STUDIES ON THE REACTION BETWEEN ETHYLENIC MOLECULES AND FREE RADICALS.

The kinetics of the addition of bromotrichloromethane to vinyl acetate and vinyl chloride.

A thesis submitted to the University of
Glasgow in accordance with the regulations
for the award of the degree of Doctor of
Philosophy.

by

Ross A.M. Thomson, B.Sc.

Dept. of Chemical Technology,
Royal College of Science and
Technology,
Glasgow.

January, 1960.

The author is greatly indebted to Dr. W.I. Bengough for his help and encouragement during the course of this work. Thanks are also due to Professor P.D. Ritchie, in whose Department the work was carried out, to the Department of Scientific and Industrial Research for the award of a maintenance allowance and to Mr S.A, McIntosh of the author's Department for many helpful discussions.

Publications.

Some of the work described in this thesis is contained in the following publications:-

The Photochemical Addition of Bromotrichloromethane to Vinyl Acetate.

Bengough and Thomson, Chem. & Ind., 1957, 426.

A Dilatometric Method of Measuring the Heats of Radiation-induced Reactions. Part 2 - The Heat of the Photochemical Addition of Bromotrichloromethane to Vinyl Acetate.

Bengough and Thomson, Trans. Faraday Soc., 1959, 55, 268.

A Modified Rotating-Sector Method of Measuring Kinetic Chain Life-times.

Bengough, McIntosh and Thomson, Nature, 1959, 184, 266.

The Addition of Bromotrichloromethane to Vinyl Acetate. Part 1 - The Products of the Photochemical and Benzoyl Peroxide Catalysed Reactions.

Bengough and Thomson, Trans. Faraday Soc., 1960, (in press)

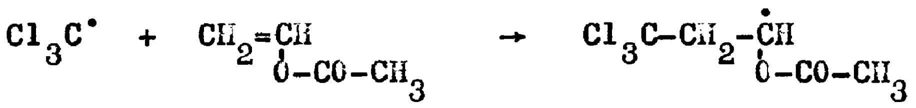
INDEX.

Index to Figures.

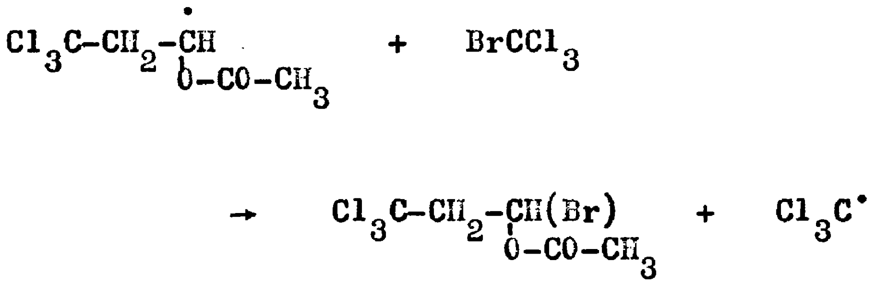
Figure page.

Summary.

The photochemical reaction between vinyl acetate and bromotrichloromethane has been investigated dilatometrically. The propagation steps in the reaction are as follows:-

(2) 

$$\mathrm{Cl_3C^{\bullet} + CH_2{=}\underset{O{-}CO{-}CH_3}{CH} \rightarrow Cl_3C{-}CH_2{-}\underset{O{-}CO{-}CH_3}{\overset{\bullet}{C}H}}$$

(3) 

$$\mathrm{Cl_3C{-}CH_2{-}\underset{O{-}CO{-}CH_3}{\overset{\bullet}{C}H} + BrCCl_3 \rightarrow Cl_3C{-}CH_2{-}\underset{O{-}CO{-}CH_3}{CH(Br)} + Cl_3C^{\bullet}}$$

The value obtained by previous workers for the velocity coefficient of reaction 3 indicated that under suitable concentration conditions, a measurable quantity of high polymer should be produced. On examination, however, no polymer was detected.

It has been found that the ratio of the velocity coefficient for reaction 3 to the velocity coefficient for the addition of the radical produced by reaction 2 to a vinyl acetate molecule is sufficiently high to preclude the formation of polymer.

A marked decrease in value has been found in the ratio of the velocity coefficient for chain transfer to the velocity coefficient for propagation with increase in radical $\overline{DP}$ for the chain transfer of bromotrichloromethane with vinyl acetate. The only apparent explanation of this is that bromotrichloromethane has a negative e-value in the Alfrey-Price Q-e Scheme.

Velocity coefficients for the photochemical reaction between vinyl chloride and bromotrichloromethane have also been evaluated where possible. Results show that vinyl chloride and vinyl acetate are similarly reactive towards the trichloromethyl radical, which would be expected from co-polymerisation studies.

The homogeneous and heterogeneous photo-sensitised polymerisations of vinyl chloride have been compared and close similarities have been found to exist.

Chapter 1. Introduction.

During the past few decades the idea has been gradually adopted that such processes as oxidation, polymerisation, telomerisation, etc., proceed by radical chain mechanisms. With respect to the latter two processes in particular, the most imposing evidence has been that substances known to produce free radicals on decomposition are capable of chain initiation and that the rate of photo-polymerisation is greatly increased in the presence of these materials. It is also known that such reactions are completely inhibited in the presence of small quantities of free radical scavengers for distinct periods, after which reaction proceeds normally (i.e., when all the inhibitor has been used up).

Kinetic analysis of experimental data from such systems offers further evidence of free radical chain mechanisms.

Initially, there was a great deal of unsatisfactory conjecture applied to the study of this topic. In 1930, however, Taylor and Jones[1] were the first to offer a good example of a chain reaction - the polymerisation of ethylene initiated by the decomposition products of mercury diethyl.

Radical reactions, unlike ionic reactions which are nearly instantaneous, proceed at measurable, reproducible rates. The most important single factor governing the rate is the ease with which the radical will react with the other components of the system. This property is normally termed 'reactivity', and in vinyl polymerisations, the rate of reaction and the nature of the reaction products will normally depend on the reactivity of two species - that of the radical and that of the monomer from which it is derived. These two factors are usually interdependent since a highly reactive monomer will yield a correspondingly unreactive radical.

Several methods of differing merit are available for estimating reactivities, for example, oxidation and co-polymerisation studies. The former suffers from the defect that complications may be introduced by the molecular structure of the reactants and by difficulty in characterising the radicals produced. Again, oxidation studies often involve two phase gas-liquid systems which also introduce difficulties. Co-polymerisation studies are much more satisfactory, and by a suitable choice of monomers it is possible to obtain a series of velocity coefficients for the interaction of one specific radical with a variety of olefins and so obtain a general picture of their reactivities.

Unfortunately, both of these methods suffers from the defect that neither the radical nor the reaction product can be characterised with any degree of certainty. It is much more satisfactory to measure the reactivity of a species by examining the addition of a simple, unambiguous radical under circumstances where a large molecule will not be produced.

With this in mind, the addition of simple organic compounds (usually halides) to olefins has been studied by a number of workers. Kharasch et al[2-4] found that simple, well-defined products are obtained in such reactions which proceed by a chain mechanism. In particular they found that the thermal catalysed addition of bromotrichloromethane to cyclohexene yielded the product 1:trichloromethyl-2-bromocyclohexane.[5] They suggested that the decomposition of bromotrichloromethane provided the trichloromethyl radicals required to initiate the kinetic chain.

Bromotrichloromethane is an excellent source of free radicals. The excitation wave-length is in the region of 3300-3900 A, so that the light obtained from an ordinary high pressure mercury vapour lamp filtered through soft glass will bring about decomposition. The nature of the breakdown too, is unambiguous. It is obvious from bond-energy considerations alone that rupture will occur preferentially across the carbon-bromine bond to give equal numbers of trichloromethyl and bromine radicals.

As would be expected from these considerations, bromotrichloromethane is an efficient chain transfer agent in vinyl polymerisations. Little was known however, about the addition of a trichloromethyl radical to start the growth of a chain. The cyclohexene - bromotrichloromethane system was thus ideal for obtaining information about this step and possibly about the interaction of hydrocarbon radicals in solution (provided the presence of a trichloromethyl grouping does not affect radical reactivity to an appreciable extent).

Similar investigations may be carried out on vinyl monomers which normally polymerise, and if sufficiently high concentrations of bromotrichloromethane are employed, then the de-bromination or transfer reaction becomes of sufficient importance to preclude the formation of polymer. Information may then be obtained about radical processes which occur in polymerisation. For example, an estimate may be obtained of the relative reactivities of a series of monomers towards one unambiguous free radical which should be strictly comparable with the results obtained from co-polymerisation studies. The effect of degree of polymerisation ($\overline{DP}$) on radical reactivity may be observed by measuring the velocity coefficients for the propagation of radicals of widely differing $\overline{DP}$. Information about the interaction of radicals may also become available.

Melville et al[6] also investigated the photochemical addition of bromotrichloromethane to cyclohexene. They suggested a kinetic scheme for the reaction and evaluated several of the velocity coefficients involved. In their work, they measured the required parameters by the usual methods of polymer chemistry.

This led to a later investigation by the same workers[7] of the photochemical addition of bromotrichloromethane to vinyl acetate, for which they proposed the following kinetic scheme:-

$$(1)\qquad Cl_3C\,Br \rightarrow Cl_3C^{\bullet}$$

$$(2)\qquad Cl_3C^{\bullet} + M \rightarrow Cl_3C(M)^{\bullet} \qquad (k_2)$$

$$(3)\qquad Cl_3C(M)^{\bullet} + Br\,CCl_3 \rightarrow Cl_3C(M)Br + Cl_3C^{\bullet} \qquad (k_3)$$

$$(4)\qquad 2\,Cl_3C^{\bullet} \rightarrow \qquad (k_4)$$

$$(5)\qquad Cl_3C^{\bullet} + Cl_3C(M)^{\bullet} \rightarrow \qquad (k_5)$$

$$(6)\qquad 2\,Cl_3C(M)^{\bullet} \rightarrow \qquad (k_6)$$

The bracketed symbols (k_3, etc.) denote the velocity coefficients for each of the reactions. M refers to the monomer in question, in this case vinyl acetate. A formula superscribed by a dot (e.g., $Cl_3C^{\bullet}$) signifies a free radical.

In future, the various radicals involved in the reaction will be denoted by the following symbols:-

$T(M)^{\bullet}$ – The radical produced by the addition of a

The above scheme is self-explanatory, the trichloromethyl radicals being obtained by the irradiation of bromotrichloromethane with light of wave-length around 3650 Å.

These workers[7] found that with excess vinyl acetate the rate-controlling reaction was the de-bromination of a bromotrichloromethane molecule (step 3) and that the principal termination reaction was the combination of two $T(VA)^{\bullet}$ radicals (step 6)

---

	trichloromethyl radical to a monomer molecule.
$T(M)_n^{\bullet}$	The radical produced by the addition of further monomer molecules to the $T(M)^{\bullet}$ radical.
$Z(M)^{\bullet}$	The radical produced by the addition of a monomer molecule to a radical derived from a normal initiator (e.g., benzoyl peroxide).
$Z(M)_n^{\bullet}$	A growing polymer chain initiated by the same type of initiator.
$R(M)^{\bullet}$	The radical produced by the addition of a monomer molecule to an unspecified initiating radical.
$R(M)_n^{\bullet}$	The propagation product of the radical $R(M)^{\bullet}$

With excess bromotrichloromethane, however, they found that reaction 2 was rate-controlling and that termination was brought about by the combination of two trichloromethyl radicals (step 4). For intermediate ranges, they derived an expression for the interaction coefficient between two dis-similar radicals (step 5). They found that second order termination occurred over the range of concentrations used. They were thus able to evaluate k_2, k_3, k_4, k_5 and k_6.

Using the same techniques as in the cyclohexene-bromotrichloromethane system they evaluated these coefficients and the results obtained which are relevant to the present discussion are shown in Table 1.

Table 1. Summary of the results obtained by Melville et al for the photochemical addition of bromotrichloromethane to vinyl acetate[7].

k_2 (30°C)	1120	$1.mole^{-1}sec.^{-1}$
k_3 (30°C)	2740	" " "
k_4 (30°C)	1.0×10^8	" " "

It was pointed out by Mayo[8] that, since the velocity coefficient for the propagation reaction in vinyl acetate polymerisation is about 1100 $l.mole^{-1} sec.^{-1}$ [9], the velocity coefficient for the following reaction

$$(7) \qquad Cl_3C(M)^{\bullet} + M \rightarrow Cl_3C(M)_2^{\bullet} \qquad (k_7)$$

might be expected to be of the same order.

