+} \xrightarrow{k_{11}} Tl(II) + HRS \qquad (94)$$

$$Tl(II) + HRSH \xrightarrow{k_{12}} Tl(I) + HRS + H^+ \qquad (95)$$

$$2HRS \xrightarrow{k_{13}} HR - S - S - RH \qquad (96)$$

It is recognised that reactions of further hydrolysed species of Tl(III) and the undissociated thiomalic acid have not been included, but under the conditions employed, the concentrations of such species are considered negligible.

Providing the protolytic reactions are sufficiently fast, the electron transfer sufficiently slow ($k_{13}, k_{12} \gg k_{10}$ and k_{11}), and an excess of thiomalic acid is maintained, the rate of decrease of Tl(III) may be described as

$$\frac{-d[\mathrm{Tl(III)}]}{dt} = k_{10}\left[\mathrm{TlHRSH}^{3+}\right] + k_{11}\left[\mathrm{TlHRS}^{2+}\right] \qquad (97)$$

and

$$k_{obs}^{-1} = \frac{([\mathrm{H}^+] + K_h')}{(k_{10}K_7[\mathrm{H}^+] + k_{11}K_8K_h')[\mathrm{HRSH}]} + \frac{(K_7[\mathrm{H}^+] + K_8K_h')}{(k_{10}K_7[\mathrm{H}^+] + k_{11}K_8K_h')} \qquad (98)$$

All kinetic runs, especially at 30° and 25°C, showed good linearity of the first order plots to at least 80 - 90% reaction, and typical plots are shown in Figure 58. Some measured values of k_{obs} at each temperature and hydrogen ion concentrations are listed in Table 28.

The inverse hydrogen ion dependence of the rate of reaction in the $[\mathrm{H}^+]$ range 0.25 - 1.00M can be correlated with the hydrolytic equilibria of Tl^{3+}, rather than any dissociated species of thiomalic acid. Since,

$$\mathrm{Tl}^{3+} + \mathrm{H_2O} \xrightleftharpoons{K_h'} \mathrm{TlOH}^{2+} + \mathrm{H}^+ \qquad (89)$$

$$\mathrm{TlOH}^{2+} + \mathrm{HRSH} \xrightleftharpoons{K_8} \mathrm{TlHRS}^{2+} + \mathrm{H_2O} \qquad (91)$$

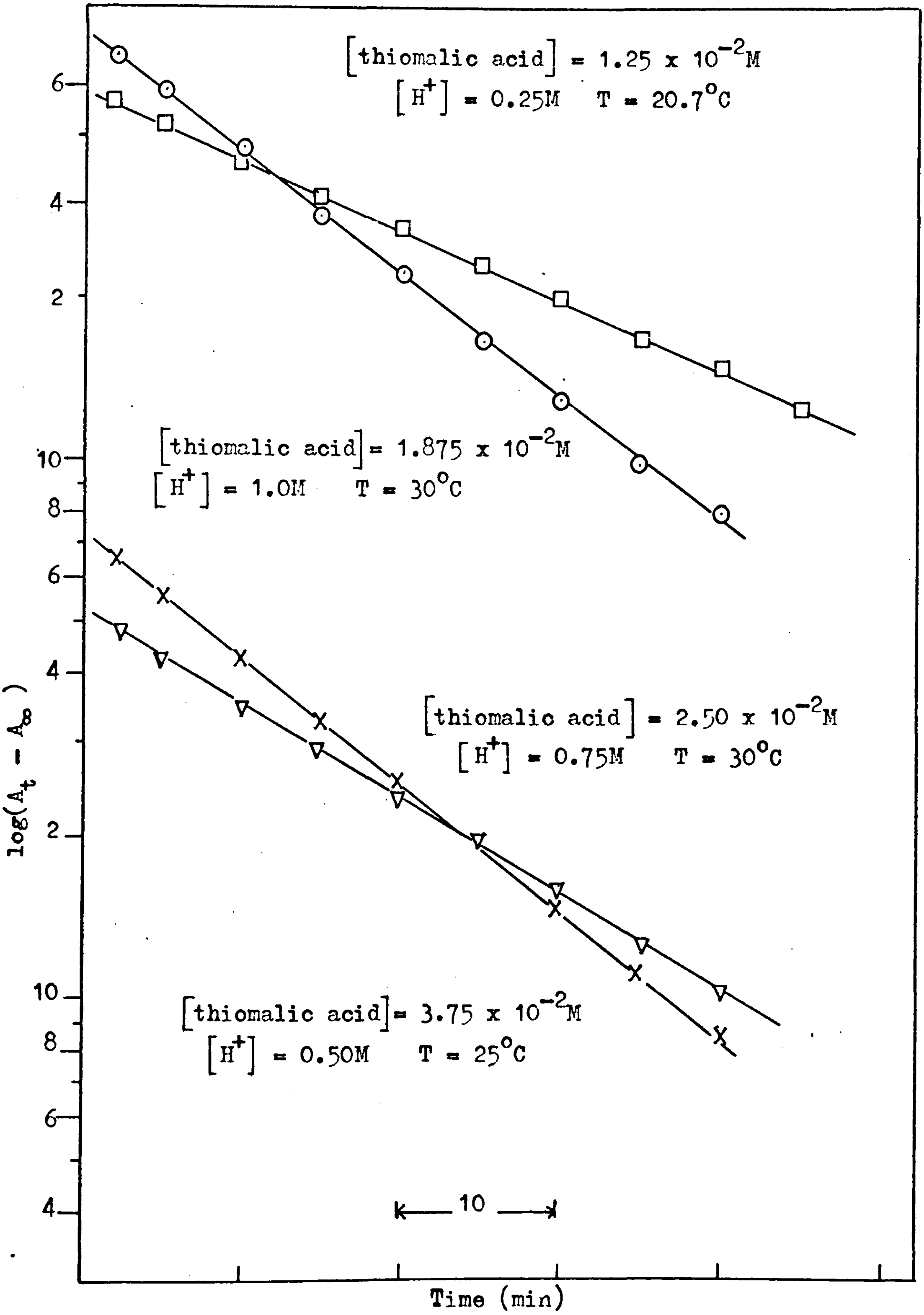


Figure 58 :- First order decay of Tl(III) at various [H$^+$] and temperatures.

the hydrolysis constant of Tl^{3+} is 0.073M at I = 3M and 25°C, and the hydrogen ion concentration employed in the present investigation, Tl(III) exists mostly as Tl^{3+}(78-94%). An alternative origin for the hydrogen ion effect may be derived from the reaction

$$TlHRSH^{3+} \underset{}{\overset{K_9}{\rightleftharpoons}} TlHRS^{2+} + H^{+} \qquad (92)$$

where $K_7K_9 = K_8K_h'$.

It is kinetically difficult to distinguish the pathways (89) and (91) or (90) and (92) by which $TlHRS^{2+}$ is formed, although equilibrium (92) has been preferred in the thallium(III) oxidation of hydrogen peroxide[210] and hypophosphorous acid[211].

According to equation (98), at constant $[H^+]$, a plot of k_{obs}^{-1} against $[HRSH]^{-1}$ should be linear and this was observed. Typical plots at various $[H^+]$ and temperatures are shown in Figure 59. Using the known values of slope and intercept (Table 28) obtained from the plots of k_{obs}^{-1} against $[HRSH]^{-1}$, the following equations may be derived :

$$\frac{([H^+] + K_h')}{\text{Slope}} = k_{10}K_7[H^+] + k_{11}K_8K_h' \qquad (99)$$

$$\frac{([H^+] + K_h')}{\text{Slope}} \times \text{Intercept} = K_7[H^+] + K_8K_h' \qquad (100)$$

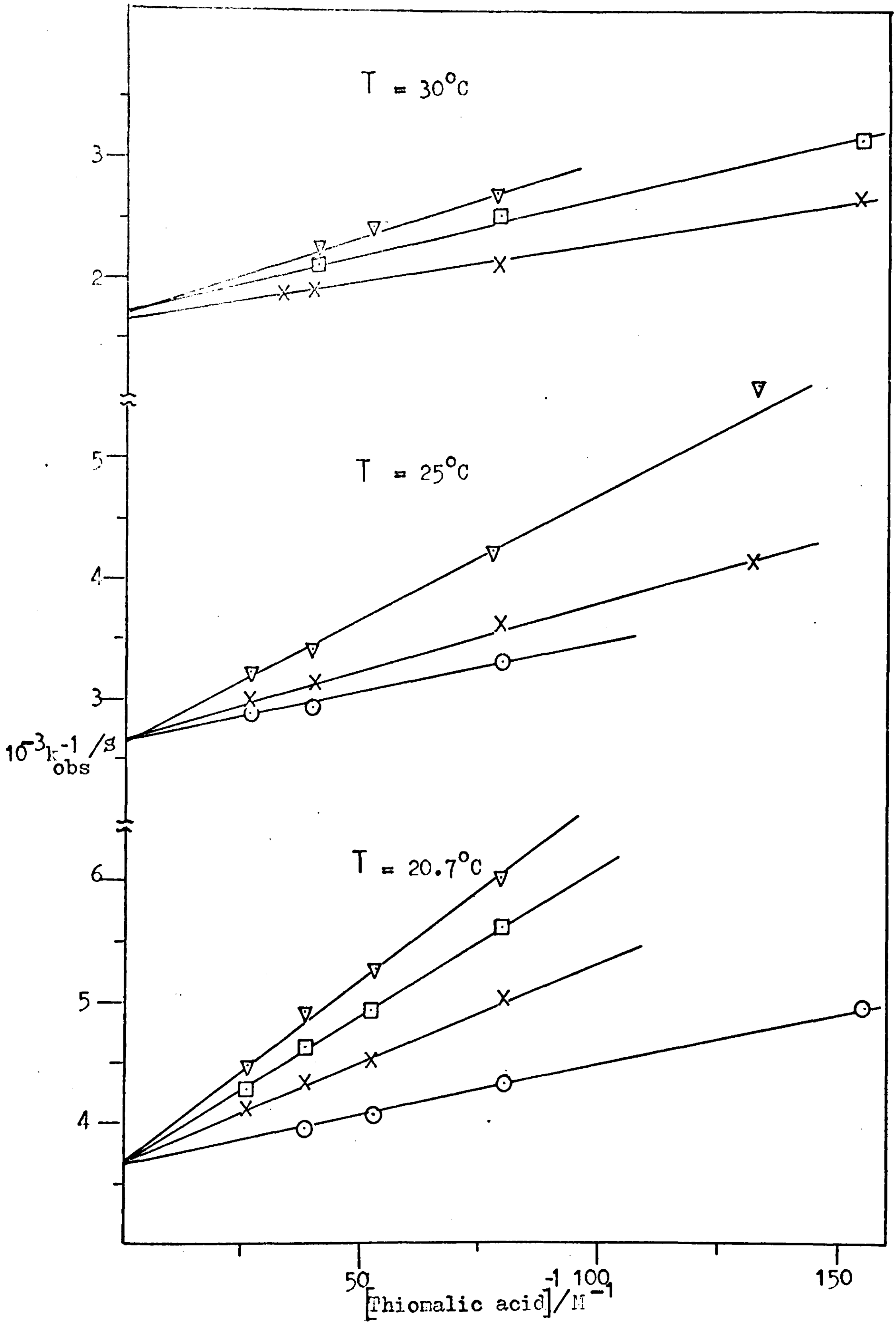


Figure 59 :- Plots of k_{obs} versus [thiomalic acid]$^{-1}$ at T = 20.7°, 25°, 30°C; [H^+] = 0.25(O), 0.50 (X), 0.75 (□), 1.00 (∇) and I = 2.0M

and in order to calculate equilibrium and rate constants, accurate values of K_h' at different temperatures are required. The most generally accepted value of K_h', based on e.m.f. measurements[212], is 0.073M at I = 3.0M and 25°C; Rogers and Waind[213] reported a value of 0.086M at I = 1.50M. Recently Thakura and Gupta[214], based on their kinetic data, found a value of 0.078M at 1.0M. Thus the hydrolysis constant of Tl(III) does not seem to be too much dependent on the ionic strength employed. The value of K_h' at 30°C was obtained by extrapolation of Thakura and Gupta's reported values at 25°, 20°, 16°C. Using the known values of slopes and intercepts (Table 28) of plots of k_{obs}^{-1} vs $[HRSH]^{-1}$ and K_h, left hand side of equation (99) was found to be independent of $[H^+]$, thus suggesting that only one complex species, namely $TlHRS^{2+}$, predominates. The values of equilibrium constants K_8 were then calculated (Table 29) by dividing the average values of $\frac{([H^+] + K_h')}{\text{Slope}}$ x Intercept with K_h' values at various temperatures. The values of $\Delta H_8 = -6.6$ k cal mole^{-1} (Figure 60) and equilibrium constant $K_8 = 1.6 \times 10^3$M may be compared with $\Delta H = -3.4$ k cal mole^{-1} and 8.6×10^2M at 25°C, obtained for Tl(III) - Oxalic acid complex[191]. The corresponding values of the equilibrium constants for formic[192] and hypophosphorous[211] acids are 16M and 7.8M at 60° and 30°C respectively.