Thus, for mixtures consisting of a molar ratio of, for example, 10 to 1 vinyl acetate to bromotrichloromethane, the rate of reaction (7) would be expected to be greater than that of reaction (3) and the dilatometric measurements would include not only the contractions due to reactions (2) and (3), as assumed by Melville et al[7] but also the contraction produced by reaction (7) and subsequent polymerisation. However, the absence of any apparent polymer formation did not favour this view.

It would appear then that if the assumption made by Melville et al[7] is correct, i.e., that no polymer is formed, then either the value obtained for the velocity coefficient of reaction (3) is incorrect or the reactivity of the $T(VA)^{\bullet}$ radical produced by reaction (2) is very low compared with, for example, a $Z(VA)_n^{\bullet}$ radical.

The object in carrying out the work described in this dissertation has been to determine whether polymerisation does take place under these conditions, and if not to attempt to explain this apparent anomaly.

The first task was an investigation of the products of reaction when carried out at various mole ratios of vinyl acetate to bromotrichloromethane. This led to a series of determinations of the ratio of the velocity coefficients for propagation and transfer using a closely allied system which gave a greater rate of formation of product. At this stage it was considered necessary to re-evaluate where possible the velocity coefficients for the reaction. The dependence of rate of reaction on reactant concentration was determined over a wide range. To evaluate the velocity coefficients, reaction rates were measured using a variation of the dilatometric method, kinetic chain life-times by the non-stationary state method and by a novel method incorporating non-stationary state and rotating sector techniques. The rate of formation of trichloromethyl radicals was measured in several media using an inhibitor technique.

As stated previously, an investigation of the photochemical addition of a series of monomers to the same radical will give information regarding, among other factors, monomer reactivities. Monomers which have been, or are being investigated from this point of view include styrene,[10] methallyl acetate,[11] acrylonitrile,[12] and of course, vinyl acetate.[7,13]

On completion of the work on vinyl acetate, it was decided to include vinyl chloride in the above list.

Unfortunately, little work has been done on the kinetics of vinyl chloride polymerisation. A literature survey indicated that only one evaluation has been made of the velocity coefficients for the solution polymerisation.[14] Bulk-polymerisation studies are difficult, as poly-vinyl chloride is insoluble in its monomer and precipitates as it forms, thus introducing many complications.

Burnett and Wright[14] evaluated the velocity coefficients for the photo-sensitised polymerisation of vinyl chloride in the presence of tetra-hydrofuran as a solvent for the polymer. They found that the velocity coefficients were rather greater in value than was expected. It was of interest to observe whether the reaction with bromotrichloromethane would under certain conditions give similarly high results.

Preliminary results indicated that at very low concentrations of bromotrichloromethane, the photo-chemical reaction with vinyl chloride yielded polymer, whereas at higher concentrations, adducts of 1:1 to approximately 5:1

vinyl chloride to bromotrichloromethane were obtained. The reaction scheme proposed is similar to that for the vinyl acetate-bromotrichloromethane reaction together with the following steps:-

(7) $\mathrm{Cl_3C(M)^{\bullet}} + \mathrm{M} \rightarrow \mathrm{Cl_3C(M)_2^{\bullet}}$ (k_7)

(8) $\mathrm{Cl_3C(M)_2^{\bullet}} + \mathrm{Cl_3C\,Br} \rightarrow \mathrm{Cl_3C(M)_2Br} + \mathrm{Cl_3C^{\bullet}}$ (k_8)

(9) $\mathrm{Cl_3C(M)^{\bullet}} + (n-1)(\mathrm{M}) \rightarrow \mathrm{Cl_3C(M)_n^{\bullet}}$ (k_9)

(10) $\mathrm{Cl_3C(M)_n^{\bullet}} + \mathrm{Cl_3C\,Br} \rightarrow \mathrm{Cl_3C(M)_nBr} + \mathrm{Cl_3C^{\bullet}}$ (k_{10})

Innumerable straight and cross-terminations are possible but they have not been quoted.

In conclusion, in this dissertation, it is hoped to explain the absence of polymer formation, if this should be the case, in the photochemical reaction between vinyl acetate and bromotrichloromethane. It is also hoped to compare the reactivities of two monomers towards the same radical and to obtain any other relevant information.

Chapter 2. Experimental.

2.1. Materials.

VINYL ACETATE, obtained from the Shawinigan Chemical Corporation was dried over calcium chloride and distilled in a six-foot vacuum-jacketed column packed with small wire-gauze rings. A high reflux ratio was maintained and a product of B.Pt. 72.2-72.3°C was collected. The monomer was transferred to a flask, a small quantity of benzoyl peroxide added and the flask was attached to the high vacuum line. The mixture was thoroughly out-gassed by repeated freezing, evacuating and thawing and irradiated with ultra-violet light until a slight increase in viscosity was noted. The monomer in this pre-polymerised mixture was distilled at room temperature on the high vacuum line shortly before use.

A cylinder of VINYL CHLORIDE, a gas at normal temperatures and pressures, was gifted by the Distiller's Company, Ltd. Initially, the gas was passed through a purification train prior to its introduction into the high vacuum line. This train contained ammoniacal cuprous chloride (to remove acetylene), water and silica gel. Such a precaution was found to be unnecessary and the monomer was purified shortly before use by distilling at room temperature on the high vacuum line. The distilled monomer was evacuated for about an hour, warmed and the vapour stored in a large glass bulb of known volume attached to the line.

BROMOTRICHLOROMETHANE (BTCM) was obtained from the Eastman-Kodak Company, Ltd. It was washed with dilute sodium carbonate solution followed by water, dried over calcium chloride and distilled under reduced pressure before use.

BENZOYL PEROXIDE (B.D.H., practical Grade) was dissolved in chloroform, vacuum concentrated and the pure reagent precipitated by absolute alcohol.

1:1' AZO-<u>bis</u>-(CYCLOHEXANE) CARBONITRILE was prepared by the method of Overberger[15] and recrystallised from absolute alcohol.

1:1'-AZO-bis-ISOBUTYRONITRILE (AIBN) was obtained from Eastman-Kodak, Ltd. and purified by recrystallisation from absolute alcohol.

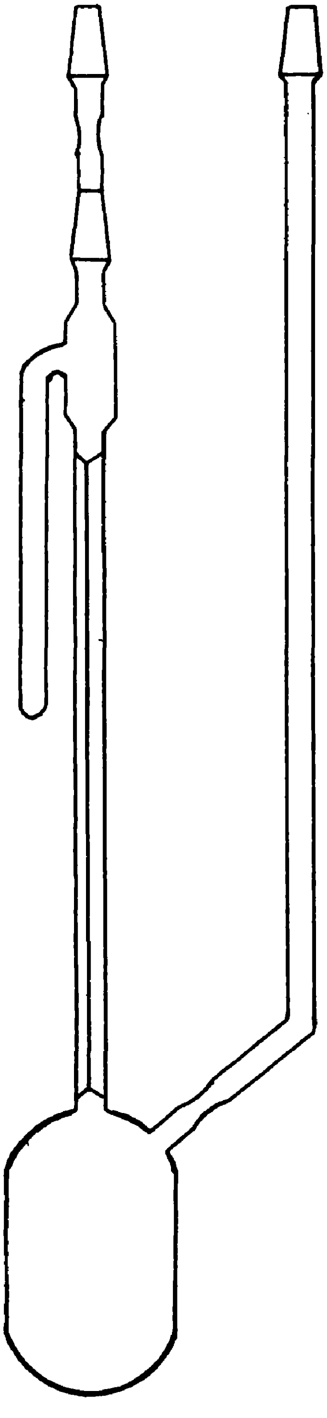
1:1'-DIPHENYL-2-PICRYLHYDRAZYL (DPPH) was prepared by the method of Goldschmidt and Renn[16] and recrystallised from a mixture of ligroin and benzene.

CHLOROFORM and CYCLOHEXANE (Analar grade) and BENZENE (molecular weight determination quality) were distilled before use.

2.2. Apparatus.

A vacuum line of standard design was built of Pyrex glass. The pumping system consisted of a two-stage mercury vapour diffusion pump backed by a 'Metrovac' rotary vacuum pump. For the present work, a vacuum gauge was considered extraneous, and from the effect of a high voltage discharge coil, the estimated vacuum was about 10^{-4} mm of mercury. Liquid nitrogen was used as the coolant when dealing with vinyl chloride and Drikold-acetone mixtures for vinyl acetate.

FIGURE 1



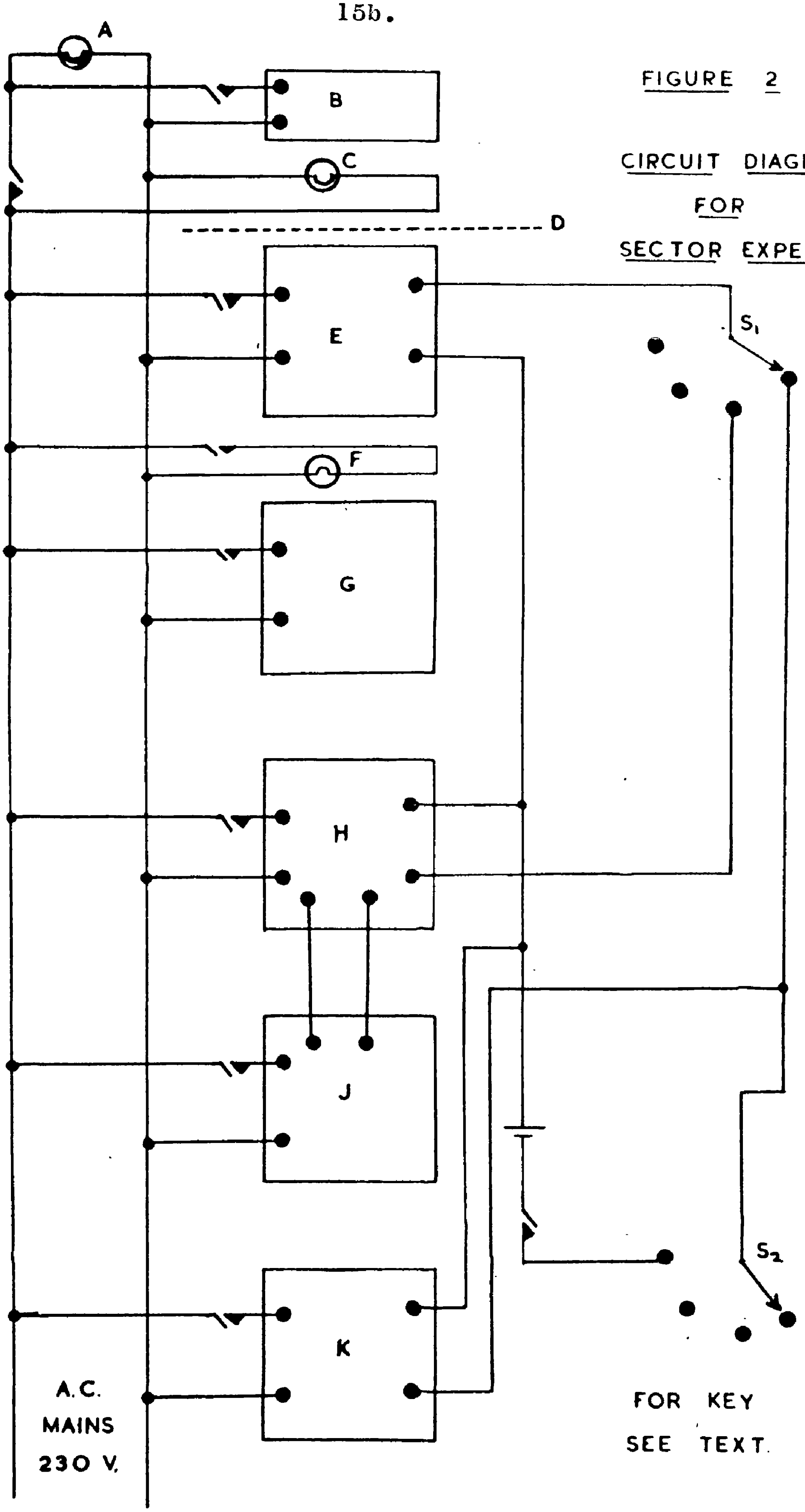


FIGURE 2

CIRCUIT DIAGRAM
FOR
SECTOR EXPERIMENTS

FOR KEY
SEE TEXT.

The thermostat was a cylindrical Pyrex glass, water-filled tank contained in a copper jacket lined with Fibreglass. The required temperature was maintained to within ±0.02°C by a Robertson Heater controlled by a relay circuit. The detecting unit was a mercury-toluene regulator.

The source of illumination was a 125 watt 'Osira' mercury vapour lamp connected to a choke and capacitor to eliminate variations in the applied current. The light was filtered through a Chance OX1 filter.

Dilatometers were usually of about 20 ml capacity and were made from Pyrex glass tubing. The special narrow-stemmed dilatometer shown in Figure 1 allowed several measurements to be made, since the liquid level in the stem could be raised by adding reaction mixture from the side-arm reservoir.

Figure 2 is a diagram of the circuit used in the modified rotating sector and non-stationary state experiments. The sector itself was a light aluminium disc divided into four equal segments, two of which had been removed, so that one complete revolution produced two light and two dark periods. It was driven through a 25:1 reduction gear by a variable speed electric motor.

Low sector speeds were measured by allowing it to rotate in front of a photo-electric cell connected through the pre-amplifier to an Elliot D.C. Pen-recording Voltmeter as shown. For high sector speeds, the pulse frequency from the photocell was balanced against the output of a signal generator, using a cathode-ray oscilloscope. For measuring reaction rates, the pen-recorder was connected in series with a 1-volt dry cell, a small resistance and a tapping key so arranged that when de-pressed, the circuit was broken. Figure 2 shows how these circuits were connected up for ease of operation, the following being the key to the diagram.

A - Viewing lamp in thermostat.
B - Shutter solenoid.
C - Excitation lamp for photo-cell.
D - Plane of sector.
E - Photo-electric cell.
F - Mercury vapour lamp.
G - Variable speed electric motor.
H - Cathode-ray oscilloscope.
J - Pre-amplifier.
K - Elliot D.C. Pen-recording Voltmeter.
S_1/S_2- 2 bank switch.

2.3. Procedure.

2.3.1. Calibration of High Vacuum Line.

It was necessary to calibrate the high vacuum line for use with vinyl chloride. The volume of one of the bulbs attached to the line was measured by weighing empty and then filled with water. The bulb was dried, replaced, filled with air at atmospheric pressure and sealed. The remainder of the line was evacuated and the reading on the mercury manometer noted. Each section of the line was opened to the bulb in turn and its volume calculated from the new manometer reading by a straightforward application of Boyle's law, assuming that air behaves as a perfect gas.

2.3.2. Filling of dilatometers.

Dilatometers were thoroughly washed with concentrated nitric acid, water and acetone and were dried on the high vacuum line before use. They were calibrated using acetone to determine the volume of the bulb and mercury for the stem.

Those containing vinyl acetate (VA) and BTCM were filled as follows:-

The required amount of BTCM was measured into the dilatometer and out-gassed on the high vacuum line by repeated freezing, evacuating and thawing. Vinyl acetate was distilled from the pre-polymerised mixture into a graduated flask and the dilatometer (immersed in freezing mixture) opened to this supply. When filled, the dilatometer was sealed off <u>in situ</u> and stored in a Drikold-acetone mixture until required.

When an initiator or inhibitor was also required, a solution of known strength was prepared in chloroform. The correct volume of this solution was placed in the dilatometer through a fine dropper and the solvent carefully pumped off on the high vacuum line. The other reactants were added exactly as above.

In experiments requiring a very small quantity of BTCM, a solution was prepared in vinyl acetate. The required amount was placed in the dilatometer, out-gassed and the remaining vinyl acetate added as above.

The 1:1 addition product of vinyl acetate and BTCM when required was weighed into the dilatometer after the initiator had been introduced.

Benzene and cyclohexane were added to the BTCM in the dilatometer and the normal filling procedure then carried out.

Dilatometers containing BTCM and vinyl chloride (VCl) were filled by introducing and out-gassing the former in the usual way. Vinyl chloride was then condensed in the dilatometer by opening it to the monomer storage bulb. As the liquid and vapour densities of the monomer were known, the amount condensed was easily measured by noting the pressure difference registered on the mercury manometer.

The dilatometer shown in Figure 1 was filled as follows:- For vinyl acetate and BTCM, a mixture of the two reactants in the required composition was added, out-gassed and the dilatometer sealed off as above. For vinyl chloride, this procedure was unsuitable and the dilatometer was filled in the usual way through the side-arm.

2.3.3. Rate measurements.

Experiments were carried out by completely immersing each dilatometer in the thermostat at the required temperature. In all cases, rates were determined by some form of the dilatometric method. The normal technique consisted of measuring the rate of contraction due to reaction by means of a cathetometer.

2.3.4. Determination of intensity exponents.

Intensity exponents were measured by following the reaction rate cathetometrically under full illumination. A wire-gauze screen of known transmission was interposed and the reaction rate measured under reduced intensity of illumination. The screen was removed and the rate was measured once more under full illumination.

2.3.5. Determination of the heat of reaction.

The heats of the various reactions were determined by a dilatometric technique using the Elliot D.C. Pen-recorder in conjunction with a graduated scale engraved on the cathetometer eye-piece.

By manipulation of the dilatometer (Figure 1), the meniscus in the stem was arranged to be at a convenient level at the reaction temperature. Irradiation was commenced by pressing a switch to open the shutter in front of the light source. Simultaneously, the previously mentioned tapping-key was depressed to give a peak on the recorder chart. As the meniscus passed suitably chosen divisions on the eye-piece scale, the key was depressed and a series of peaks was obtained on the chart. The scale was calibrated for each experiment and the distance between the peaks measured. The rate of contraction due to reaction was also measured in this way, the measurement being repeated several times to ensure that it was linear. The rate of contraction due to cooling immediately on the cessation of irradiation was measured by shutting off the light suddenly and following the rate as before. Each of these measurements was made several times at 20 minute intervals to ensure reproducibility.

2.3.6. Determination of specific heat.

The specific heats of vinyl acetate and BTCM were determined by the method of Newton's cooling curves. A weighed copper calorimeter containing a known weight of BTCM was heated to about 35°C, placed in an air-jacket and partially immersed in the thermostat at 25°C. The cooling rate was measured while the liquid was steadily stirred. This procedure was repeated for the same volumes of vinyl acetate and carbon tetrachloride.

2.3.7. Determination of expansion coefficient.

Calibrated dilatometers were filled to a convenient level with vinyl acetate, vinyl chloride and BTCM. Each dilatometer was immersed in the thermostat at 25°C and the liquid level noted by means of a cathetometer. The temperature of the tank was slowly increased to 30°C and the liquid level noted at 1 degree intervals.

2.3.8. Determination of the life-time of the kinetic chain by the non-stationary state method.

For this measurement, the initial expansion due to self-heating was followed over the first 10 seconds of irradiation using the technique described for the determination of the heat of reaction.

2.3.9. Determination of the life-time of the kinetic chain by the modified rotating sector method.

In this method, the initial expansion rate due to self-heating was determined over the first 10 seconds of steady illumination as before. The sector motor was started and when a steady speed was attained, it was measured as described previously. The initial expansion rate was measured under these conditions. The sector speed was re-determined and from the average of the two speeds, the mean flash-time was obtained. This procedure was carried out at least twelve times, at different sector speeds, with about 20 minutes between each measurement to allow the system to reach thermal equilibrium.

2.3.10. Determination of rate of initiation.

This was determined in several solvents and monomers by measuring the rate of removal of DPPH from DPPH-BTCM-solvent (or monomer) mixtures on irradiation. A Unicam SP 1400 Spectrophotometer was used for this purpose. In one case, the rate of initiation was determined from the lengths of the periods of inhibition produced by several concentrations of inhibitor.

2.3.11. Isolation of reaction products.

Either a distillation or a precipitation technique was used to isolate the reaction products. In the former, the contents of the dilatometer were transferred to a flask on the high vacuum line. The more volatile unreacted materials were distilled off to a large extent on heating to about 50°C. The residue was placed in a molecular still and carefully distilled at as low a temperature as possible. The product was in some cases freeze-dried from benzene. The materials thus obtained were sealed in glass ampoules and stored in Drikold-acetone mixtures for further investigation.

In the precipitation method, much of the unreacted material was removed at room temperature on the high vacuum line. The residue was precipitated from toluene by petroleum ether (boiling range 40/60°C). In this case, the product was freeze-dried from benzene on the high vacuum line.

2.3.12. Investigation of reactants and reaction products.

Densities were determined using a pyknometer of about 1 ml capacity, calibrated with water at 25°C, and refractive indices by means of an Abbé refractometer. The molar extinction coefficient of the 1:1 adduct of vinyl acetate and BTCM was measured using a Unicam SP 600 Spectrophotometer. Infra-red absorptions and microanalyses were carried out in the Department.

Cryoscopic molecular weight determinations were made by measuring the freezing-point depression produced in a known volume of benzene by a known weight of material.

The degree of polymerisation was determined viscosimetrically using a Ubbelohde viscometer modified to allow the solution to be diluted in situ. A known weight of the material was dissolved in benzene and the time taken for a fixed volume to flow through the capillary tube of the viscometer was noted. The solution was successively diluted and the time of flow for each concentration as well as for pure benzene was obtained.

Chapter 3. Preliminary work.

3.1.1. Investigation of the products of reaction between vinyl acetate and BTCM.

A number of experiments were carried out at various mole ratios to determine whether polymerisation occurred in the photochemical reaction between vinyl acetate and BTCM. Obviously, it was of major importance to examine the range covered by Melville et al[7]. Experiments were carried out at 25°C using mole ratios of 1:1 and 10:1 vinyl acetate to BTCM and the reaction products were compared after isolation by the distillation technique described in Chapter 2. Experiments were also carried out at much higher mole ratios of vinyl acetate to BTCM, and the results obtained are shown later.

3.1.2. Investigation of the effect of the 1:1 adduct of vinyl acetate and BTCM on the photo-sensitised polymerisation of vinyl acetate.

It is necessary to anticipate here some of the results obtained in the investigation described in paragraph 3.1.1.

If the products of the photochemical reaction between vinyl acetate and BTCM are of much lower molecular weight than would be expected, a possible explanation is that the $T(VA)^{\bullet}$ radical produced by reaction 2 (page 6) is so unreactive towards vinyl acetate that reaction 7 (page 9) is unlikely to occur. The presence of these radicals should thus ensure complete inhibition of the photo-sensitised polymerisation of vinyl acetate. Initiator radicals, obtained by the photo-decomposition of benzoyl peroxide, for example, would abstract the labile bromine atom in the reactive T(VA)Br molecules. If the $T(VA)^{\bullet}$ radical is very unreactive towards vinyl acetate as suggested, no propagation should occur. This hypothesis was tested by irradiating mixtures of vinyl acetate, benzoyl peroxide and the 1:1 adduct (T(VA)Br) at 25°C.

3.2.1. Results obtained in the investigation of the photochemical reaction between vinyl acetate and BTCM.

Table 2. Some properties of the products of the photochemical reaction between vinyl acetate and BTCM at 25°C.

Mole Ratio (VA/BTCM)	1:1	10:1
Molecular weight	287	286
Liquid density (25°C) ($gm.ml^{-1}$)	1.660	1.658
Refractive Index	1.496	1.495
%age Carbon	21.4	21.32
%age Hydrogen	3.02	2.17

The 1:1 vinyl acetate/BTCM adduct would have a molecular weight of 284, a carbon content of 21.1% and a hydrogen content of 2.10%.

Infra-red absorption spectra were obtained for each of the above materials and in both cases, peaks were obtained at the following wave-numbers:-

Table 3. Principal I.R. absorption peaks for the above reaction products.

687	708	813	849	940	1007
1057	1096	1192	1328	1360	1374
1416	1730	2390	3020	(cm^{-1})	

Further experiments were carried out at much higher mole ratios of vinyl acetate to BTCM to determine whether polymer was produced under these conditions. The following table shows the results which were obtained:-

Table 4. The products of the photochemical reaction between vinyl acetate and BTCM over a wide range of concentrations.

Initial mole-ratio x 10^4 (BTCM/VA)	F.Pt. Depression (C^o)	Molecular Weight	Measured $\overline{DP}$	Calc.* $\overline{DP}$	$\frac{k_{tr}}{k_p}$ +
8.75	0.240	447	2.9	421	600
111	0.028	320	1.4	42	214
113	0.314	396	2.29	41	69
1,000	0.252	287	1.0	5.1	-
10,000	0.413	287	1.0	1.4	-

[*] Calculated using the value obtained for k_3 by Melville et al.[7]

[+] Calculated using Mayo's equation for low molecular weight polymer (see Chapter 4).