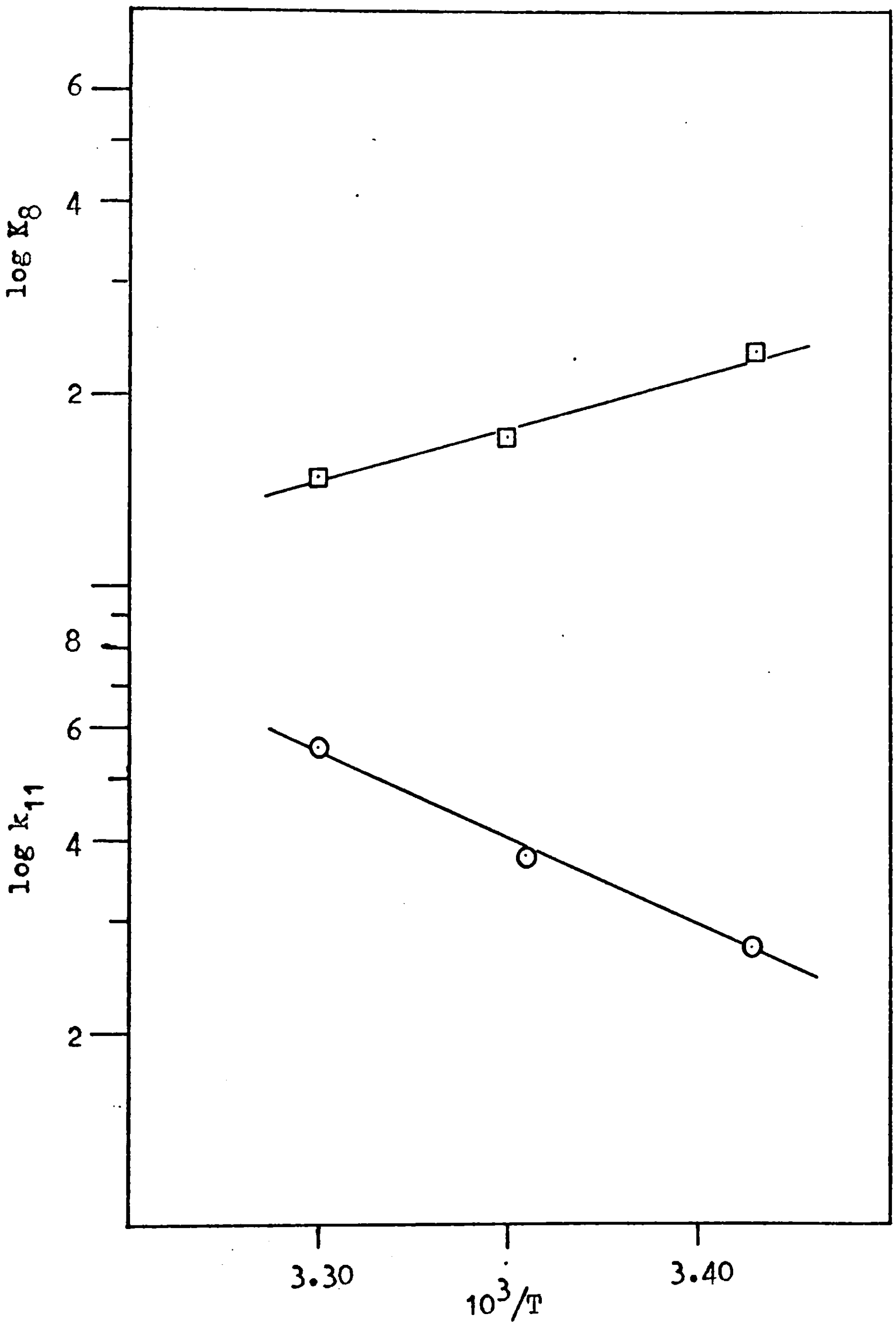


Figure 60 :- Plots of log k_{11} and log K_8 against $^I/_T$

Since there is a very slight $[H^+]$ dependence on the intercepts of plots of k_{obs}^{-1} against $[HRSH]^{-1}$ (equation (98)) it may be that either $k_{10} \approx k_{11}$ or $K_7 \ll K_8$, or both. Thus from treatment of data (Table 28) according to equation (100) it should be possible to calculate the values of k_{10} and k_{11}. Using the known values of slopes (Table 28) and K_h', the plots of $([H^+] + K_h')$/Slope were also found to be $[H^+]$ independent. The values of k_{11} were obtained by dividing the average values of $k_{11}K_8K_h'$ with K_8K_h' ,derived above, and are given in Table 29. The absence of path (93) may thus be explained from the negligible concentration of $TlHRSH^{3+}$ compared to $TlHRS^{2+}$ in solution. In this connection this reaction pathway may be compared with k_2 observed in the oxidation of malic acid (the oxygen analogue of thiomalic acid) by cerium(IV) in perchlorate media (Chapter 4, Section I).

The enthalpy of activation (ΔH^*_{11} = 11.8 k cal mole^{-1}) calculated from an Arrhenius plot (Figure 60) may be compared with that of $CoOH^{2+}$ [172] (ΔH^* = 15.2 k cal mole^{-1}). Although transient complexes have been identified in the oxidation of thiomalic acid by Cu(II)[215] and V(V)[176], no temperature effect, i.e. $\Delta H^* \approx$ zero, on the rate of reaction was observed in the latter case, whereas with Cu(II) the kinetics are more complex than expected and the complete understanding of this system is still not very clear. Moreover, in the Fe(III) oxidation of thiomalic acid, the dimerisation of the intermediate complex has been shown[132] to be the rate determining step. Thus a direct comparison of the oxidation of thiomalic acid by the one electron oxidants, Fe(III), Cu(II) and V(V), and with Tl(III), cannot be made. However, it is interesting to note that the enthalpies of activation for the decomposition of various complexes, formed with the oxygen containing substrates, of Tl(III) [with formic[193] (26.0), oxalic[191] (27.8) and phosphorous acid[216] (25.9 k cal mole^{-1})] are almost twice that (11.8 k cal mole^{-1}) obtained in this study.

It is acknowledged that this preliminary kinetic and spectrophotometric study on Tl(III) and thiols is incomplete and a full discussion will have to await more experimental data. For example, a more thorough kinetic investigation, especially with an excess of oxidant, and complete product analysis would certainly help in understanding the mechanism by which thiols are oxidised. It is hoped that further work on a much simpler thiol, i.e. $CH_3CH_2NH_2SH$ where no carboxyl group interference arising from dissociation would provide much of the necessary information.

TABLE 28

OBSERVED RATE CONSTANTS AT VARYING THIOMALIC ACID AND HYDROGEN ION CONCENTRATIONS

$[Tl(III)] = 3.0 \times 10^{-4}M$, $I = 2.00M$, $\lambda = 308nm$.
Slopes (S) and intercepts(I) were derived from plots according to equation (98)

$T/^{o}C$	$[H^{+}]/M$	$10^{2}[\text{Thiomalic Acid}]/M$	$10^{4}k_{obs}/s^{-1}$
20.5	0.25	0.625	2.02
		1.25	2.31
		1.876	2.45
		2.50	2.53
	$S = 8.25 \pm 0.22$	$10^{-3}I = 3.64 \pm 0.02$	
	0.50	1.25	1.99
		1.876	2.22
		2.50	2.31
		3.75	2.43
	$S = 16.1 \pm 1.1$	$10^{-3}I = 3.65 \pm 0.06$	
	0.75	1.25	1.79
		1.876	2.05
		2.50	2.14
		3.75	2.35
	$S = 24.4 \pm 1.5$	$10^{-3}I = 3.62 \pm 0.08$	

$T/^\circ C$	$[H^+]/M$	10^2[Thiomalic Acid]/M	$10^4 k_{obs}/s^{-1}$
20	1.00	1.25	1.67
		1.876	1,89
		2.5	2.06
		3.75	2.26
	S = 29.4 ± 1.2	10^{-3}I = 3.67 ± 0.06	
25	0.25	1.25	3.03(a)
		2.50	3.35
		3.75	3.40
	S = 6.83 ± 0.9	10^{-3}I = 2.74 ± 0.05	
	0.50	0.75	2.41(b)
		1.25	2.74
		2.50	3.19
		3.75	3.40
	S = 11.3 ± 0.7	10^{-3}I = 2.67 ± 0.06	
	1.00	0.75	1.78(c)
		1.25	(2.32)[d] 2.36
		2.50	2.92
		3.75	3.12
	S = 22.7 ± 1.2	10^{-3}I = 2.53 ± 0.1	
30	0.50	0.625	(3.72)[d] 3.74
		1.25	4.74
		1.875	5.15
		3.125	5.29
	S = 6.34 ± 0.5	10^{-3}I = 1.64 ± 0.05	

T/°C	$[H^+]$/M	10^2[Thiomalic Acid]/M	$10^4 k_{obs}/s^{-1}$
30	0.50	0.625	$(3.19)^d$ 3.16
		1.25	3.98
		2.50	4.69
	S = 8.52 ± 0.3	10^{-3}I = 1.80 ± 0.04	
	1.00	1.25	3.73
		1.875	4.15
		3.125	4.63
	S = 10.8 ± 0.46	10^{-3}I = 1.82 ± 0.027	

(a) λ = 330nm

(b) λ = 290nm

(c) λ = 350nm

(d) using degassed solutions

TABLE 29

TEMPERATURE DEPENDENCE OF K_8 AND k_{11}

$T/^{\circ}C$	K_8K_h'	$10^{-3}K_8/M^{-1}$	$10^2k_{11}K_8K_h'/s^{-1}$	$10^4k_{11}/s^{-1}$
20.5	124 ± 5	2.34 ± 0.09	3.42 ± 0.11	2.76 ± 0.3
25	129 ± 12	1.65 ± 0.15	4.88 ± 0.16	3.78 ± 0.5
30	180 ± 11	1.50 ± 0.09	10.1 ± 0.5	5.61 ± 0.6

at 25°C

$-\Delta H_8 = 6.6 \pm 0.7$ k cal mole^{-1} $\Delta H^*_{11} = 11.8 \pm 1.2$ k cal mole^{-1}

$-\Delta S_8 = 8 \pm 2$ cal deg^{-1}mole^{-1} $\Delta S^*_{11} = -33 \pm 6$ cal deg^{-1}mole^{-1}

The values of K_h' used for the above calculations were 0.053M, 0.78M, and 0.12M at 20.5°, 25° and 30°C respectively.

Chapter 6

THE VANADIUM(V) OXIDATION OF THIOUREA

INTRODUCTION

Some Features of the Chemistry of Vanadium(V)

In aqueous solution (pH <1) vanadium(V) is mainly present as VO_2^+ [217], whereas in more basic solution the various equilibria among vanadium(V) species are more complicated due to the presence of polynuclear species. There has been considerable discussion as to whether or not VO_2^+ should be more correctly written $V(OH)_4^+$ [218], or even $V(OH)_4H_2O^+$ [219]. It seems to be agreed, however, that a lower co-ordination number than six is probably correct for cations which are devoid of d - electrons.

The oxidation of organic substrates by vanadium(V) in acid media may be classified as either acid catalysed exhibiting $C_{H_3^+O}$ or h_0 (Hammet acidity function) dependences, or if the substrate is easily attacked, an uncatalysed path may also be observable. The prevalence of these types of reaction can be rationalised by assuming the presence of a small proportion of a further vanadium species, $V(OH)_3^{2+}$, as the oxidant in the acid-catalysed reaction. Though it is difficult, on the basis of kinetics, to estimate the extent of formation of this cation, there is spectrophotometric evidence for ternary complex formation from VO_2^+, H_3O^+, and alcohol molecules[220]; the shift of the charge-transfer spectrum of vanadium(V) in this complex, and the general ideas of polarity, indicate that $V(OH)_3^+$ must be a better oxidant than is VO_2^+ itself. As an attempt at distinction between $C_{H_3O^+}$ and h_o dependences on the rate of oxidation of organic substrates, it has been shown empirically that reactions occurring via chelate complex formation exhibit an h_o dependence and others occurring via complex formation vary with $C_{H_3O^+}$. This $C_{H_3O^+}$ and h_o dependence has been attributed to the difference in degree of hydration, not only of the transition state of the reaction, but also of the reversibly formed complex, the appropriate functions have been found to fit more closely than in reactions where the water molecule is taking part merely as a nucleophile. A typical example where a distinction between the $C_{H_3O^+}$ and h_o acidity dependence can be made is in the oxidation of monofunctional alcohols (where no possibility of chelate formation exists) and of pinacol. It may be pointed out that in both cases the complex has a tetrahedral structure.

Thus the general feature of the oxidation of organic compounds is the formation of a transient complex followed by a slow decomposition to V(IV) and an organic radical. The further oxidation of this radical by another molecule of V(V) takes place in the fast step. Vanadium(V) oxidations of α-hydroxy acids, unlike the cerium(IV) systems, exhibit a kinetic isotopic effect and on this basis it has been suggested that C - H bond fission is appreciable, in these reactions. A distinction has been made, on the basis of overall thermodynamic parameters between systems involving C - H bond rupture and those where C - C bond is broken and it is suggested that a fairly large negative entropy of activation is associated with C - H bond fission in the rate determining step[197].

Wells and Kuritsyn[221] have suggested that the reduction of V(V) by hydroquinone may proceed via an inner-sphere mechanism giving the products V(IV) and p-benzoquinone. The rate is first order in V(V), but less than first order in hydroquinone at higher concentrations of reductant, suggesting complexation of V(V) prior to electron transfer. The rate increases with increasing hydrogen ion concentration, further suggesting that the equilibrium constant for the complex depends upon a hydrogen equilibrium. Recently the oxidation of hydroquinone under conditions of excess V(V) has been studied and the same mechanism was suggested to be operating[189].