Molar extinction coefficient at 3650 Å.

Figure 3 shows the optical density at 3650 Å of a solution of the 1:1 adduct of vinyl acetate and BTCM in *iso*-octane as a function of the concentration. From this curve, the molar extinction coefficient was found to be 0.66.

3.2.2. Results obtained in the investigation of the effect of the 1:1 adduct on the photo-sensitised polymerisation of vinyl acetate.

Results of experiments carried out at 25°C and using 1×10^{-3} mole.l.$^{-1}$ benzoyl peroxide as initiator are as follows:-

Complete inhibition was not produced. Instead, chain termination altered from second to first order with increase in adduct concentration (Figure 4). The rate of contraction due to reaction decreased, rapidly at first and

FIGURE 3

MOLAR EXTINCTION COEFFICIENT

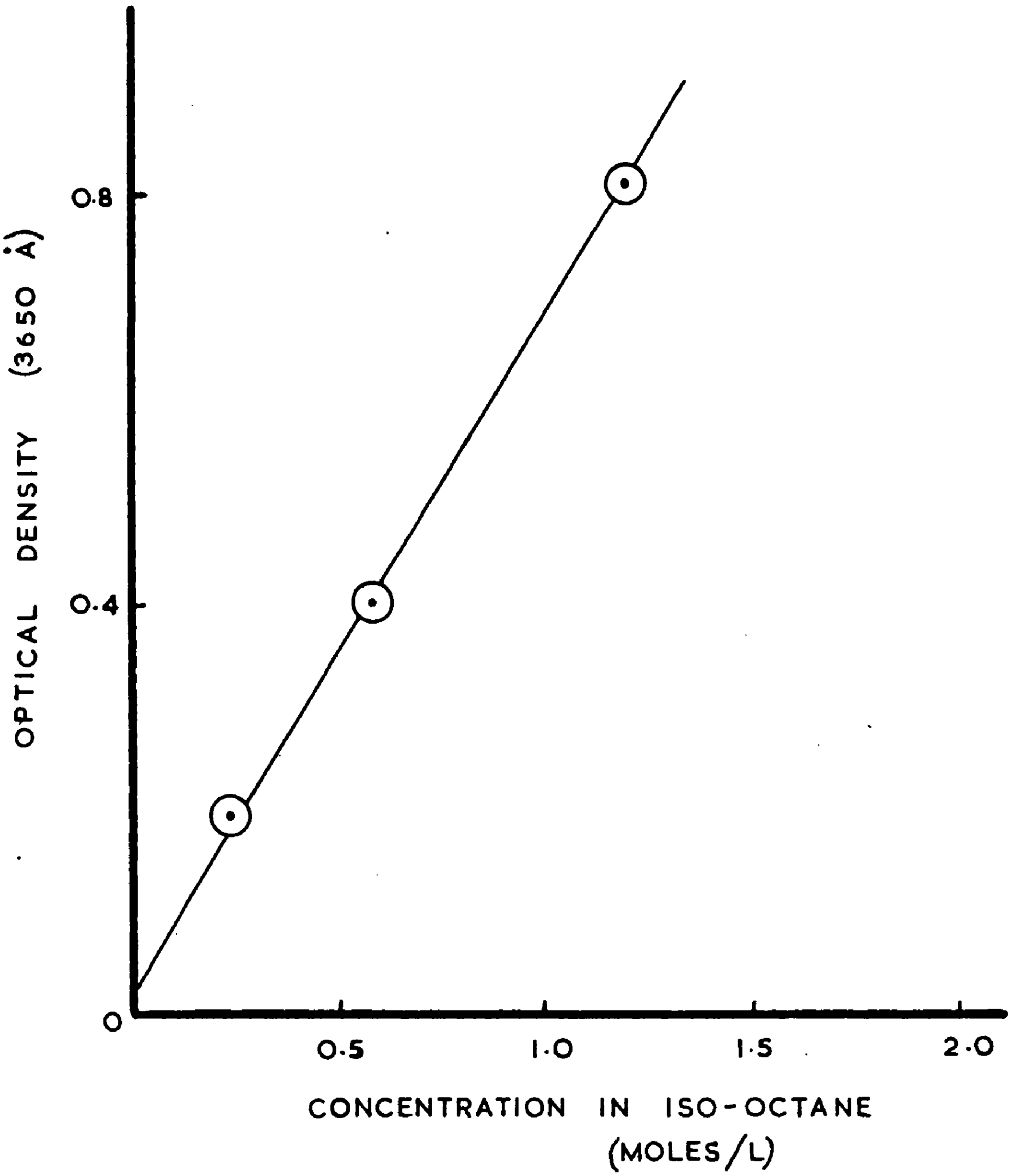


FIGURE 4

ORDER OF TERMINATION IN PRESENCE OF 1:1 ADDUCT.

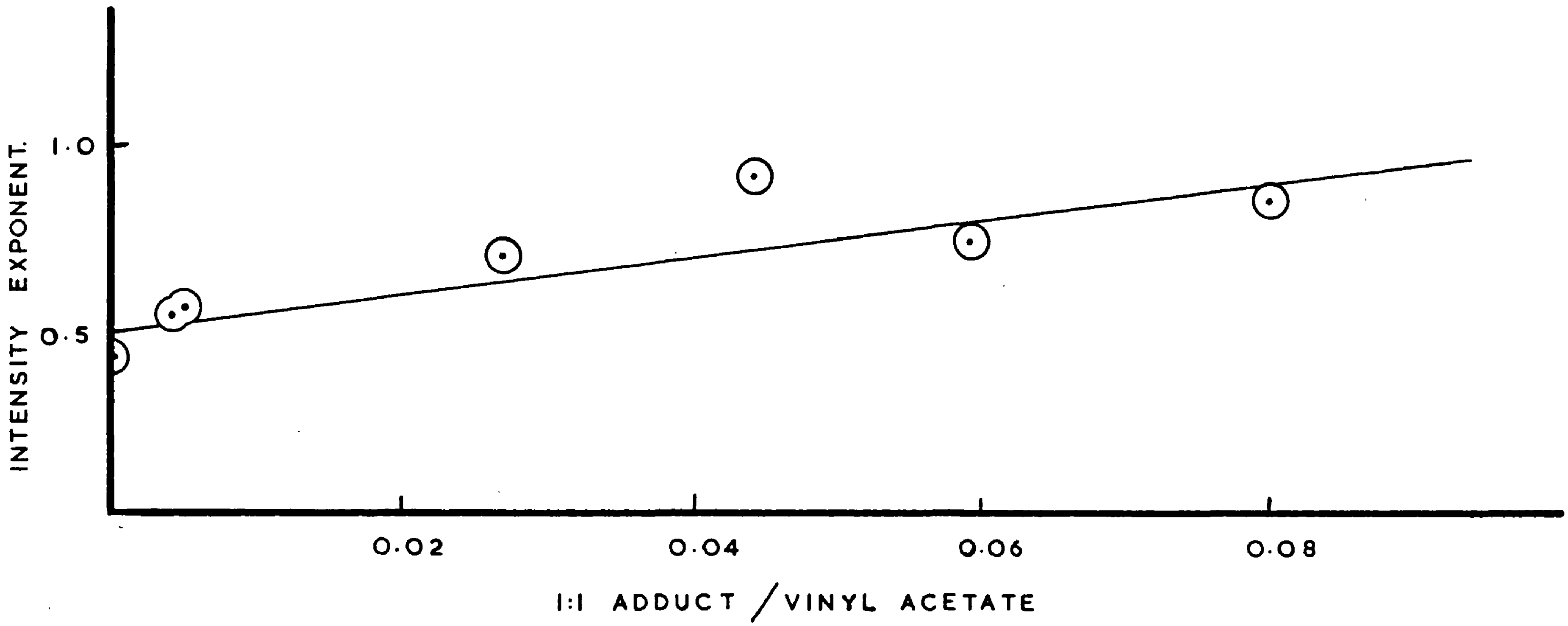
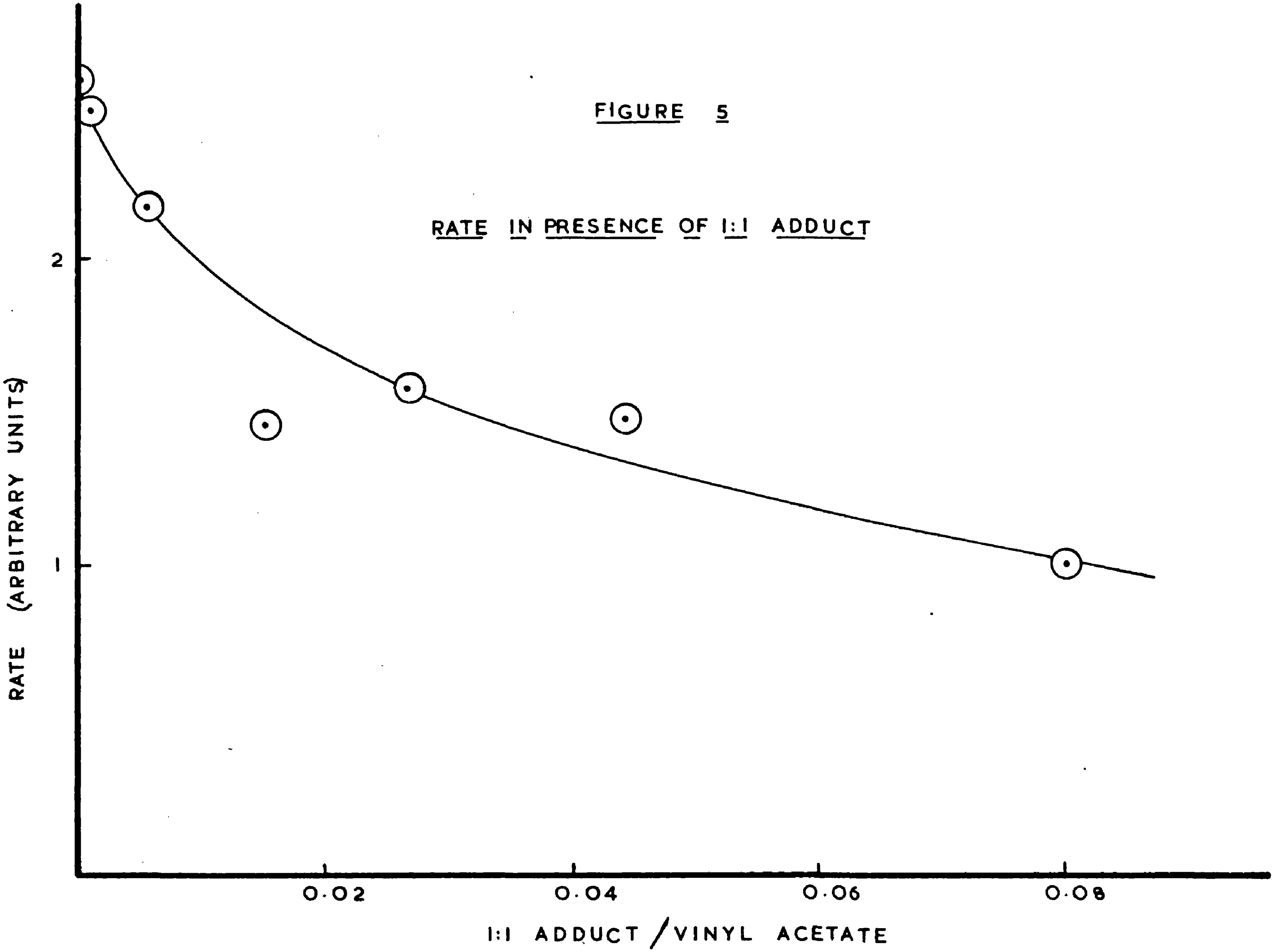


FIGURE 5

RATE IN PRESENCE OF 1:1 ADDUCT



then more slowly with increase in adduct concentration (Figure 5).

It was also found that in general, metal screens, rather than photographic plates must be used for the determination of intensity exponents and that the adduct should be freshly prepared.

3.3.1. Discussion of results.

Melville et al[6] found that BTCM absorbed very little radiation of wave-length 3650 Å. The present work indicated however, that the 1:1 adduct of the two reactants absorbed very strongly at this wave-length. Unless the concentration of the product in the reacting mixture is very low, therefore, it will absorb most of the incident radiation close to the glass-mixture interface nearest the source of illumination. This "skin effect" will produce unreliable results and conditions must be so chosen that the intensity of illumination is practically constant throughout the mixture. Thus, other reasons apart, reaction should only be taken to a low extent, when the product concentration will be low.