In the kinetic study[222] of oxidation of L-ascorbic acid under excess of V(V) both kinetic and spectrophotometric data suggest the formation of an intermediate followed by its decomposition in the rate determining step.

The V(V) oxidation of oxalic acid has been extensively studied[223-225]. The dependence of rate on acidity shows a sharp minimum[226] in the region of 3M, and the early determinations of Bobtelsky and Glasner[223] showing second and first order dependence upon oxalic acid and V(V) concentrations respectively, have been confirmed for lower acidity (1M). At low $[H^+]$ a 1 : 1 complex is formed between VO_2^+ and oxalic acid (OX) which further reacts with another molecule of oxalic acid. The slow decomposition of $V(V)\ (OX)_2$ would then produce the unusual kinetics. At lower acidities, ionisation of this complex produces an uncharged species which reacts with another molecule of oxalic acid and this tris-oxalato-V(V) complex then undergoes internal oxidation.

McAuley and Pickering[176] studied the kinetics of oxidation of thiomalic acid by V(V) under an excess of reductant using fast reaction techniques and again in this instance there is spectrophotometric evidence for the formation of an intermediate complex. Product studies indicated that the overall reaction involved 1 mole of vanadate per 1.1 ± 0.1 moles of α-thiol, with the formation of the corresponding disulphide. Over the pH range 2.4 - 4.4, the rate constant for the formation of the intermediate remained constant.

(b) Oxidation of Thiourea by Transition Metal Ions

Recently fast reaction techniques have been used to study the oxidation of thiourea by various metal ions. In the case of cerium(IV) sulphate[107] oxidation under an excess of reductant, the overall reaction is strictly second order with no evidence for extensive complex formation. Attempts to correlate the data for these systems according to Marcus theory have shown that whilst the plot of $-\Delta G^{\circ}$ (the overall free energy) against ΔG^{*} for thiourea and substituted thiourea, oxidations showed good linearity, the slope of -0.14 is markedly different from the theoretical value of 0.5.

In a similar study on the oxidation of thiourea by Co(III)[173] the marked curvature obtained in the plots of free energy of reaction against free energy of activation suggests that an outer-sphere mechanism is not operating. Although the overall reaction is second order with no evidence of complex formation, the rate determining step is thought to be complex formation as compared to fast electron transfer step.

A similar mechanism (inner-sphere substitution controlled) has also been suggested in the Mn(III) oxidation of thioureas[175]. At higher acidities (>3M) kinetic data support the involvement of doubly protonated thioureas, which react slower than the monoprotonated species. The overall reaction is again shown to be first order with respect to each reactant.

Recently in the oxidation of thioureas by Cr(VI) spectrophotometric[130] evidence strongly suggests the formation of a transient complex, Cr – L , followed by a slow decomposition in the rate determining step. Disulphide has been shown to be the final product in these metal ion oxidations, although product analysis suggests that in the case of Cr(VI) reaction some of the disulphide is co-ordinated to Cr(III).

In some preliminary investigations of reactions of V(V) with sulphur containing substrates it was observed that L-cysteine and DL-penicillamine do not form transient complexes and undergo slow oxidation ($t_{\frac{1}{2}} >$ several minutes). On the other hand, reactions of α-thiols are comparatively fast compared with thiourea and undergo oxidation via a transient complex.

EXPERIMENTAL

Vanadium(IV) perchlorate solutions were prepared as follows : To a solution of vanadyl sulphate (B.D.H. Reagent Grade) concentrated ammonium hydroxide was added dropwise until the precipitation was complete. The dark blue grey precipitate was digested for several hours, filtered, washed repeatedly with distilled water and dried. A portion was then dissolved in $\sim 0.2M\ HClO_4$ and the resulting blue solution analysed spectrophotometrically at $\lambda = 750nm$ ($\varepsilon = 15.9$)[218]. Vanadium(V) solutions were prepared by dissolving ammonium metavanadate (Hopkin and Williams, AnalaR) in aqueous perchloric acid. Thiourea (Hopkin and Williams, Reagent Grade) was twice recrystallised from ethanol-water mixtures (1 : 1) and the purity was confirmed by elemental analysis.

	Found (%)	Calculated (%)
Thiourea	C = 16.0	C = 15.8
	N = 36.6	N = 36.8
	H = 5.2	H = 5.3

The preparation and standardisation of perchloric acid and sodium perchlorate were as described in Chapter 3. Grade 'A' glassware was used whenever possible and all solutions were prepared using water obtained from an all-glass still. Solutions of thiourea were prepared immediately before use.

Spectrophotometric Measurements

The complex formation between V(IV) and thiourea was studied using Job's variation method. Appropriate dilutions were made using freshly prepared stock solutions of V(IV) and thiourea, and standard perchloric acid to give solutions of the required concentration and acidity. The volume of the solution made was 25ml. All optical density measurements were made with a Unicam S.P. 800D spectrophotometer using 10mm and 40mm path length quartz and glass cells. A blank containing perchloric acid solution appropriate to V(IV) - thiourea solution was used as a reference.

Stoicheiometric Measurements

The stoicheiometry of the V(V) - thiourea reaction was determined using spectrophotometric titrations. Spectra of solutions containing various concentrations of V(V) and a constant ligand concentration were measured after reaction had occurred, the residual V(V) being monitored at wavelengths where there was little or no absorbance from V(IV) or the organic products.

In order to determine the total number of moles of reductant reacting with V(V), experiments were carried out in which thiourea was in excess (V(V) = 1.2m moles, thiourea = 5.0m moles, $[H^+]$ = 0.2M) and immediately after reaction the solution was transferred to an ion-exchange (Dowex 50W x 8)column. In previous studies[171,228] on thiourea and its derivatives, it has been considered that one of the nitrogens is protonated in accord with the data of Lane et al[229]. These data in fact relate to dioxan-water mixtures and may not be extrapolated to acidic aqueous media[230,231]. Under such conditions, the pK_a of the conjugate acid of thiourea and its derivatives fall in the range -1.2 to -1.9[232] so that no protonation would be expected even in the most acidic media studied here. The uncharged, unreacted thiourea in the solution transferred to the ion-exchange column was therefore eluted without retention and was monitored using a silver-ion titration in basic media[117], in which a known volume of silver (I) is added to the thiourea solution. After removal of the silver sulphide formed,

$$(NH_2)_2CS + 2Ag^+ + 2NH_3 \longrightarrow CNNH_2 + Ag_2S + 2NH_4^{+1} \qquad (101)$$

the excess silver ion was titrated with ammonium thiocyanate using ferric alum as an indicator. Repeated determinations indicated that 2.2 ± 0.1 moles of thiourea reacted per mole of V(V).

Kinetic Measurements

The disappearance of V(V) in the presence of excess thiourea ($\geqslant$ 20 fold excess) was monitored at λ=360nm, using the 'slow' stopped-flow apparatus described in Chapter 2.

In some experiments where the formation of V(IV) was followed (λ = 760nm) identical rate constants were obtained. The $[H^+]$ range employed was 0.20 - 1.40 M at a total ionic strength of 1.50M. All the kinetic measurements were made at 25°C. Each kinetic run was repeated at least twice with replicate measurements using agreeing to ± 3%.

Polymerisation

The formation of free radicals as intermidiates in the V(V) and thiourea reaction was demonstrated by experiments with acrylonitrile. It is known that free radicals initiate its polymerisation. When V(V) ~ 0.02M and thiourea ~ 0.05M in

~ 0.3M $HClO_4$, were reacted in the presence of 5% V/V acrylonitrile, a cloudy suspension formed within a few minutes. A large amount of precipitate was observed after a lapse of about 40 minutes. Blank experiments with either V(V) or thiourea excluded gave no detectable polymerisation. While these experiments do not serve to identify free radical species unambiguously, they do indicate that the reaction between V(V) and thiourea produces species which are capable of the initiation of acrylonitrile polymerisation.

RESULTS AND DISCUSSION

Stoicheiometry and Products

The spectrophotometric measurements establish that the reaction occurring is

$$V(V) + 2(NH_2)_2CS \longrightarrow V(IV)(NH_2)_2CS + \tfrac{1}{2}N_4H_6C_2S_2 + H^+ \quad (102)$$

with an experimental uncertainty of ± 5%. Because of analytical difficulties connected with the low concentrations of V(V) available and the small extinction coefficients of the thiourea reactant and disulphide product the stoicheiometry of reaction (102) was first measured with excess V(V) (2 moles of thiourea per mole of V(V), Figure 61)

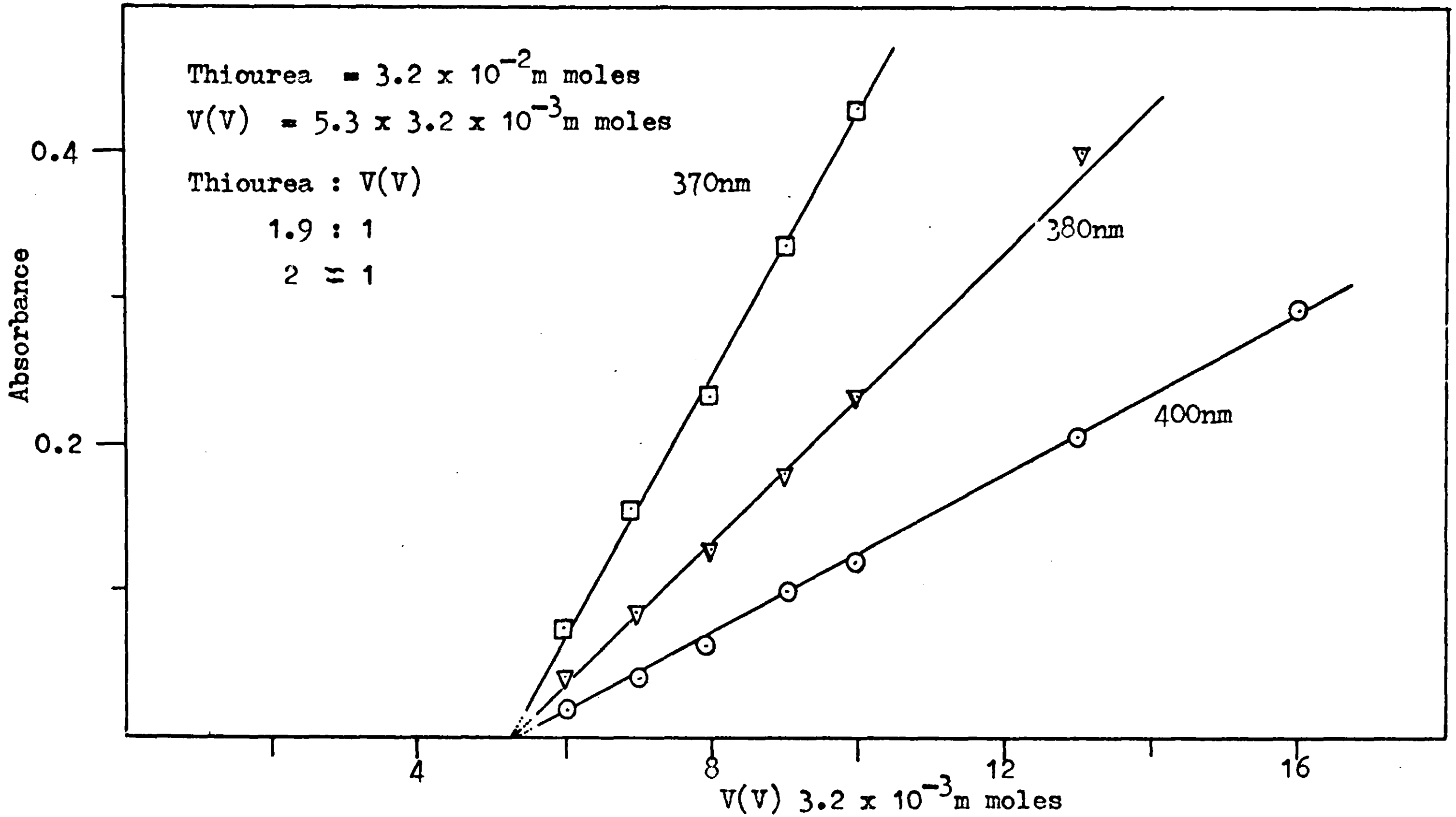


Figure 61 :- Spectrophotometric estimation of V(V) for the stoicheiometry of V(V) - thiourea reaction, at $[H^+] = 1.0M$ and $I = 1.50M$.

while, for practical reasons, the kinetics were followed with excess thiourea. However, from the preliminary kinetic experiments it was observed that at low acidity $<0.3M$ $[H^+]$, the reaction order with respect to thiourea, is nearly two. Because it was desirable to measure the stoicheiometry under conditions directly related to the kinetic measurements, quantitative estimation of unreacted thiourea was made. This also indicated the overall stoicheiometry corresponding to reaction (102). Although the disulphide was not positively identified because of analytical difficulties, it has, however, been shown to be the only product in the Ce(IV)[107], Mn(III)[175], Co(III)[173], and Cr(VI)[130] oxidation of thiourea. However, an indirect confirmation of the formation of formamidine disulphide was given by its ready decomposition to sulphur in acid media.

The above measurements suggest that at least two moles of thiourea are involved in the overall reaction and since V(V) is probably behaving as a one electron oxidant, the other molecule of thiourea must then be co-ordinated to V(IV). This is further substantiated by the fact that an increase of 10% in optical density ($\lambda = 750$nm) of the reaction mixture compared with V(IV) alone was observed. This observation is strongly suggestive of the product not being a simple $V(IV)_{aq}$ ion. Spectra of reaction products along with calculated spectra are shown in Figure 62. Attempts were made to determine the composition of the V(IV) - thiourea complex. The Job's variation method was attempted, but due to the small optical density changes when thiourea solution was added to V(IV) and also the small value of $\varepsilon_{V(IV)}$, accurate measurements were not possible. However, it has been shown that a 1:1 complex is formed between V(IV) and SCN^- having spectrum similar to V(IV) and since similar behaviour is also observed with thiourea, it may be concluded that an interaction of this type occurs in both cases, presumably through sulphur bonding.

Spectrum of the Intermediate

Preliminary kinetic measurements made at 360nm indicated that a complex between V(V) and thiourea is formed within the time of mixing. It is seen that while thiourea itself does not absorb appreciably at wavelengths above its presence markedly increases the absorption of V(V) in this region (Figure 63). It may be added that at 360nm the increase in optical density with increasing concentration of thiourea was not large enough to determine the stability

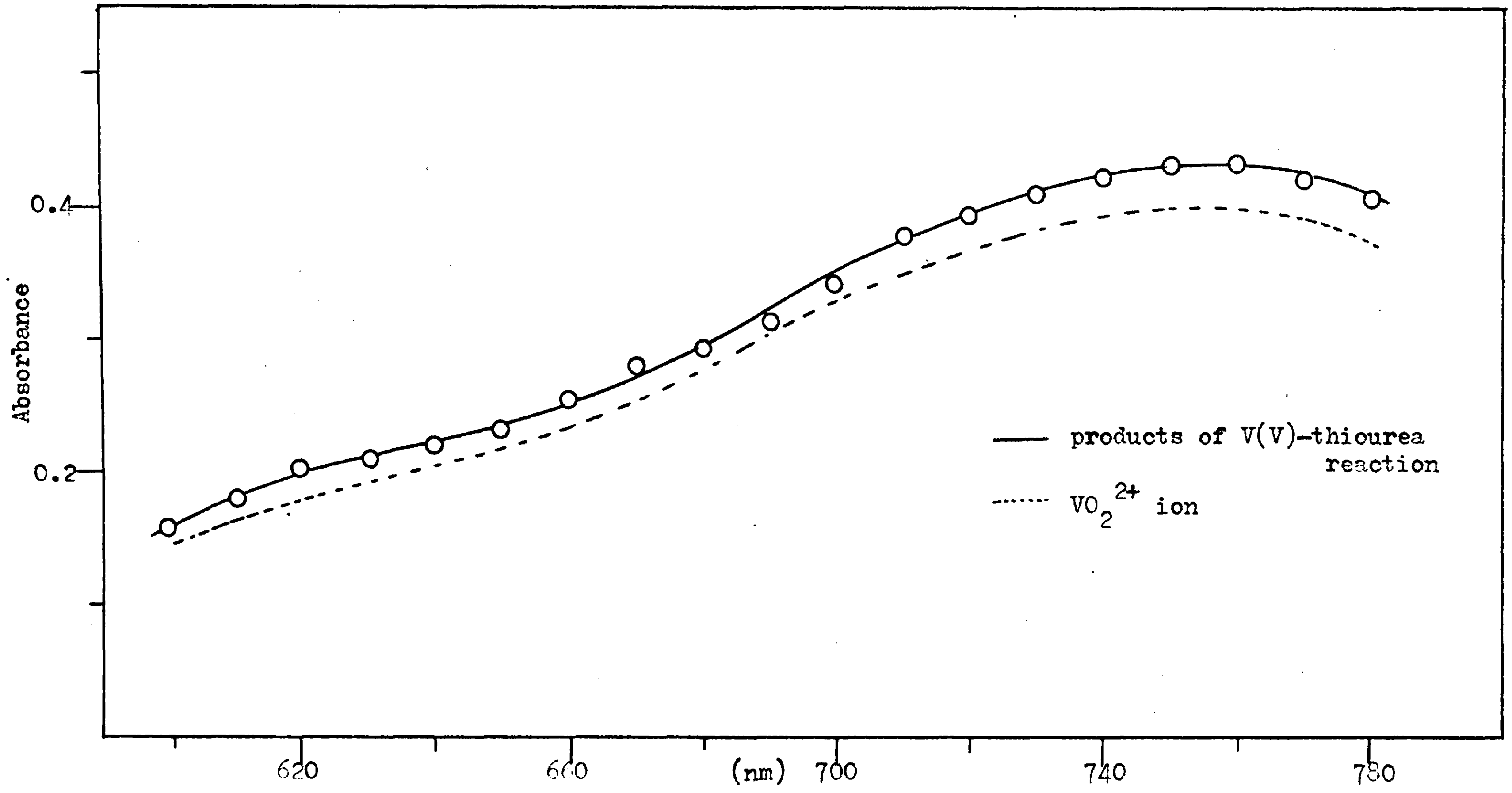


Figure 62 :- Comparison of spectra of reaction products of $[V(V)] = 2.5 \times 10^{-2}M$, $[\text{thiourea}] = 2.5 \times 10^{-1}M$ in $1.0M\ [H^+]$ and VO_{aq}^{2+} ion.

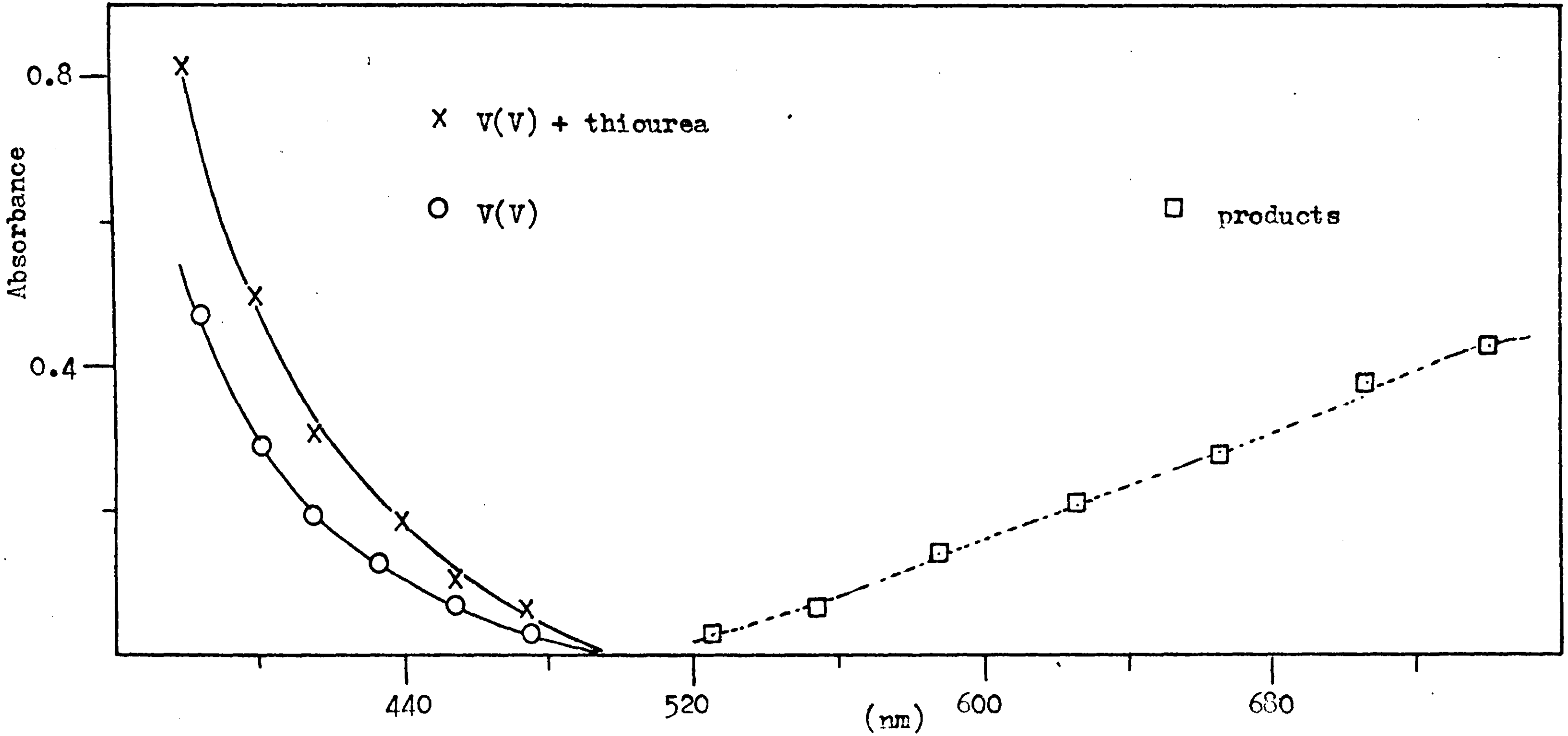


Figure 63 :- Spectra of (O) V(V) (2.5×10^{-2}M), (X) in the presence of thiourea and (□) of reaction products, $[H^+] = 1.0$M, I = 1.50M and T = 25°C

constant with any certainty.

Kinetics and Mechanism

First order plots of $\ln(A_t - A_\infty)$ versus time where A_t and A_∞ are measured optical densities at time, t, and after several half-lives respectively, were linear for at least 80 - 90% reaction in the presence of twenty fold or greater excess of thiourea, thus establishing a first order dependence of the rate on V(V). In cases where the formation of V(IV) was followed, linear plots of $\ln(A_\infty - A_t)$ vs time up to at least three half-lives, were obtained and typical plots are shown in Figure 64. No effect of oxygen was observed as the degassed solutions gave identical rate constants, as in the presence of air. The observed rate constants in the $[H^+]$ 0.2 to 1.40M at constant ionic strength of 1.50M, are given in Table 30.

The general kinetic features of this redox reaction are that at low acidity, i.e. $<$ 0.4M, the order of the reaction, with respect to thiourea, is nearly two. However, as the acidity is increased, the order changes, suggesting the involvement of another molecule of thiourea in the overall reaction. Typical plots of k_{obs} against $[\text{thiourea}]^2$ at different $[H^+]$ are illustrated in Figure 65. Furthermore,

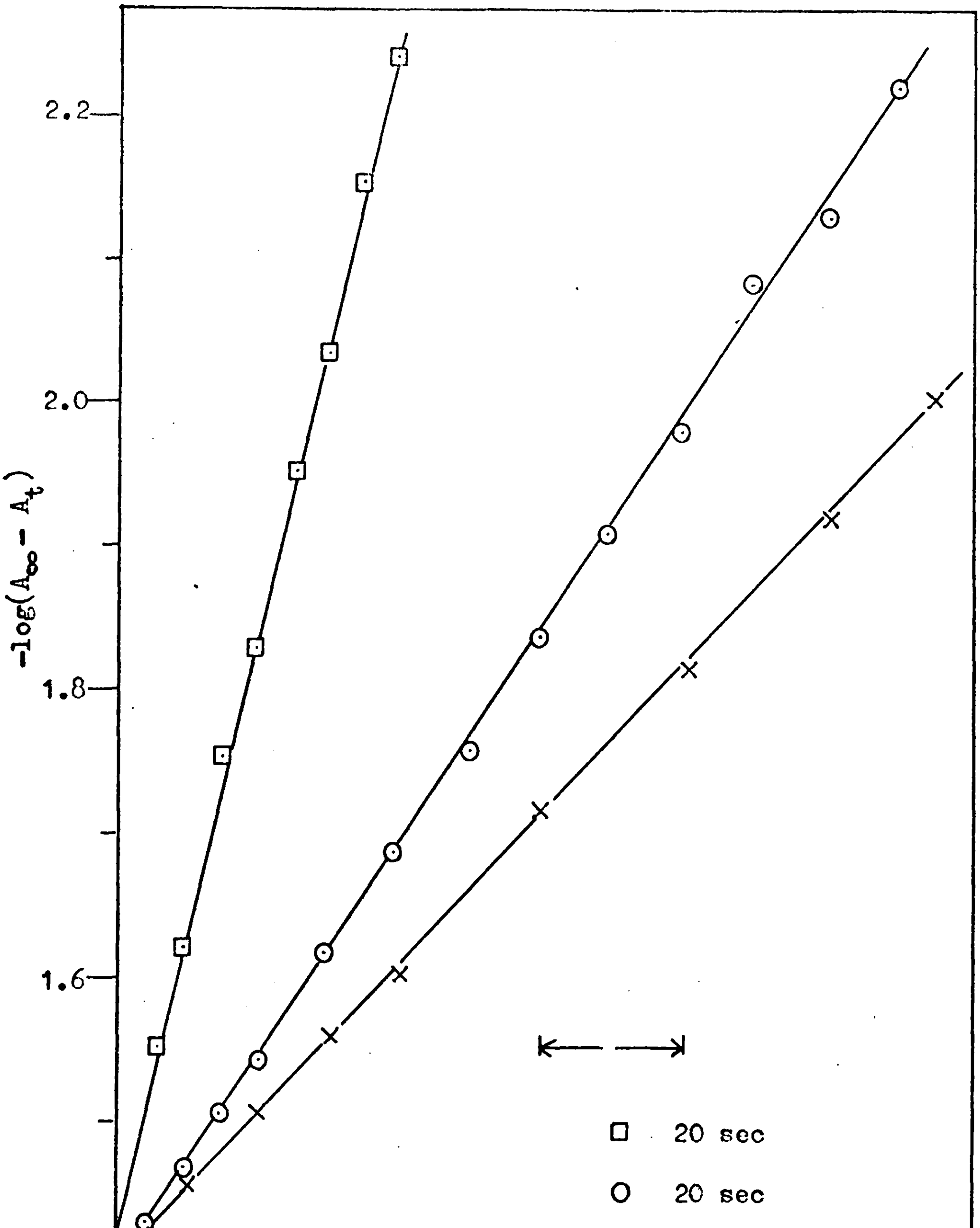


Figure 64 :- First order increase of V(IV) products with $[V(V)] = 5.0 \times 10^{-3}$M; (□) [thiourea] = 0.15M; $[H^+]$ = 1.40M; (○) [thiourea] = 0.20M, $[H^+]$ = 0.60M; (X) [thiourea] = 0.10M, $[H^+]$ = 0.20M