From Table 2, it is seen that over the concentration range employed by Melville et al[7], only the 1:1 adduct of the two reactants (molecular weight 284) was produced. This was confirmed by the other analyses. According to the values obtained by these workers for the velocity coefficients involved in the reaction, a product of molecular weight 320 would be expected for a feed-composition of 1:1 vinyl acetate to BTCM and 630 at the higher mole ratio.

The products of the reaction carried out at higher feed ratios of vinyl acetate to BTCM were also of much lower molecular weight than would be expected (Table 4). Although the individual results obtained here probably involve a considerable error, the general trend is significant. Severe experimental difficulties were encountered. For example, several of the experiments involved the use of a 1000 ml dilatometer and the subsequent removal of about 999 ml of unreacted materials to yield a very small quantity of product.

It would appear from these results therefore, that Melville's assumption [7] is correct, i.e., that no polymer is formed by the photochemical reaction between vinyl acetate and BTCM at experimentally possible mole ratios of the two reactants.

The results detailed in section 3.2.2. of this dissertation suggest that the presence of the T(VA)Br molecule has a retarding, rather than an inhibiting effect on the polymerisation of vinyl acetate. This might indicate that, although the reactivity of the $T(VA)^{\bullet}$ radical is low, it is still capable of propagating further via reaction 7 (page 9) and subsequent similar additions. Alternatively, the retardation may be ascribed to the effect of cross-termination of the various radical species as suggested by Jenkins.[17]

The results obtained here were inconclusive, however, and the problem was attacked from another angle. The subsequent work is described in Chapter 4.

Chapter 4. Evaluation of the ratio of the velocity coefficient for chain transfer to the velocity coefficient for propagation.

For almost any reaction involving chain transfer it is possible to measure the ratio of the velocity coefficients for transfer and propagation by the method due to Mayo.[18] This method was limited initially to reactions in which high polymer was produced[18] but by a suitable modification it may be applied to reactions producing low molecular weight polymers (or telomers).[19] This modification was derived independently in the present work.

By applying this method, it should be possible to evaluate the ratio of the velocity coefficients for reactions 3 and 7 (pp. 6,9) and from this measurement explain the absence of polymer formation.[20]

4.1.1. The ratio of the velocity coefficient for transfer to the velocity coefficient for propagation in a chain transfer reaction producing long chain polymers.[18]

In a chain transfer reaction, the following are the principal steps which occur.

$$R(M)_n^\bullet + M \rightarrow \text{propagation} \qquad (k_p)$$

$$R(M)_n^\bullet + M \rightarrow R(M)_n + M_1^\bullet \quad \text{(monomer transfer)} \qquad (k_{tr}')$$

$$R(M)_n^\bullet + S \rightarrow R(M)_n + S^\bullet \quad \text{(solvent transfer)} \qquad (k_{tr})$$

$$2\,R(M)_n^\bullet \rightarrow \text{termination} \qquad (k_t)$$

where $R(M)_n^\bullet$ represents the growing radical and S the material which is undergoing transfer with the monomer (M)

Now,

$$\overline{DP} = \frac{\text{rate of chain growth}}{\text{rate of chain termination}}$$

$$= \frac{k_p[R][M]}{k_t[R]^2 + k_{tr}'[R][M] + k_{tr}[R][S]} \qquad \text{..................(4.1)}$$

where $\overline{DP}$ is the degree of polymerisation, $[R]$ the radical concentration at the steady state, $[M]$ the monomer concentration and $[S]$ the concentration of the transfer agent.

At the steady state,

$$I = k_t[R]^2$$

where I is the rate of initiation.

Thus,

$$[R] = (I/k_t)^{\frac{1}{2}} = (k_1[M][B]/k_t)^{\frac{1}{2}} \quad \text{......(4.2)}$$

where $[B]$ is the initiator concentration and k_1 the velocity coefficient for the initiation step.

Inverting equation (4.1) and substituting the value of $[R]$ from equation (4.2) gives:-

$$\frac{1}{\overline{DP}} = \frac{(k_1.k_t)^{\frac{1}{2}}[B]^{\frac{1}{2}}}{k_p[M]^{\frac{1}{2}}} + \frac{k_{tr}'}{k_p} + \frac{k_{tr}[S]}{k_p[M]} \quad \text{....(4.3)}$$

Now, let $\overline{DP}_o$ be the degree of polymerisation when $[S] = 0$, i.e., in straight polymerisation.

Then,

$$\frac{1}{\overline{DP}_o} = \frac{(k_1.k_t)^{\frac{1}{2}}[B]^{\frac{1}{2}}}{k_p[M]^{1/2}} + \frac{k_{tr}'}{k_p} \quad \text{..........(4.4)}$$

Substitution in equation (4.3) gives,

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + \frac{k_{tr}[S]}{k_p[M]} \quad ....(4.5)$$

4.1.2. The ratio of the velocity coefficient for transfer to the velocity coefficient for propagation in a chain transfer reaction producing short chain polymers.

In a chain transfer reaction, in view of the competition between transfer and propagation, the following considerations are valid:-

$$\frac{\text{Chance of propagation}}{\text{Chance of transfer}} = \frac{k_p[R][M]}{k_{tr}[R][S]}$$

The symbols have been defined previously.

Thus,

$$\text{Probability of propagation} = \frac{k_p[M]}{k_{tr}[S] + k_p[M]}$$

$$\text{probability of transfer} = \frac{k_{tr}[S]}{k_{tr}[S] + k_p[M]}$$

From these expressions it is comparatively easy to calculate the number of each type of molecule which is formed, viz.,

Material	Number of molecules x $\overline{DP}$
T(VA)Br	$\dfrac{k_{tr}[S]}{k_{tr}[S] + k_p[M]}$
$T(VA)_2Br$	$\dfrac{2\,k_p[M] \cdot k_{tr}[S]}{\left\{k_{tr}[S] + k_p[M]\right\}^2}$
$T(VA)_3Br$	$\dfrac{3\left\{k_p[M]\right\}^2 \cdot k_{tr}[S]}{\left\{k_{tr}[S] + k_p[M]\right\}^3}$
$T(VA)_nBr$	$\dfrac{n\left\{k_p[M]\right\}^{n-1} \cdot k_{tr}[S]}{\left\{k_{tr}[S] + k_p[M]\right\}^n}$

The overall theoretical degree of polymerisation will be obtained by calculating the sum to infinity of the above series.

Let $k_{tr}[S] = A$, $k_p[M] = B$ and let the series be represented by Ω.

Thus,

$$Q \;=\; A/(A + B),\;\; 2AB/(A + B)^2;\;\; 3AB^2/(A + B)^3;\; \ldots\ldots.$$

$$= \frac{A}{(A + B)}\left\{1 + \frac{2B}{(A + B)} + \frac{3B^2}{(A + B)^2} + \frac{4B^3}{(A + B)^3} + \ldots\ldots.\right\}$$

$$= AC/(A + B)$$

and $C = 1 + 2\lambda + 3\lambda^2 + 4\lambda^3 + \ldots\ldots.$

if $\lambda = B/(A + B)$

Now, $\lambda C = \lambda + 2\lambda^2 + 3\lambda^3 + \ldots\ldots\ldots$

Hence,

$$(1 - \lambda C) = 1 + \lambda + \lambda^2 + \lambda^3 + \ldots..$$

$$= 1/(1 - \lambda)$$

So that, $C = 1/(1 - \lambda)^2$

Thus,

$$Q = \frac{A}{(A + B)} \times \frac{1}{\left\{1 - \dfrac{B}{(A + B)}\right\}^2}$$

$$= \left\{1 + B/A\right\}$$

i.e., $$\overline{DP} = 1 + \frac{k_p[M]}{k_{tr}[S]}$$

or, $$\frac{1}{\overline{DP} - 1} = \frac{k_{tr}[S]}{k_p[M]} \qquad \text{.................(4.6)}$$

By plotting the functions on the left-hand side of equations (4.5) and (4.6) as a function of $[S]/[M]$ (depending on the nature of the reaction product) where $[S]$ in this case refers to the BTCM concentration, a linear graph should be obtained, the gradient of which will be numerically equal to k_{tr}/k_p. For the propagation of the T(VA)$^\cdot$ radical, this ratio corresponds to k_3/k_7, so that a confirmation might be expected for the results obtained by Melville et al.[7]

4.1.3. Determination of the degree of polymerisation.

Degrees of polymerisation were determined cryoscopically if low and viscosimetrically if high. In the former, the principle involved is that one mole of a solute lowers the freezing point of a known amount of solvent by a characteristic quantity.[21]

In the latter case, the increase in viscosity (η) of a polymer solution over that of the pure solvent (η_0) is expressed as a fraction termed the specific viscosity:-

$$\text{i.e.,} \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1,$$

where η_r is the relative viscosity ($= \eta / \eta_0$)

The specific viscosity is dependent on the concentration, so that to define a quantity characteristic of a given molecule in a solvent it is necessary to measure the initial slope of the η_{sp}-concentration curve, i.e.,

$$\lim_{c \to 0} \eta_{sp}/c = \lim_{c \to 0} \frac{\ln \eta_r}{c} = [\eta]_i$$

This limiting value of η_{sp}/concentration at infinite dilution is termed the intrinsic viscosity.

The simplest and most widely-used method of determining the molecular weights of long chain polymers is by measuring their intrinsic viscosities in a suitable solvent. Staudinger suggested that there was a linear relationship between them[22] but his expression was not generally applicable. A modification of his equation is generally used, viz.,

$$[\eta]_i = K.m^{\beta}$$

where m is the molecular weight, β and K are experimental constants for each solute-solvent system. In the present work, the relationship used for the polyvinyl acetate-benzene system is that due to Nakajima[23]:-

$$\overline{DP} = 2040\,[\eta]_i^{1.615} \qquad \ldots\ldots\ldots\ldots(4.7)$$

where $[\eta]_i$ is in units of 100 ml/gm and concentrations in units of gm/100 ml.

4.2.1. Determination of the ratio of k_{tr}/k_p for the thermal catalysed polymerisation of vinyl acetate in the presence of BTCM.(60°C).

When the photochemical addition is carried out at very high mole ratios of vinyl acetate to BTCM, low rates and extremely low yields of product are obtained. It is possible to avoid these difficulties to some extent by initiating the reaction thermally at 60°C using benzoyl peroxide as initiator. The benzoyloxy and phenyl radicals obtained through the decomposition of the peroxide will either transfer directly with the BTCM or react with the vinyl acetate to produce growing chains which subsequently transfer with BTCM. In either event, trichloromethyl radicals are produced and these can either propagate by reactions 2 and 3 or produce growing chains by reaction 7 and further addition of vinyl acetate. (see Chapter 1).

4.3.1. Results and preliminary discussion.

In Table 4 (page 30) the ratio of k_{tr}/k_p has been calculated for the photo-addition of BTCM to vinyl acetate by means of equation (4.6) (page 41). At mole ratios of the order of 100:1 or less vinyl acetate to BTCM, very low molecular weight materials are produced. A small error in measurement of $\overline{DP}$ thus involves a considerable error in the evaluation of k_{tr}/k_p, since the function appearing in the equation is $(\overline{DP} - 1)$. This partly explains the scatter of the results (ca 70–600). The general trend is significant, however, so it was of interest to carry out the reaction at much higher mole ratios of vinyl acetate to BTCM. This necessitated the investigation of the thermal catalysed reaction described in section 4.2.1.

The results of such experiments carried out in the presence of 1.9×10^{-3} mole/l benzoyl peroxide at 60° C

FIGURE 6

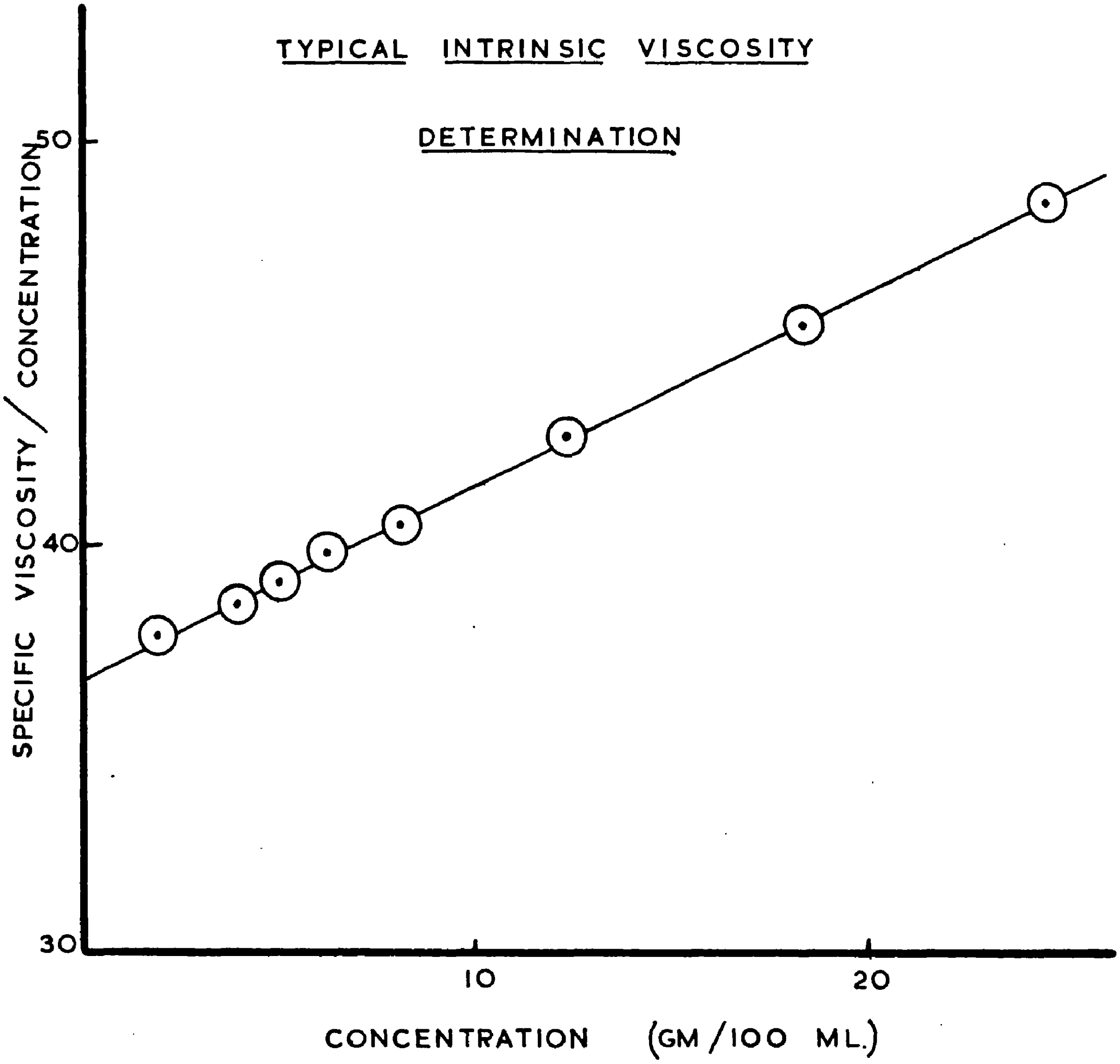

TYPICAL INTRINSIC VISCOSITY DETERMINATION
SPECIFIC VISCOSITY / CONCENTRATION
50
40
30
10
20
CONCENTRATION (GM / 100 ML.)

FIGURE 7

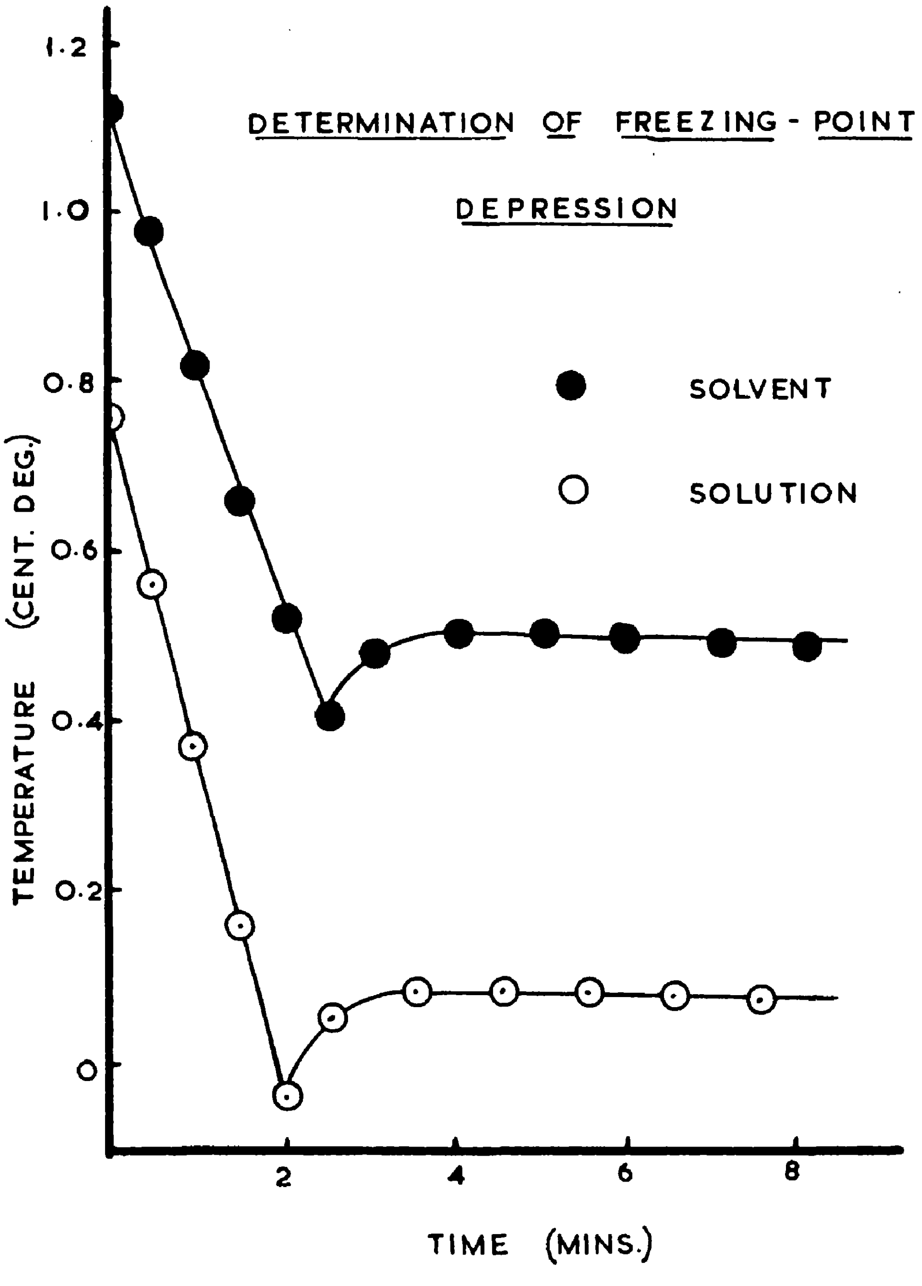

DETERMINATION OF FREEZING - POINT DEPRESSION
● SOLVENT
○ SOLUTION
TEMPERATURE (CENT. DEG.)
1·2
1·0
0·8
0·6
0·4
0·2
0
2
4
6
8
TIME (MINS.)