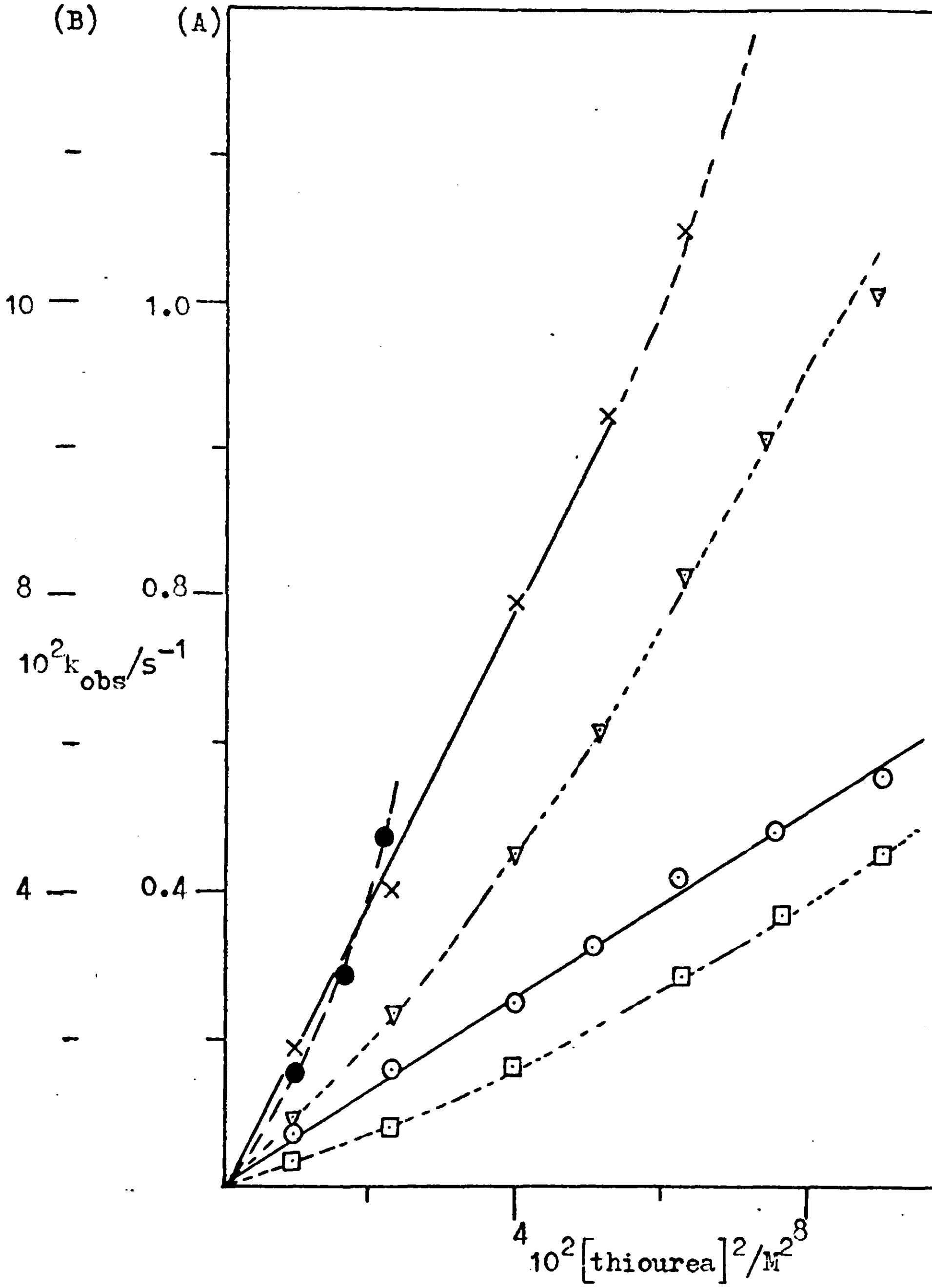


Figure 65 :- Plots of k_{obs} against $[\text{thiourea}]^2$ at $[H^+]$ = 0.20M(O), 0.40M(X)(Scale A); 0.60M(□), 1.0M(▽) and 1.40M(●)(Scale B)

it is also interesting to note that the order of reaction, with respect to $[H^+]$, is between one and two up to 0.60M where it changes to second order as shown graphically in Figure 66.

Reactions (103) to (108) are consistent with the above observations

$$VO_2^+ + H^+ + L \underset{}{\overset{K_{10}}{\rightleftharpoons}} V(OH)_3^{2+}L \qquad (103)$$

$$V(OH)_3^{2+} + H^+ + L \overset{K_{11}}{\rightleftharpoons} V(OH)_2^{3+}L_2 \qquad (104)$$

$$V(OH)_3^{2+}L + L \xrightarrow{k_{14}} V(IV)L + L \qquad (105)$$

$$V(OH)_2^{3+}L_2 \xrightarrow{k_{15}} V(IV)L + L \qquad (106)$$

$$V(OH)_2L_2^{3+} + L \xrightarrow{k_{16}} V(IV)L_2 + L \qquad (107)$$

$$2L \xrightarrow{k_{17}} L - L \qquad (108)$$

In these equations L represents a thiourea molecule, L is the radical produced by oxidation, and L_2 is the disulphide formed in the rapid dimerisation reaction. For this mechanism, assuming equilibria K_{10} and K_{11} are rapidly established and $k_{17} \gg k_{14}, k_{15}$ and k_{16} equation 109 is deduced for the rate of

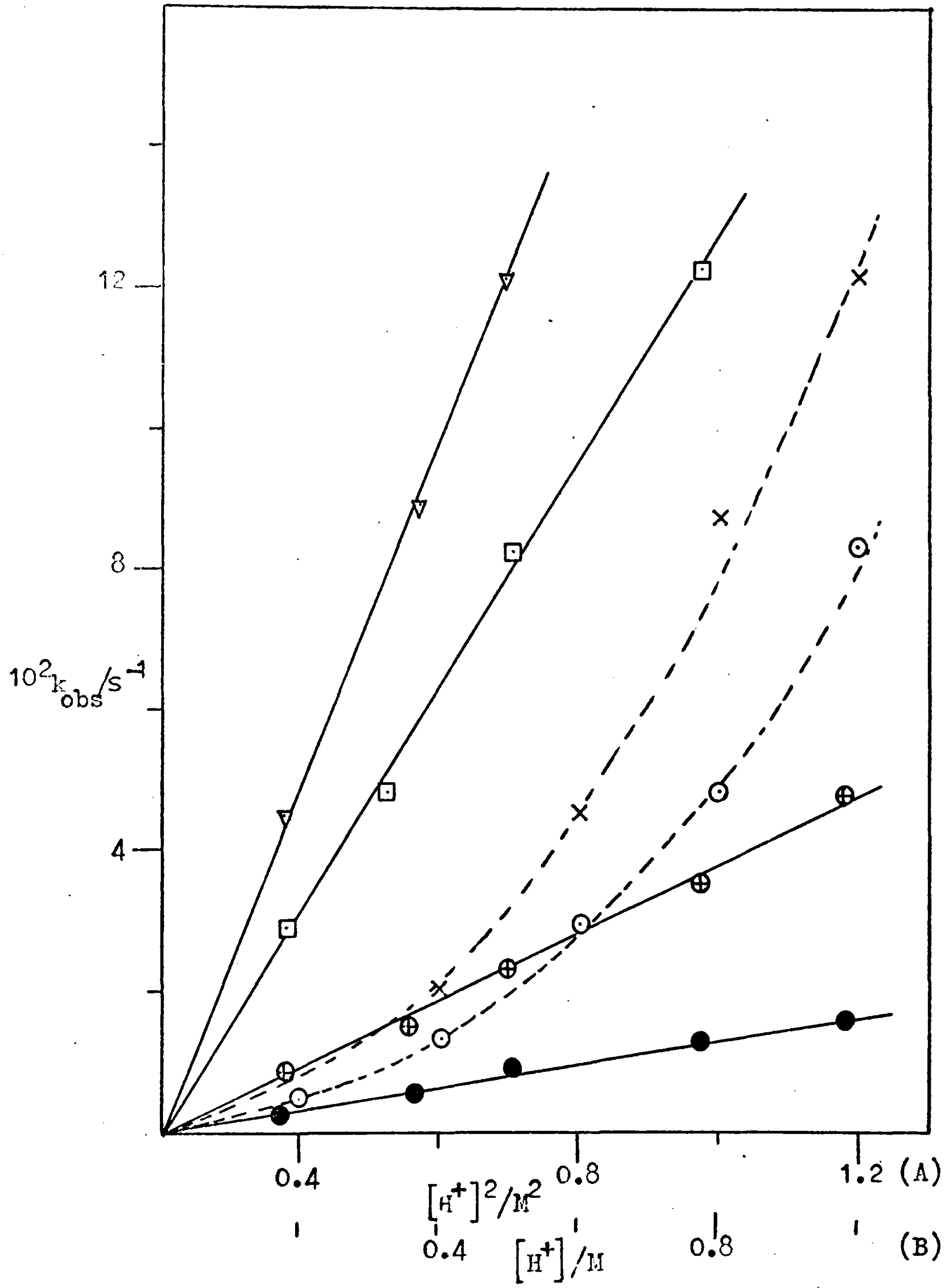


Figure 66 :- Plots of k_{obs} versus $[H^+]^2$ and $[H^+]$ at

[thiourea] = 0.10M (●), 0.15M (⊕) 0.25M (□), 0.30M (▽) (Scale A);

[thiourea] = 0.25M (O), 0.30M (X).

disappearance of V(V). Equation (110) for the observed rate constants, k_{obs}, follows from equation (109)

$$-\frac{d[V(V)]}{dt} = (k_{14}K_{10}[L^{2}][H^{+}] + k_{15}K_{11}[H^{+}]^{2}[L^{2}] + k_{16}K_{11}[H^{+}]^{2}[L^{3}])[V(V)] \quad (109)$$

$$k_{obs} = \frac{(k_{14}K_{10}[H^{+}] + k_{15}K_{11}[H^{+}]^{2} + k_{16}K_{11}[H^{+}]^{2}[L])[L]^{2}}{1 + K_{10}[L][H^{+}] + K_{10}K_{11}[H^{+}]^{2}[L]^{2}} \quad (110)$$

If $1 \gg K_{10}[L][H^{+}] + K_{11}K_{12}[H^{+}]^{2}[L]^{2}$ and

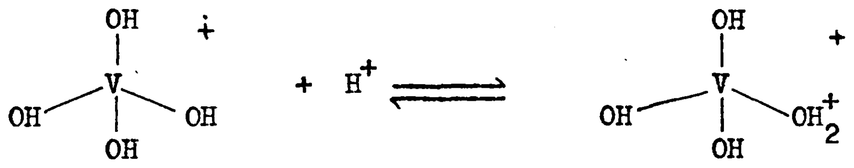
$$k_{14}K_{10}[H^{+}] \ll (k_{15}K_{11}[H^{+}]^{2} + k_{16}K_{11}[H^{+}]^{2}[L])$$

then equation (110) reduces to

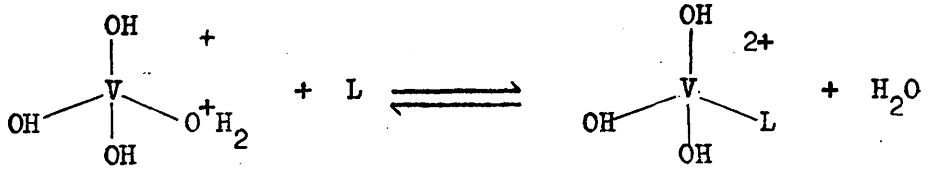
$$k_{obs} = (k_{15}K_{11} + k_{16}K_{11}[L])[L]^{2}[H^{+}]^{2} \quad (111)$$

so that a plot of $k_{obs}/[L]^{2}$ at constant $[H^{+}]$ against $[L]$ should be a straight line. Such a treatment of data in the range $[H^{+}]$ = 0.60 to 1.40M (Table 30) yielded good straight lines (Figure 65). From the plots of slopes and intercepts of $k_{obs}/[L]^{2}$ vs $[L]$, against $[H^{+}]^{2}$, $k_{15}K_{11}$ ($0.59M^{-4}s$) and $k_{16}K_{11}$ ($2.6M^{-3}s$) were calculated. The situation at $[H^{+}]$ 0.60M is somewhat different from that described above. Since the order of reaction, with respect to both thiourea and $[H^{+}]$, changes in this region and as measurements were made only at $[H^{+}]$ = 0.20 and 0.40M, makes it difficult to comment further on this behaviour. More kinetic data, particularly at lower acidity, i.e. 0.1, 0.3 and 0.5M, is required before any rationalisation is made.