FIGURE 8

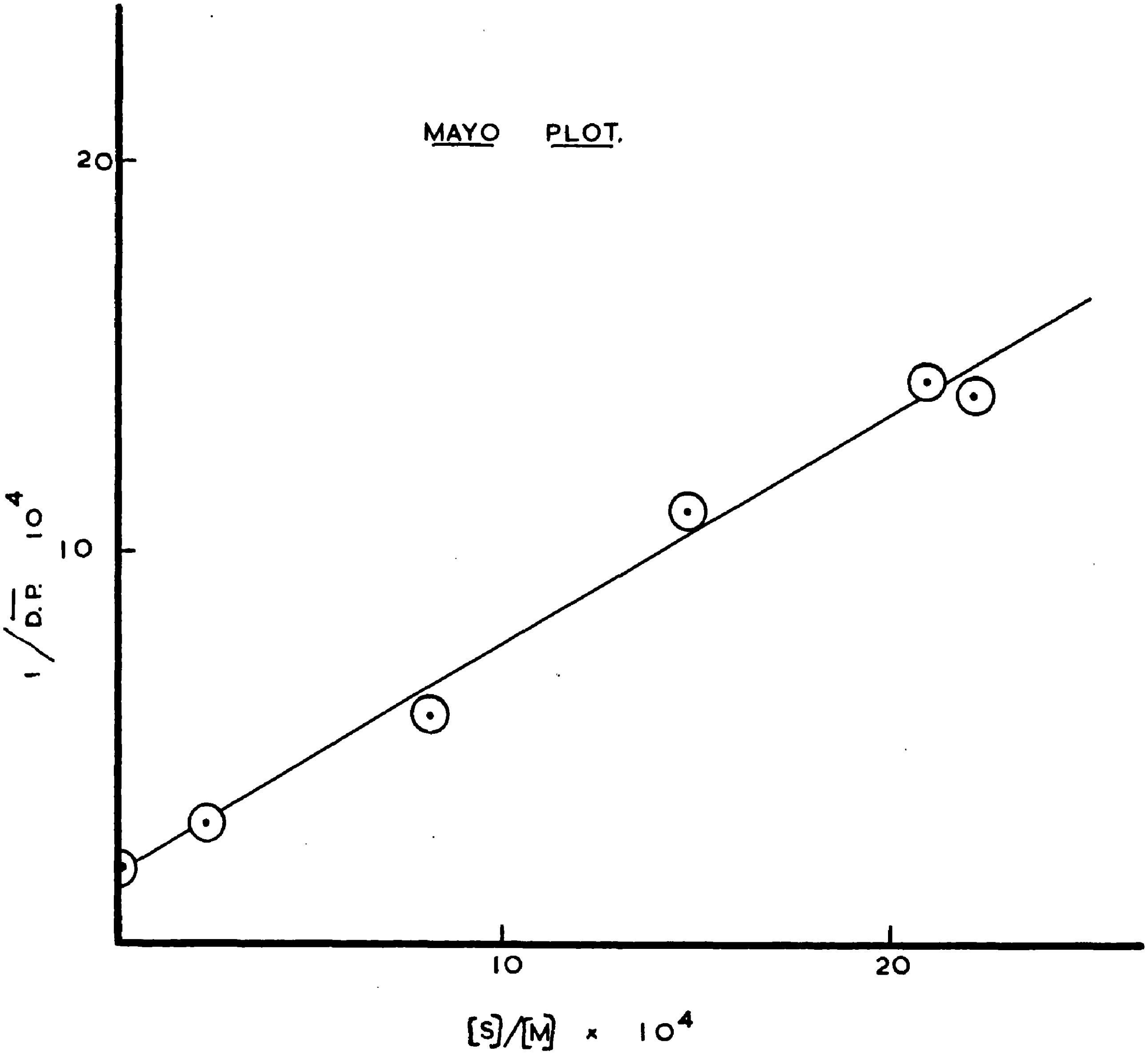


FIGURE 9

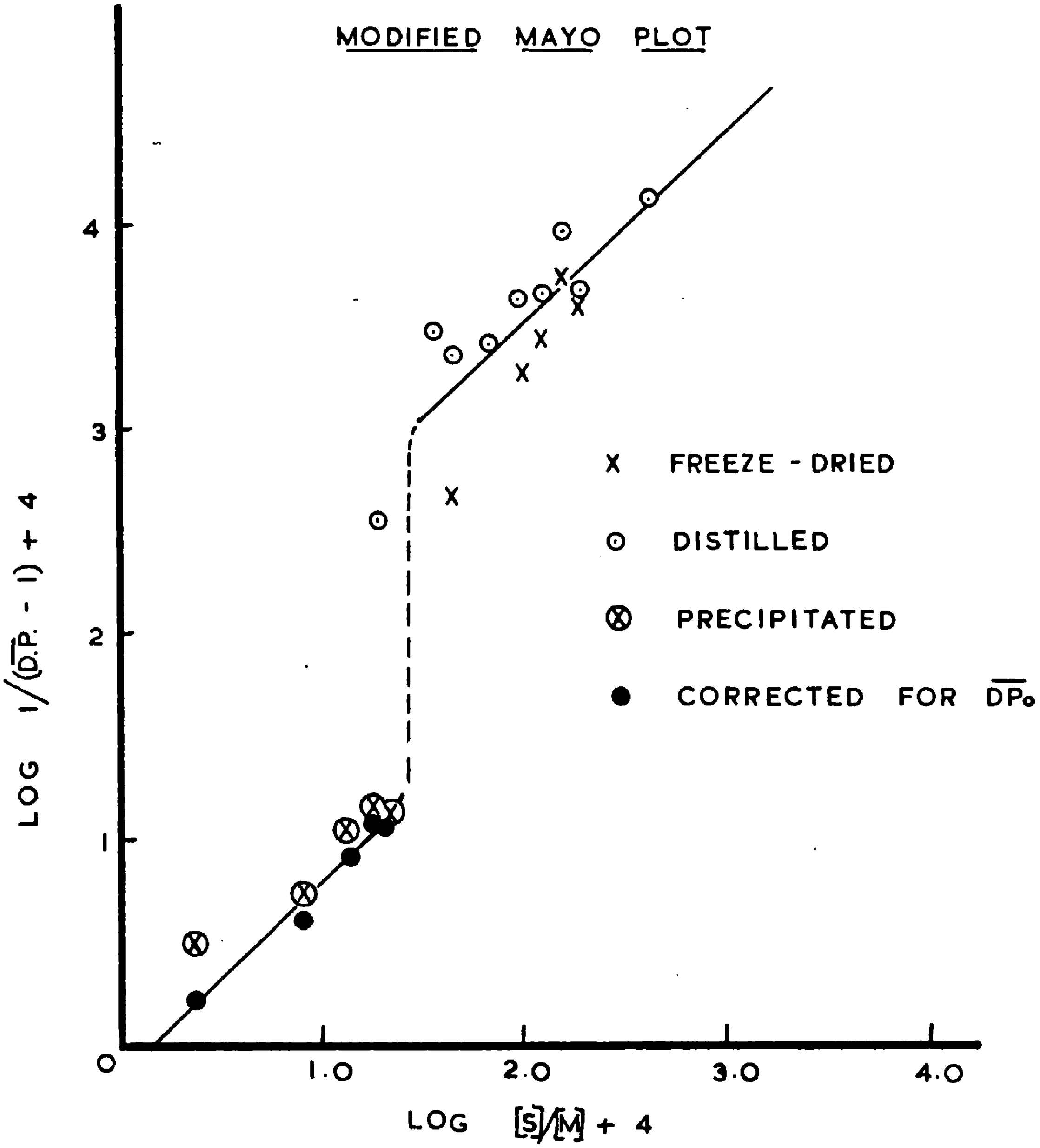

MODIFIED MAYO PLOT
X FREEZE - DRIED
⊙ DISTILLED
⊗ PRECIPITATED
● CORRECTED FOR $\overline{DP_o}$
LOG $1/(\overline{D.P.} - 1) + 4$
LOG $[S]/[M] + 4$
0
1
2
3
4
1.0
2.0
3.0
4.0

FIGURE 10

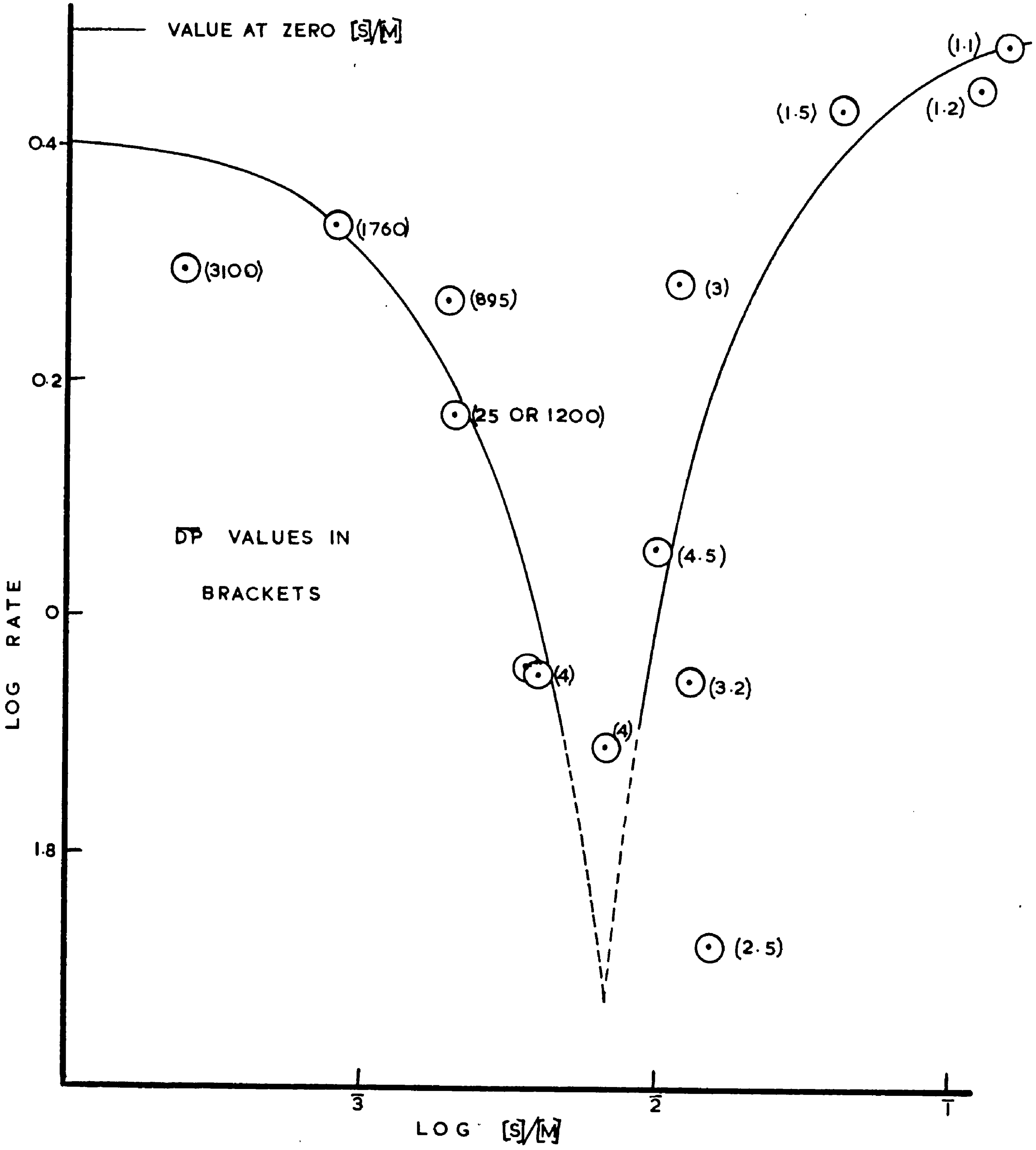
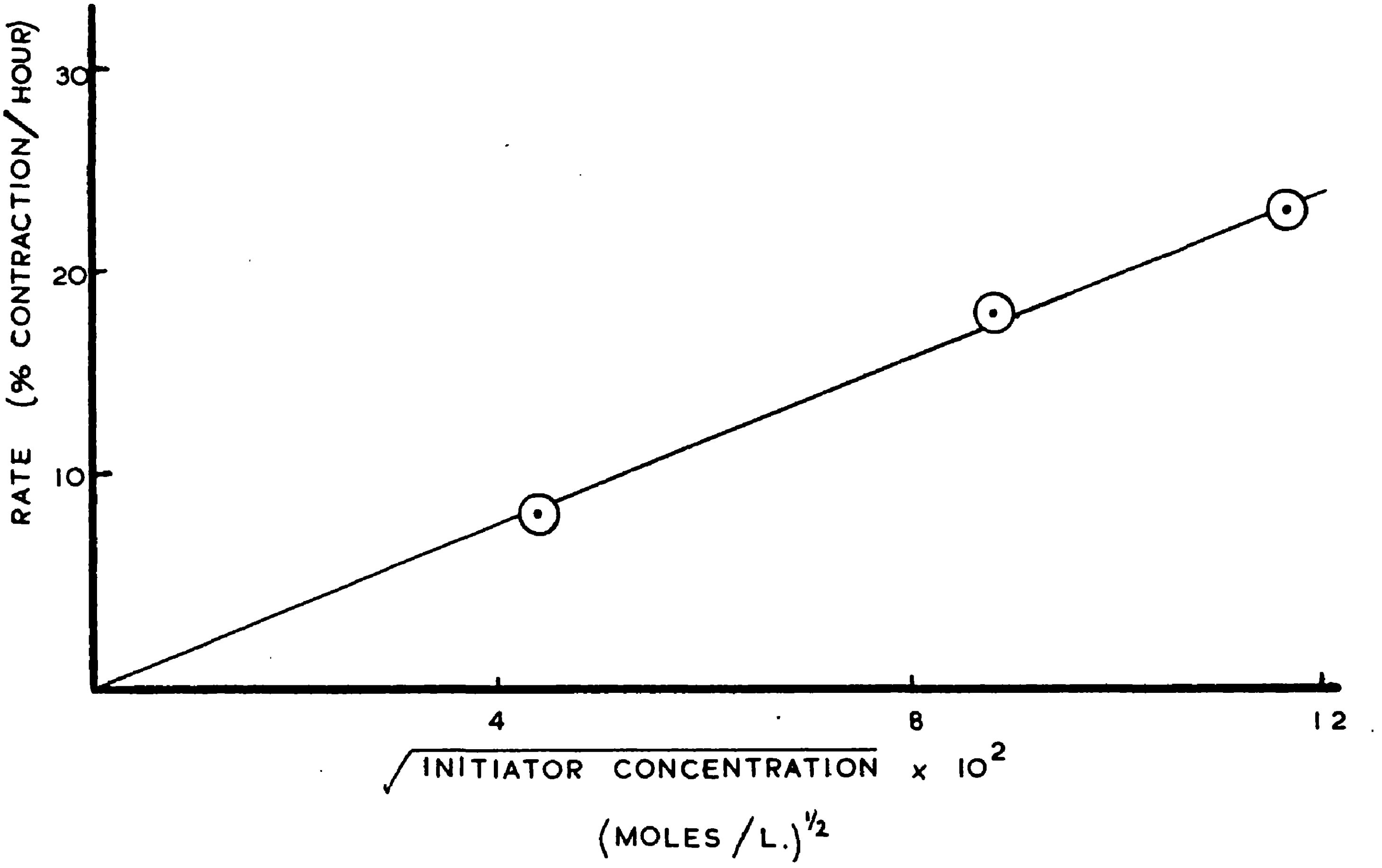

VALUE AT ZERO [S]/[M]
(1.1)
(1.5)
(1.2)
0.4
(1760)
(3100)
(895)
(3)
0.2
(25 OR 1200)
DP VALUES IN BRACKETS
(4.5)
0
LOG RATE
(4)
(3.2)
(4)
1.8
(2.5)
3̄
2̄
1̄
LOG [S]/[M]

FIGURE 11

ORDER OF TERMINATION



for BTCM/vinyl acetate mole ratios of from 2×10^{-4} to 1.35×10^{-1} are shown in Figures 6 to 11. The polymer produced in the range of BTCM/vinyl acetate mole ratios of from 2×10^{-4} to 2.1×10^{-3} was isolated by precipitation with petroleum ether as described in Chapter 2 (page 25), while that formed in the range of ratios from 2.1×10^{-3} to 1.35×10^{-1} was isolated by the distillation technique, and in some cases, distillation followed by freeze-drying. In the former case, degrees of polymerisation were determined viscosimetrically and in the latter, cryoscopically.

Figure 6 shows a typical viscosimetric molecular weight determination and Figure 7 a typical cryoscopic determination. In the distillation procedure, small amounts of initiator would, of course, remain in the polymer, but these were calculated not to affect very greatly the measured value of the molecular weight of the polymer.

In Figure 8, the reciprocal of the degree of polymerisation has been graphed as a function of the BTCM/vinyl acetate mole ratio for values of the latter of from 2×10^{-4} to 2.1×10^{-3}. It will be seen that the points lie on a straight line as would be expected from the theory. The gradient of this line gives a value of 0.6 for k_{tr}/k_p, and the intersection of the line with the reciprocal $\overline{DP}$ axis gives a value of 1.6×10^{-4} for $1/\overline{DP}_o$, where $\overline{DP}_o$ is the degree of polymerisation of the polymer produced in the absence of added BTCM.