Since plots of k_{obs} against $[H^+]^2$ (where $[H^+] > 0.60M$) at constant $[L]$ (equation (111)) pass through the origin, it is suggested that VO_2^+ is a much weaker oxidising agent compared to $V(OH)_3^{2+}$. The role of the proton in reaction (103) is thus to weaken the strong bond between the negative oxygen atom and the positive central atom. Alternatively, the reaction (103) can also occur via (112) and (113)



(112)



(113)

where the hydroxide group is converted into water which can easily be lost, and the increased positive charge thus facilitates the attck by L. The nearly second order dependence of the rate on $[L]$ and less than second order with respect to $[H^+]$ at $[H^+] < 0.6M$, may thus be explained by considering the above equilibria (112) and (113). As the acidity is increased, the complex $V(OH)_3L^{2+}$ reacts with another proton and a ligand molecule in a manner described above.

It is of some interest to compare the present reaction of thiourea with the corresponding systems involving bromide[233,234], iodide[235-239] and oxalic acid[223-226] which have been the subject of a number of studies. The common kinetic feature of these reactions (thiourea, iodide and bromide), however, is the acid catalysed formation of a 1 : 1 complex between V(V) and the ligand similar to reaction (103). This complex is then further protonated with the subsequent reaction with another molecule of ligand to give a 1 : 2 complex. which either undergoes redox decomposition itself, or further interacts with another molecule of ligand by pathways corresponding to (106) and (107) to give the final products. The oxidation of oxalic acid is somewhat different from that described above in that the rate of reaction first decreases with increasing $[H^+]$ in the range 0 to 3.5M, reaches a minimum[226] at $[H^+] \approx 3.5M$, and thereafter increases with increasing $[H^+]$. Although such a situation was not observed in the present system with thiourea, the kinetics of both systems are quite similar.

For example, the orders of reactions observed, with respect to $[H^+]$ and oxalic acid are between one and two, which may be compared with reactions (105) and (106). Furthermore, the oxidation of the tris-oxalato - V(V) complex was also postulated to be the rate determining step. The order of reaction (between two and three), with respect to thiourea observed in the present system at $[H^+] > 0.60M$, is in this way similar to the above observations.

The situation regarding whether these redox reactions, where more than one complex is formed, would occur via a single electron transfer step or two electron transfer to form V(III) and product followed by fast oxidation of V(III) by V(V), is not yet clear. Both possible pathways have been suggested in the oxidation of iodide and bromide. Oxidation of oxalic acid by V(V) failed to induce the reduction of mercuric chloride[224]. This indicates that transient formation of radicals or radical ions, such as $HC_2O_4^{\cdot}$, $^{\cdot}C_2O_4^-$ or $^{\cdot}CO_2^-$ are not formed in the course of reduction. This may be taken as an indication of the predominance of a two electron oxidation, although, Jones and Waters[224] have preferred the mechanism involving one electron transfer. It is interesting to note that in a more recent kinetic study on the oxidation of L-ascorbic acid[222], which is a two electron reductant and where the decomposition of the transient 1 : 1 complex has been shown to be the rate determining step, one electron oxidation was suggested on the basis of induced polymerisation of acrylonitrile. This was further supported by the fact that under the experimental conditions employed in that study, although k_{obs} was found to be of the same order of magnitude as for the reaction of V(III) and V(V), the hydrogen dependence favours the one electron oxidation. Thus from the induced polymerisation of acrylonitrile observed in the V(V) and thiourea reaction, it may be concluded that one electron oxidation is taking place in reactions (105) - (107).

While these results are interesting, further work will be necessary in order to completely elucidate the V(V) - thiourea system. There are several possible approaches which could be useful in the study of species present in these solutions. Raman spectroscopy may prove useful for carrying out product studies, e.g. for determining the amount of disulphide present under various concentration conditions. Flow e.s.r. studies will give more information on the radicals first formed in solution. Furthermore, the complete product analysis would be more helpful in order to decide about the possible number of thiourea molecules attached to V(IV) under various $[H^+]$.

Above all, studying the kinetics of this interesting reaction under an excess of V(V) concentration would eliminate the possibility of the reactions (105) and (107). It may be added that the kinetic measurements under an excess of oxidant were not possible due to some experimental difficulties.

TABLE 30

OBSERVED RATE CONSTANTS AT VARYING THIOUREA AND HYDROGEN-ION CONCENTRATIONS.

I = 1.50M, T = 25°C, λ = 750nm,

$[V(V)] = 5 \times 10^{-3}M$

$10[\text{Thiourea}]/M$	$10^{2}k_{obs}/s^{-1}$	$10[\text{Thiourea}]/M$	$10^{2}k_{obs}/s^{-1}$
$[H^+]$ = 0.20M		$[H^+]$ = 0.40M	
1.00	0.080	1.00	0.19
1.50	0.017	1.50	0.41
2.00	0.25	2.00	0.79
2.25	0.32	2.25	1.05
2.50	0.41	2.50	1.30
2.75	0.48	2.75	1.72
3.00	0.55	3.00	2.12
$[H^+]$ = 0.60(a)		$[H^+]$ = 0.80M	
1.00	0.30	1.00	0.55
1.50	0.82	1.50	1.45
2.00	1.68	2.00	$(2.92)^{b}$ 2.90
2.50	2.90	2.50	4.83
2.75	3.73	2.75	6.45
3.00	4.51	3.00	$(8.9)^{b}$ 8.75
$[H^+]$ = 1.00		$[H^+]$ = 1.25	
1.00	0.90	1.00	1.33
1.50	2.30	1.50	$(3.49)^{b}$ 3.56
2.00	4.60	2.00	7.24

$10[\text{Thiourea}]/M$	$10^2k_{obs}/s^{-1}$	$10[\text{Thiourea}]/M$	$10^2k_{obs}/s^{-1}$
2.25	6.21	2.25	9.89
2.50	8.28	2.50	12.3
2.75	10.1	2.75	15.2
3.00	12.1		

$[H^+]$ = 1.40M

1.00	1.63
1.25	2.94
1.50	4.84

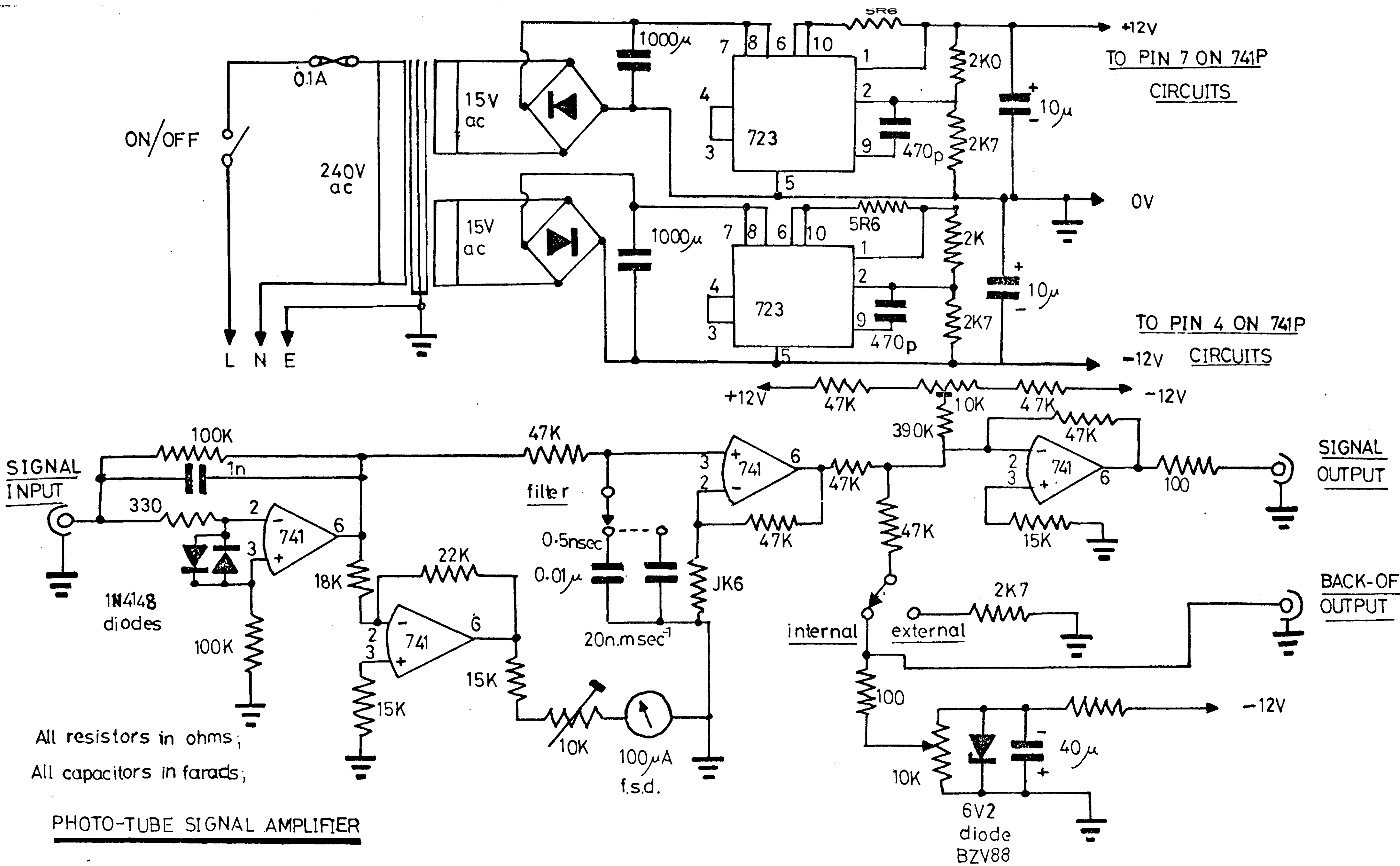
(a) $\lambda = 360$nm

(b) using degassed solutions

APPENDIX

COMPUTER PROGRAMME FOR OPTICAL DENSITY (O.D.) CALCULATIONS

```
* 0001    PRINT "  GAIN            B.O.          R.B.O.      R.I."
* 0002    INPUT X;
* 0003    PRINT ,;
* 0004    INPUT B;
* 0005    PRINT ,;
* 0006    INPUT C;
* 0007    PRINT ,;
* 0008    INPUT F
* 0009    LET A = 1.032*X
* 0010    PRINT "  R.O.T.          TIME          O.D.      LN(O.D.)"
* 0012    INPUT D;
* 0013    IF D = 999 THEN GO TO 0026
* 0014    LET Q = (B*.005575) - (C*A)
* 0015    LET Y = Y+1
* 0017    LET G = Q + (D*A)
* 0018    LET J = Q + (F*A)
* 0019    LET Z = (LOG(G) -LOG(J))/2.303
* 0020    LET Z = ABS(Z)
* 0021    LET M =LOG(Z)
* 0022    PRINT ,Y,;Z,;M,;
* 0023    PRINT ""
* 0025    GO TO 0012
* 0026    END
```



All resistors in ohms;

All capacitors in farads;

PHOTO-TUBE SIGNAL AMPLIFIER

References

(1) J.O. EDWARDS, "Inorganic Reaction Mechanisms", W.A. Benjamin, Inc., 1965, New York.

(2) M.L. TOBE, "Inorganic Reaction Mechanisms", Thomas Nelson and Sons Ltd., 1972, London.

(3) A.G. SYKES, "Kinetics of Inorganic Reactions", Pergamon Press Ltd., 1966, London.

(4) R.A. MARCUS, J. Chem. Phys., 24, 966 (1956); 26, 867, 872 (1972).

(5) R.J. MARCUS, B.J. ZWOLINSKI, and H. EYRING, J. Phys.Chem., 58, 432 (1954).

(6) K.J. LAIDLER, Can. J. Chem., 37, 138 (1959).

(7) W.F. LIBBY, J. Phys. Chem., 56, 863 (1952).

(8) A.C. WAHL and C.F. DECK, J. Amer. Chem. Soc., 76, 4054 (1954).

(9) J.C. SHEPPARD and A.C. WAHL, J. Amer. Chem. Soc., 79, 1021 (1957).

(10) L. GJERTSEN and A.C. WAHL, J. Amer. Chem. Soc., 81, 1573 (1959).

(11) E.N. SLOTH and C.S. GARNER, J. Amer. Chem. Soc., 77, 1440 (1955).

(12) E.EICHLER and A.C. WAHL, J. Amer. Chem. Soc., 80, 4145 (1958).

(13) D.R. STRANKS, Disc. Far. Soc., 29, 73 (1960).

(14) R.A. MARCUS, J. Phys. Chem., 67, 853 (1963).

(15) R.J. CAMPION, N. PURDIE and N. SUTIN, Inorg. Chem., 3, 917 (1964).

(16) G. GULZ and N. SUTIN, Inorg. Chem., 2, 9175 (1963).

(17) H. DEIBLER and N. SUTIN, J. Phys. Chem., 68, 174 (1964).

(18) J.F. ENDICOTT and H. TAUBE, J. Amer. Chem. Soc., 86, 1686 (1964).

(19) M.G. ADAMSON, F.S DAINTON and P. GLENTWORTH, Trans. Far. Soc., 61, 689 (1965).

(20) H. TAUBE, H. MYERS and R.L. RICH, J. Amer. Chem. Soc., 75, 4118 (1953); H. TAUBE and H. MYERS, J. Amer. Chem. Soc., 76, 2103 (1954).

(21) H. TAUBE, J. Amer. Chem. Soc., 77, 4481 (1955).

(22) H. TAUBE and E.S. GOULD, Accounts Chem. Res., 11, 322 (1969).

(23) R.A. MARCUS, J. Phys. Chem., 24, 979 (1956); Ann. Rev. Phys. Chem., 15, 155 (1964).

(24) T.J. CONNCCHIOLI, G.H. NANCOLLAS and N. SUTIN, Inorg. Chem., 5, 156 (1965).

(25) Y. SASAKI and A.G. SYKES, J. Chem. Soc. (Dalton), 1048 (1975).

(26) N. SUTIN and B.M. GORDON, J. Amer. Chem. Soc., 83, 70 (1961).

(27) N. SUTIN and M.H. FORD-SMITH, J. Amer. Chem. Soc., 83, 1830 (1961).

(28) J. HALPERN, J. Chem Educ., 45, 372 (1968).

(29) E. CHAFFEE and J.O. EDWARDS, Prog. Inorg. Chem., 13, 1970 (1970).

(30) J.O. EDWARDS, J. Chem Educ., 31, 270 (1954).

(31) T.C. HOERING, F.T. ISHIMORI and H.O. McDONALD, J. Amer. Chem., 80, 3876 (1958).

(32) H. TAUBE, J. Chem. Educ., 45, 452 (1968).

(33) K. EVERETT in "Handbook of Laboratory Safety", Ed. N.V. Steere, The Chemical Rubber Company, Cleveland, p.205 (1967).

(34) L. JOHANSSON, Coord. Chem. Revs., 12, 241 (1974).

(35) A. McAULEY and J. HILL, Quart. Rev., 23, 18 (1969).

(36) G.L. EICHHORN, Ed., "Inorganic Biochemistry" Vol. 2, Elsevier Publishing Company, 1973, New York.

(37) J. BURGESS (Senior Reporter) in "Inorganic Reaction Mechanisms", Vol. 4, (A specialistic Periodical Report), The Chemical Society, 1974, London.

(38) I. AMDUR and G.G. HAMMES, "Chemical Kinetics", McGraw Hill, 1966, New York, Chapter 6.

(39) E.M. EYRING, "Survey of Progress in Chemistry", 2, 57 (1964).

(40) G.G. HAMMES and SCHIMMEL P.R., "Rapid Reactions and Transient States", in "The Enzymes", Vol. II, Ed. P.D. Boyer, Academic Press, 1970, New York.

(41) G.G. HAMMES, Ann. Rev. Phys. Chem., 15, 13 (1964); E.M. EYRING and B.C. BENNION, Ann. Rev. Phys. Chem., 19, 129 (1968); H. STREHLOW, Ann. Rev. Phys. Chem., 16, 167 (1965).

(42) D.N. HAGUE, "Fast Reactions", Wiley Interscience, (1971), New York.

(43) E.F. CALDIN, "Fast Reactions in Solution", Blackwell Scientific Publications (1964), Oxford.

(44) K.KUSTIN (ed), "Fast Reactions", Vol. XVI of "Methods in Enzymology", Eds-in-chief: S.P. Colowich and N.O. Kaplan, Academic Press, (1969), New York.

(45) G.G. HAMMES (Ed)., "Investigation of Rates and Mechanisms of Reactions", Part II, 3rd. Edition, Vol. VI of "Techniques of Chemistry", ed. A. Weissberger, Wiley Interscience (1974),New York.

(46) M. ERGEN and R.G. WILKINS, "Mechanisms of Inorganic Reactions", J. Amer. Chem. Soc., Advances in Chemistry Series, No. 49 (1965).

(47) B. CHANCE, R. EISERHARDT, Q.H. GIBSON and K.K. LONBERG-HOLM, (eds), "Rapid Mixing and Sampling Techniques in Biochemistry", Academic Press (1964),New York.

(48) S. CLAESSON (ed) "Fast Reactions and Primary Processes in Chemical Kinetics", Fifth Nobel Symposium, Almquist and Wiksell (1967), Stockholm.

(49) Ref. 45, Chapters III - VII.

(50) S. PETRUCCI (Ed), "Ionic Interactions", Vol. 2,Chapter 7, Academic Press, (1971), New York.

(51) M. EIGEN and L. De. MAEYERS, in "Investigation of Rates and Mechanisms of Reactions", Part II, 2nd. edition, Vol. VIII of "Techniques of Organic Chemistry", S.L. Friess and A. Weissberger (eds) Interscience, (1963), New York.

(52) M. EIGEN and L. De. Maeyers in Ref. 47, pp 175 - 181.

(53) C. CZERLINSKI, in Ref. 47, pp 183 - 190.

(54) G.G. HAMMES, in Ref. 45, p.2.

(55) H. HARTRIDGE and F.T. ROUGHTON, Proc. Roy. Soc., London, A104, 376 (1923).

(56) B. CHANCE, J. Franklin Inst., 228, 229, 230, 455, 613, 737 (1940).

(57) Q.H. GIBSON and L. MILNES, J. Biochem., 91, 161 (1964).

(58) Ref. 43, p.39.

(59) B. CHANCE, in Ref. 47, pp 39 - 45.

(60) B. CHANCE, in Ref. 45, p.26.

(61) R.L. BERGER, in Ref. 47, p. 364.

(62) R.L. BERGER, B. BALKO and H.F. CHAPMAN, Rev. Sci. Inst., 39, 493 (1968).

(63) B. CHANCE, Rev. Sci. Inst., 22, 627 (1951).

(64) Q.H. GIBSON, Disc. Farad. Soc., 71, 137 (1954).

(65) J.F. BELOW, R.W. CONNICK and C.P. COPPEL, J. Amer. Chem. Soc., 80, 2961 (1958); R.E. CONNICK and C.P. COPPEL, J. Amer. Chem. Soc., 81, 6389 (1959); P. MATTHIES and H. WENDT, Z. Physik. Chem. (Frankfurt), 30, 137 (1961).

(66) G.F. SMITH, "Cerate Oxidimetry", G.F. Smith Chemical Co., (1964), Columbus, Ohio.

(67) E. WADSWORTH, F.R. DUKA and C.A. GOETZ, Anal. Chem., 29, 1824 (1957).

(68) B.D. BLAUSTEIN and J.W. GRYDER, J. Amer. Chem. Soc., 79, 540 (1957); M.K. DORFMAN and J.W. GRYDER, Inorg. Chem., 1, 709 (1962).

(69) I.A. LABEDEV, B.F. MYASOEDOV and V.Ya. FRANKEL, Russ. J. Inorg. Chem., 18, 1716 (1973).

(70) T.J. HARDWICK and E. ROBERTSON, Can. J. Chem., 29, 828 (1951).

(71) K.B. WIBERG and P.C. FORD, Inorg. Chem., 7, 369 (1968).

(72) M. SAUNDERS and J.B. HYNE, J. Chem. Phys., 29, 1319 (1958).

(73) G.E. SMITH and C.A. GETZ, Ind. Eng. Chem. Anal. Edn., 10, 191 (1938).

(74) M.S. SHERRILL, C.B. KING and R.C. SPOONER, J. Amer. Chem. Soc., 65, 170 (1943).

(75) L.J. HEIDT and M.E. SMITH, J. Amer. Chem. Soc., 70, 2746 (1948).

(76) E.L. KING and M.L. PANDOW, J. Amer. Chem. Soc., 74, 1966 (1952).

(77) T.J. HARDWICK and E. ROBERTSON, Can. J. Chem., 29, 818 (1951).

(78) F.B. BAKER, T.W. NEWTON and M. KAHN, J. Phys. Chem., 64, 109 (1960).

(79) H.G. OFFNER and D.A. SKOOG, Anal. Chem. 38, 1520 (1966).

(80) M. RANGASWAMY and M. SANTAPPA, Ind. J. Chem., 7, 473(1969).

(81) I.M. MATHAI and R. VASUDEVAN, J. Chem. Soc., (B), 1361 (1970).

(82) A.K. WADHAWAN, P.S. SANKHLA and R.J. MEHROTRA, Ind. J. Chem., 11, 567 (1973).

(83) F.R. DUKE and R.F. BREMER, J. Amer. Chem. Soc., 73, 5179 (1951).

(84) C.F. WELLS and M. HUSAIN, J. Chem. Soc., (A),1013 (1970).

(85) A. SAMUNI and G. CZAPSKI, J. Chem. Soc., (Dalton), 487 (1973).

(86) R.E. CONNICK and W.H. McVEY, J. Amer. Che. Soc., 71, 3182 (1948).

(87) S. HIETNEN, Acta Che. Scand., 10, 1531 (1956).

(88) L Th. LANG, J. Prak. Chem., 82, 133 (1861).

(89) W.H. RICHARDSON, in "Oxidation of Organic Chemistry", Vol A, Ed. K.B. Wiberg, Academic Press, (1965),

(90) F.R. DUKE, J. Amer. Chem. Soc., 69, 2885 (1947).

(91) F.R. DUKE and A.A. FORRIST, J. Amer. Chem. Soc., 71, 2790 (1949).

(92) H.L. HINTZ and D.C. JOHNSON, J. Org. Chem., 32, 556(1967).

(93) J.S. LITTLER and W.A. WATERS, J. Chem. Soc., (A),
2767 (1967).

(94) G. MINO, S. KAIZERMAN and E. RASMUSSEN, J. Amer.Chem.
Soc., 81, 1494 (1958).

(95) S.P. RAO, J.N. GAUR and S.K. SHARMA, Naturwiss, 48,
98 (1961).

(96) G. HARGREARES and L.H. SUTCLIFFE, Trans. Far. Soc.,
51, 1105 (1955).

(97) J. SHORTER and C.N. HINSHELWOOD, J. Chem. Soc.,
3276 (1950).

(98) J.B. CONANT and J.G. ASTON, J. Amer. Chem. Soc., 50,
2783 (1928).

(99) V.H. DODSUN and A.H. BLACK, J. Amer. Chem. Soc., 79,
3657 (1957).

(100) A. McAULEY, J. Chem. Soc., 4054 (1965).

(101) B. KRISHNAW and K.C. TEWARI, J. Chem.Soc., 3097 (1961).

(102) A. McAULEY and C.H. BRUBAKER Jr., J. Chem. Soc., (A),
966 (1966).

(103) J.S. LITTLER, J. Chem Soc., 832, (1962).

(104) R. DAYAL and G.V. BAKORE, Ind. J. Chem., 10, 1165 (1972).

(105) R. DAYAL, K.K. BANERJI and G.V. BAKORE, Ind. J. Chem.,
9, 1017 (1971).

(106) J. HILL and A. McAULEY, J. Chem. Soc. (A), 156 (1968).

(107) U.D. GOMWALK and A. McAULEY, J. Chem. Soc. (A),
2948 (1968).

(108) R.J. MEYERS and R. JACOBY, Z. Anorg. Chem.,27, 359 (1901).

(109) F.R. DUKE and G.F. SMITH, Ind. Eng. Chem. Anal. Edn., 12, 201 (1940).

(110) C.F. WELLS and M. HUSAIN, Trans. Far. Soc., 66, 679 (1970).

(111) C.F. WELLS and M. HUSAIN, Trans. Far. Soc., 66, 2855 (1970).

(112) S.S. MOHAMMAD and K.V. RAO, Bull. Chem. Soc. Japan, 36, 943 (1963).

(113) M. ARDON, J. Chem. Soc., 1811 (1957).

(114) G.G. GUELBAULT and W.H. McCURDY Jr., J. Phys. Chem., 67, 283, (1963).

(115) C.F. WELLS and M. HUSAIN, J. Chem. Soc. (A), 380 (1971).

(116) J.W. HOPTON, Anal. Chim. Acta., 8, 429 (1953).

(117) J. MITCHELL Jr., in "Organic Analysis", Vol. I, J. Mitchell Jr., et al.,(Eds), Interscience Publishers, Inc. (1953), New York.

(118) V.K. GROVER and Y.K. GUPTA, Bull. Chem. Soc. Japan, 43, 2445 (1970).

(119) S. VENKATAKRISHAN and M. SANTAPPA, Z. Physik. Chem.(N.F.) 16, 73 (1958).

(120) J. HILL and A. McAULEY, J. Chem. Soc. (A), 1169 (1968).

(121) A. McAULEY, Unpublished work.

(122) Ref. (19) in ref. (119).

(123) T.J. KEMP and W.A. WATERS, J. Chem. Soc., 3193 (1964).

(124) S.E. SCHAAFSMA, H. STEINBERG and Th. J. de BOER, Recl. Trav. Chim. Pays-Bas, 85, 73 (1966).

(125) K. MEYERS and J. ROCEK, J. Amer. Chem. Soc., 94, 1209 (1972).

(126) C.F. WELLS and C. BARNES, J. Chem. Soc. (A), 1626(1968).

(127) C.F. WELLS, D. MEYERS and C. BARNES, J. Inorg. Nucl. Chem., 30, 1341 (1968).

(128) O.J. PARKER and J.H. ESPENSON, J. Amer. Chem. Soc., 91, 1313 (1969); J.P. BIRK and J.H. ESPENSON, Inorg. Chem., 7, 991 (1968).

(129) C. LAVALLEE and T.W. NEWTON, Inorg. Chem., 11, 2616(1972).

(130) M.A. OLATUNGIand A. McAULEY, J. Chem. Soc. (Dalton), 682 (1975).

(131) A. McAULEY and M.A. OLATUNGI, to be published.

(132) A. McAULEY and A.G. LAPPIN, J. Chem. Soc., (Dalton), in press.

(133) G.H. CARTLEDGE, J. Amer. Chem. Soc., 62, 3057 (1940).

(134) H. TAUBE, Chem. Rev., 50, 69 (1952).

(135) A.Y. DUMOND and W.A. WATERS, J. Chem. Soc., 2456 (1954).

(136) C.F. HUEBNER, S.R. AMES and E.C. BUBL, J. Amer. Chem. Soc., 68, 1621 (1946).

(137) R.L. YADER and W.V. BHAGWAT, J. Ind. Chem.Soc., 41, 389 (1964).

(138) K.K. SENGUPTA and S. ADITYA, Z. Physik. Chem. Frankfurt, 38, 25 (1963).

(139) T.J. KEMP, Ph.D. Thesis, (1963) Oxford.

(140) M. IGNACZAK, Soc. Sci. Lodz. Acta. Chim., 17, 135 (1972) (Chemical Abstract 78, 34427v (1973).

(141) T. TANG, K.S. RAJAN and N. GREEZ, Biophys. J., 8, 1458 (1968).

(142) H. SHINDO and T.L. BROWN, J. Amer. Chem. Soc., 87, 1904 (1965).

(143) G.R. LENZ and A.E. MARTELL, Biochemistry, 3, 745 (1964).

(144) D.D. PERRIN and I.G. SAYCE, J. Chem. Soc. (A)., 53 (1968).

(145) J.M. WHITE, T.J. WEISEMANN and N.C. LI, J. Phys. Chem., 61, 126 (1957).

(146) R.G. NEVILLE, J. Amer. Che. Soc., 79, 518 (1957).

(147) G. GORIN, J.E. SPESSARD, G.A. WESSLER and J.P. OLIVER, J. Amer. Chem. Soc., 81, 3193 (1959).

(148) M. CHANDRASEKHARAN, M.R. UDUPA and G. ARAVAMUDAN, Inorg. Chim. Acta., 7, 88 (1973).

(149) G.A. NEVILLE and T. DRAKENBERG, Can. J. Chem., 52, 616 (1974).

(150) D.F.S. NATUSCH and L.J. PORTER, J. Chem. Scc.,(A), 2527 (1971).

(151) W. STRICKS and I.M. KOLTHOFF, J. Amer. Chem. Soc,, 73, 1723 (1951).

(152) C.A. McAULIFFE and S.G. MURRAY, Inorg. Chim. Acta. Rev., 6, 103 (1972).

(153) Y. SUGIURA, A.YOKOYOMA and H. TANAKA, Chem. Pharm. Bull., 18, 693 (1970).

(154) Y. SUGIURA and H. TANAKA, Chem. Pharm. Bull., 18, 746 (1970).

(155) I.H. SCHIENBERG, J. Chron. Dis., 293 (1964).

(156) C.M. BELL, E.D. McKENZIE and J. OVERTON, Inorg. Chimica. Acta., 5, 109 (1971).

(157) Y. SUGIURA, Y. HOJO and H. TANAKA, Chem. Pharm. Bull., 20, 1362 (1972).

(158) A. McAULEY, unpublished data.

(159) A. TOMITA, H. HIRAI and S. MAKISHIMA, Inorg. Chem., 7, 760 (1968).

(160) J.T. SPENCE, Coord. Chem. Rev., 4, 425 (1969).

(161) R.C. BRAY and J.C. SWAN, Structure and Bonding, 11, 107 (1972).

(162) J.R. KNOX and C.K. PROUT, Acta. Cryst., B 25, 1857 (1969).

(163) T.J. HUANG and G.P. HAIGHT, J. Amer. Chem. Soc., 92, 2336 (1970).

(164) A. KAY and P.C.H. MITCHELL, J. Chem. Soc. (A), 2421 (1970).

(165) J.F. MARTIN and J.T. SPENCE, J. Phys. Chem., 74, 2863 (1970).

(166) J.P. McCANN and A. McAULEY, J. Chem. Soc. (Dalton), 783 (1975).

(167) M.A. OLATUNGI, Ph.D. Thesis, University of Glasgow, 1975.

(168) D.K. LAVELLEE, J.C. SULLIVAN and E. DEUTSCH, Inorg. Chem., 12, 1440 (1973).

(169) R. BENESCH and R.E. BENESCH, Biochim. et Biophys. Acta, 44, 183 (1957).

(170) J.I. MORROW and G.W. SHEERES, Inorg. Chem., 11, 2606 (1972).

(171) G. DAVIES, Coord. Chem. Rev., 4, 199 (1969).

(172) J. HILL and A. McAULEY, J. Chem. Soc. (A), 2405 (1968).

(173) A. McAULEY and U.D. GOMWALK, J. Chem. Soc. (A), 977 (1969).

(174) C. WALLING, "Free Radicals in Solution", J. Wiley and Sons. Inc., (1957), New York.

(175) G. DAVIES, Inorg. Chem., 11, 2488 (1972).

(176) W.F. PICKERING and A. McAULEY, J. Chem. Soc., (A), 1173 (1968).

(177) A.G. LEE, "The Chemistry of Thallium", Elsevier Publishing Co., (1971), London.

(178) N. SUTIN, Ann. Rev. Nucl. Sci., 12, 285 (1962); Ann. Rev. Phys. Chem., 17, 119 (1966).

(179) A.G. SYKES, Adv. Inorg. Chem. Radiochem., 10, 153 (1967); Chemistry in Britain, 159 (1970).

(180) B. CERĚCK, M. EBERT and A.J. SWALLOW, J. Chem. Soc.(A), 612 (1966).

(181) C.E. BURCHILL and W.H. WOLODARSKY, Can. J. Chem., 48, 2955 (1970).

(182) B. FALCINELLA, P.D. FELGATE and G.S. LAWRENCE, J. Chem. Soc. (Dalton), 1367 (1974); 1 (1975).

(183) W.C.E. HIGGINSON, Disc. Far. Soc., 29, 135 (1960).

(184) N. HUSH, Trans. Far. Soc., 57, 557 (1961).

(185) D. MEYERSTEIN, Inorg. Chem., 10, 638 (1971).

(186) R.R. GRINSTEAD, J. Org. Chem., 26, 238 (1961).

(187) P.M. HENRY, J. Amer. Chem. Soc., 87, 990, 4423 (1965).

(188) E. PELIZZETTI, E. MENTASTI and G. SAINI, J. Chem. Soc. (Dalton), 721 (1974).

(189) E. PELIZZETTI, F. MENTASTI, E. PRAMAURO and G. SAINI, J. Chem. Soc. (Dalton), 1940 (1974).

(190) V.S. SRINIVASAN and N. VENKATASUBRAMANIA, Ind. J. Chem., 11, 702 (1973).

(191) L.B. MONSTEAD, Ole MONSTEAD and G. NOND, Trans. Far. Soc., 66, 936 (1970).

(192) H.N. HALVORSON and J. HALPERN, J. Amer. Chem. Soc., 78, 5562 (1956).

(193) J. HALPERN and S.M. TAYLOR, Disc. Far. Soc., 29, 174 (1960).

(194) G.E. CHENEY, Q. FERMANDO and H. FREISER, J. Phys. Chem., 63, 2055 (1959).

(195) G.R. LENZ and A.E. MARTELL, Inorg. Chem., 4, 378 (1965).

(196) I.M. KLOTZ, G.H. CZERLINSKI and H.A. FIESS, J. Amer. Chem. Soc., 80, 2920 (1958).

(197) A. McAULEY, Coord. Chem.Rev., 5, 245 (1970).

(198) C. WESCHTER, J.C. SULLIVAN and E. DEUTSCH, Inorg. Chem., 10, 2360 (1974).

(199) K.J. ELLIS and A. McAULEY, J. Chem. Soc.,(Dalton), 1533 (1973).

(200) K.J. ELLIS and A. McAULEY, unpublished data.

(201) J.P. McCANN, Ph.D. Thesis, University of Glasgow, 1975.

(202) G.R. LENZ and A.E. MARTELL, Biochemistry, 3, 745 (1964).

(203) G.L. EICHHORN (ed) Inorganic Biochemistry, Vol. I, II, Elsevier Publishing Co., (1973), New York.

(204) F. FEIGEL, Nature, 161, 436 (1948).

(205) E. HOYER, W. DIETZSCH, H. MULLER, A. ZSCHUNKE and W. SCHROTH, Inorg. Nucl. Chem. Letter, 3, 457 (1967).

(206) A. HEYNDRICKS, in "Progress in Toxicology", A. Stolman (Ed.), Vol. 4, Academic Press, (1969).

(207) H. HEYDLOUF, European J. Pharm., 6, 340 (1969).

(208) F.J. KAYNE and J. REUBEN, J. Amer. Chem. Soc., 92, 220 (1970).

(209) K.J. ELLIS and A. McAULEY, J. Inorg. Nucl. Chem., 37, 567 (1975).

(210) P.D. SHARMA and Y.K. GUPTA, J. Chem. Soc.(Dalton), 81 (1975).

(211) K.S. GUPTA and Y.K. GUPTA, J. Chem. Soc. (A), 256(1970).

(212) G. BIEDERMAN, Arkiv Kemi., 6,(5), 527 (1964).

(213) T.E. ROGERS and G.M. WAIND, Trans. Far. Soc., 57, 1360 (1961).

(214) B.M. THAKURIA and Y.K. GUPTA, J. Chem. Soc. (Dalton), 77 (1975).

(215) J. HILL, Ph.D. Thesis, University of Strathclyde (1968).

(216) K.S. GUPTA and Y.K. GUPTA, J. Chem. Soc. (A), 1180(1971).

(217) F.J.C. ROSSOTTI and H. ROSSOTTI, Acta. Chem. Scand., 10, 957 (1956); J. MEIER and G. SCHWARZENBACH, Chimica (Aurau) 12, 328 (1958); N. IGRI and F. BRITO, Acta. Chem. SCand., 13, 1971 (1959).

(218) M,J, LaSALLE and J.W. COBBLE, J. Phys. Chem., 59, 519 (1959).

(219) H.C. MISHRA and R.C. SYMONS, J. Chem. Soc., 4411 (1962); G. SCHWARZENBACH and G. GEIER, Helv. Chim. Acta., 46, 906 (1963).

(220) J.S. LITTLER and W.A. WATERS, J. Chem. Soc., 4046(1959).

(221) C.F. WELLS and L.V. KURITSYN, J. Chem. Soc. (A), 1372 (1970).

(222) K. KUSTIN and D.A. TOPPEN, Inorg. Chem., 12, 1404(1973).

(223) M. BOBTELSKY and A. GLASNER, J. Amer. Chem. Soc., 64, 1462 (1942).

(224) J.R. JONES and W.A. WATERS, J. Chem. Soc., 4757 (1961).

(225) H. KURIHARA and T. NOZAKI, J. Chem. Soc. Japan, 83, 708 (1962).

(226) N.C. BHARGAVA, R. SHANKER and G.V. BAKORE, Z. Phys. Chem., (Leipzig), 229, 238 (1965).

(227) D.N. SATHYANARYANA and C.C. PATEL, Bull. Chem. Soc. Japan, 37, 1736 (1964).

(228) A. McAULEY and R. SHANKER, J. Chem. Soc. (Dalton), 2321 (1973).

(229) J.L. WALTER, J.A. RAYAN and T.J. LANE, J. Amer. Chem. Soc., 78, 5560 (1956).

(230) M.J, JENSSEN, Recueil, 81, 650 (1962).

(231) R. ZAHRADNIK, Coll. Czech. Chem. Comm., 24, 3678 (1959).

(232) Ref. 12 in ref. (130).

(233) M. BOBTEISKY and S. CZOSNEK, Z. Anorg. Allegen. Chem., 205, 401 (1932).

(234) K. JULIAN and W.A. WATERS, J. Chem. Soc., 818 (1962).

(235) J.B. RAMSEY, E.L. COLCHIMAN and L.C. POCK, J. Amer. Chem. Soc., 68, 3373 (1950).

(236) M.H. BOYER and J.B. RAMSEY, J. Amer. Chem. Soc., 75, 3802 (1957).

(237) G. St. NIKOLOV and D. MIHAILOVA, J. Inorg. Nucl. Chem., 31, 2499 (1969).

(238) W.C. BRAY, R.B. RAMSEY, J. Amer. Chem. Soc., 55, 2279 (1933).

(239) F. SECCO, S. CELSI and C. GRAITI, J. Chem. Soc.,(A), 1675 (1972).