The graph of log $1/(\overline{DP} - 1)$ as a function of the logarithm of the BTCM/vinyl acetate mole ratio is given in Figure 9 for mole ratios of from 2×10^{-4} to 1.35×10^{-1}. For the lower end of this range, the modified plot of log $(\overline{DP}^{-1} - \overline{DP}_o^{-1})$ versus log (BTCM/vinyl acetate) is also included. The experimental points lie mainly on two straight lines of unit gradient, indicating that the theoretical equations,

$$\overline{DP} = 1 + \frac{k_p[M]}{k_{tr}[S]} \quad \ldots\ldots\ldots(4.6)$$

and,

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_o} + \frac{k_{tr}[S]}{k_p[M]} \quad \ldots\ldots\ldots(4.5)$$

apply to the regions giving low and high polymer respectively. The effect of the $\overline{DP}$ correction is clearly only appreciable for the one experimental point obtained at the lowest BTCM/vinyl acetate mole ratio measured. Values for log (k_{tr}/k_p) are directly obtained from the intersection of the extrapolated lines with the ordinate at log (BTCM/vinyl acetate) equal to zero. The values of k_{tr}/k_p were found to be 40 and 0.6 for the regions of low and high polymer respectively, whereas a single value might have been expected for the whole range on the basis of current theory. The most striking feature of the graph is the discontinuity which occurs in the region of BTCM/vinyl acetate mole ratios of about 2 x 10^{-3}. To investigate further this peculiarity, the following experiment was performed.

The product from a reaction initiated with benzoyl peroxide at 60°C and with an initial BTCM/vinyl acetate mole ratio of 2.1 x 10^{-3} was divided into two equal parts. The polymer in one half was isolated by the precipitation method while the other half was isolated by the distillation technique. It was noted that the residue obtained after distilling off the reactants was a tacky polymer which smelled strongly of the 1:1 adduct, whereas the polymer obtained by the precipitation method was a white powder. $\overline{DP}$'s of 1200 and 25.5 were found for the polymer isolated by the precipitation and distillation methods respectively. This fifty-fold difference can only be explained if the product residue contains very low molecular weight telomers as well as some high polymer which is insoluble in petroleum ether.

The rate of contraction due to reaction was measured for the various BTCM/vinyl acetate mole ratios and is shown in Figure 10. The logarithmic plot is given in order to show the effect of a 10^3 variation in the BTCM/vinyl acetate mole ratio. The $\overline{DP}$ of the products is shown bracketed beside the experimental points in the figure.

Figure 11 shows the rate of contraction due to reaction as a function of the square root of the benzoyl peroxide concentration. It will be seen that a linear relationship is obtained. Termination is thus second order, indicating that the method used for determining the ratio of k_{tr}/k_p is suitable from this point of view. (The significance of second order termination has been discussed in Chapter 7).

The significance of the results obtained in this part of the work has been discussed in Chapter 9, but briefly stated here, it would appear that for the production of low molecular weight telomers, the value of the ratio of k_{tr}/k_p is greater than 40:1, which indicates that the value obtained by Melville et al[7] for k_3 is in error if k_7 is similar in value to the velocity coefficient for propagation in vinyl acetate polymerisation (k_p). It was decided therefore to re-evaluate the velocity coefficients for the reaction to determine whether in fact the value obtained by these workers for k_3 was too low. If this were the case, the absence of polymerisation would be explained. The following chapters describe how this task was carried out.

Chapter 5. Formal kinetics and the measurement of the rate-dependence on reactant concentration for the photochemical reaction between vinyl acetate and BTCM.

Before it is possible to evaluate any velocity coefficient for chain propagation, it must be ensured that the step which is governed by that particular coefficient is the slow step in the propagation process. This arrangement is made possible in many reactions by a suitable choice of reactant concentrations.

For the present reaction, three concentration conditions are possible:- excess BTCM, excess vinyl acetate and large excess vinyl acetate. A consideration of these conditions follows, based on the arguments proposed by Melville et al.[6,7]

5.1.1. BTCM in excess.

If in this case the rate-controlling step is the addition of a trichloromethyl radical to a monomer molecule (step 2, page 6) and termination occurs through the combination of pairs of trichloromethyl radicals (step 4, page 6), then, from the kinetic scheme outlined previously (page 6), the rate of production of trichloromethyl radicals can be represented by:-

$$\frac{d[Cl_3C^\bullet]}{dt} = I - k_2[Cl_3C^\bullet][M] + k_3[Cl_3C(M)^\bullet][Cl_3C\,Br] - k_4\,[Cl_3C^\bullet]^2 \quad \text{........(5.1)}$$

and the rate of production of $T(VA)^\bullet$ radicals by:-

$$\frac{d[Cl_3C(M)^\bullet]}{dt} = k_2[Cl_3C^\bullet]\,[M] - k_3[Cl_3C(M)^\bullet]\,[Cl_3C\,Br] \quad \text{...(5.2)}$$

At the steady radical concentration, the rate of formation of each of these radical species is equal to their rate of removal, so that,

$$\frac{d[Cl_3C^{\cdot}]}{dt} = 0 \quad \text{and} \quad \frac{d[Cl_3C(M)^{\cdot}]}{dt} = 0$$

Thus,

$$I = k_4[Cl_3C^{\cdot}]^2 \qquad \text{...........(5.3)}$$

Now, the rate of removal of monomer will be given by:-

$$-\frac{d[M]}{dt} = k_2[Cl_3C^{\cdot}][M] \qquad \text{........(5.4)}$$

Hence, $$-\frac{d[M]}{dt} = k_2.I^{\frac{1}{2}}[M]/k_4^{\frac{1}{2}} \qquad \text{........(5.5)}$$

As the rate of initiation (I) should be directly proportional to the BTCM concentration, then if the reaction scheme is obeyed and step 2 is rate-controlling in excess BTCM, the rate of reaction should be proportional to the square root of the BTCM concentration and to the first power of the vinyl acetate concentration.

5.1.2. Monomer in excess.

In this case, the initiation step is as above. If, however, the rate-controlling reaction is the debromination of a BTCM molecule by a $T(VA)^{\cdot}$ radical (step 3) and termination is predominantly by the combination of pairs of such radicals (step 6), to derive the kinetics of this system, the above principles are applied, which gives:-

$$\frac{d[Cl_3C^\bullet]}{dt} = I - k_2[Cl_3C^\bullet][M] + k_3[Cl_3C(M)^\bullet][Cl_3C\,Br]$$

$$= 0 \quad \text{........(5.6)}$$

$$\frac{d[Cl_3C(M)^\bullet]}{dt} = k_2[Cl_3C^\bullet][M] - k_3[Cl_3C(M)^\bullet][Cl_3C\,Br]$$

$$- k_6[Cl_3C(M)^\bullet]^2 \quad \text{....(5.7)}$$

$$= 0$$

Thus,

$$I = k_6[Cl_3C(M)^\bullet]^2 \quad \text{...........(5.8)}$$

or, $$[Cl_3C(M)^\bullet] = I^{\frac{1}{2}}/k_6^{\frac{1}{2}} \quad \text{............(5.9)}$$

Equation (5.6) on re-arrangement gives,

$$[Cl_3C^\bullet] = \frac{I + k_3[Cl_3C(M)^\bullet][Cl_3C\,Br]}{k_2[M]} \quad \text{...(5.10)}$$

The rate of disappearance of monomer is given by:-

$$-\frac{d[M]}{dt} = k_2[Cl_3C^\bullet][M] \quad \text{..............(5.4)}$$

$$= k_2[M] \frac{I + k_3[Cl_3C(M)^{\cdot}][Cl_3C\ Br]}{k_2[M]} \quad \ldots\ldots(5.11)$$

$$= I + \frac{k_3 . I^{\frac{1}{2}} [Cl_3C\ Br]}{k_6^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots(5.12)$$

The numerical value of I, the rate of initiation will be extremely small compared with the second term in equation (5.12), so that to a close approximation, it may be written,

$$-\frac{d[M]}{dt} = \frac{k_3 . I^{\frac{1}{2}} [Cl_3C\ Br]}{k_6^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots(5.13)$$

Thus, in the case of excess monomer, if the kinetic scheme holds and reaction 3 is rate-controlling, the rate of reaction should be proportional to the three-halves power of the BTCM concentration and should be independent of the monomer concentration.

5.1.3. Monomer in large excess.

With a sufficiently large excess of monomer, polymerisation might be expected to occur. The following relationships, which have been derived earlier are still valid under these conditions.

$$[Cl_3C(M)^{\bullet}] \quad = \quad I^{\frac{1}{2}}/k_6^{\frac{1}{2}} \quad ....(5.9)$$

$$[Cl_3C^{\bullet}] \quad = \quad \frac{I \quad + \quad k_3[Cl_3C\ Br]\,[Cl_3C(M)^{\bullet}]}{k_2[M]} \quad ...(5.10)$$

The rate of consumption of monomer will be given by:-

$$-\frac{d\,[M]}{dt} \quad = \quad k_2[Cl_3C^{\bullet}][M] \quad + \quad k_p[Cl_3C(M)^{\bullet}][M]...(5.14)$$

where k_p is the velocity coefficient for propagation in the polymerisation of vinyl acetate initiated by trichloromethyl radicals.

Substituting equations (5.9) and (5.10) in equation (5.14) gives,

$$\frac{d[M]}{dt} = k_2[M]\left\{\frac{I \quad + \quad k_3[Cl_3C\ Br] \quad I^{\frac{1}{2}}/k_6^{\frac{1}{2}}}{k_2[M]}\right\} + \quad \frac{k_p . I^{\frac{1}{2}}[M]}{k_6^{\frac{1}{2}}}$$

$$...............(5.15)$$

$$= \quad \frac{k_2[M]\ I}{k_2[M]} \quad + \quad \frac{k_3 \quad I^{1/2}[Cl_3C\ Br]}{k_6^{1/2}} \quad + \quad \frac{k_p \quad I^{1/2}[M]}{k_6^{1/2}}$$

$$..............(5.16)$$

Under the present conditions, I will be extremely small compared with the other terms in equation (5.16), thus,

$$-\frac{d\,[M]}{dt} = \frac{I^{\frac{1}{2}}}{k_6^{\frac{1}{2}}}\left\{k_3\,[Cl_3C\ Br] \quad + \quad k_p[M]\right\} \text{......}(5.17)$$

also, $k_p[M] \gg k_3\,[Cl_3C\ Br]$

Thus,

$$-\frac{d\,[M]}{dt} = \frac{k_p.I^{\frac{1}{2}}[M]}{k_6^{\frac{1}{2}}} \qquad \text{......}(5.18)$$

Under conditions where polymerisation occurs, the rate of reaction will be proportional to the square root of the BTCM concentration and to the first power of the monomer concentration. Thus, normal kinetics are applicable in this case, with the BTCM acting as initiator.

If these rate-dependences on concentration are obtained experimentally, it is possible to evaluate the velocity coefficients for the various steps. Alternatively, only under conditions where the predicted rate-dependences are experimentally obtained can the velocity coefficients be measured.

5.2.1. The use of an inert diluent in the measurement of rate-dependences.

The dependence of rate of reaction on the concentration of both vinyl acetate and BTCM was measured by observing the rate of reaction of mixtures of the two reactants at various concentrations. It soon became apparent, however that an inherent error was involved in this method.

In a fixed volume of a two-component system, variation in the concentration of one component automatically produces an alteration in the concentration of the other. If an attempt is made to measure the dependence of reaction rate on BTCM concentration by this method, changes in rate are not produced completely by the change in concentration of this reactant, but by changes in concentration of both reactants. A composite effect is actually observed and the measured rate-dependence is not the true dependence.

This error can be avoided by the use of a suitable inert diluent. To measure the true dependence of rate of reaction on, for example, BTCM concentration, the same concentration of vinyl acetate must be maintained in each experiment. Thus, it is most convenient to use the same dilatometer for each series of experiments. In filling the dilatometer for a series of experiments, the same volume of vinyl acetate should be added throughout, together with different volumes of BTCM, the deficiency being made up with the necessary volume of the diluent. Provided the diluent takes no part in the chemical reaction, a true measure of the rate-dependence on concentration will be obtained. A diluent is also essential in any attempt to measure the dependence of the rate of reaction on the concentration of the reactant which is in considerable excess.

Mixtures of benzene and BTCM and benzene and vinyl acetate did not react on irradiation, which indicates that this might be a suitable diluent, as would be expected from resonance stabilisation considerations. Several experiments were carried out in cyclohexane as a check.

5.3.1. Results.

Figures 12 to 19 depict reaction rate as a function of reactant concentration on linear and logarithmic axes. The dependences deduced from these curves are shown in the following Tables.

FIGURE 12

RATE-DEPENDENCE ON CONCENTRATION OF EXCESS REAGENT.

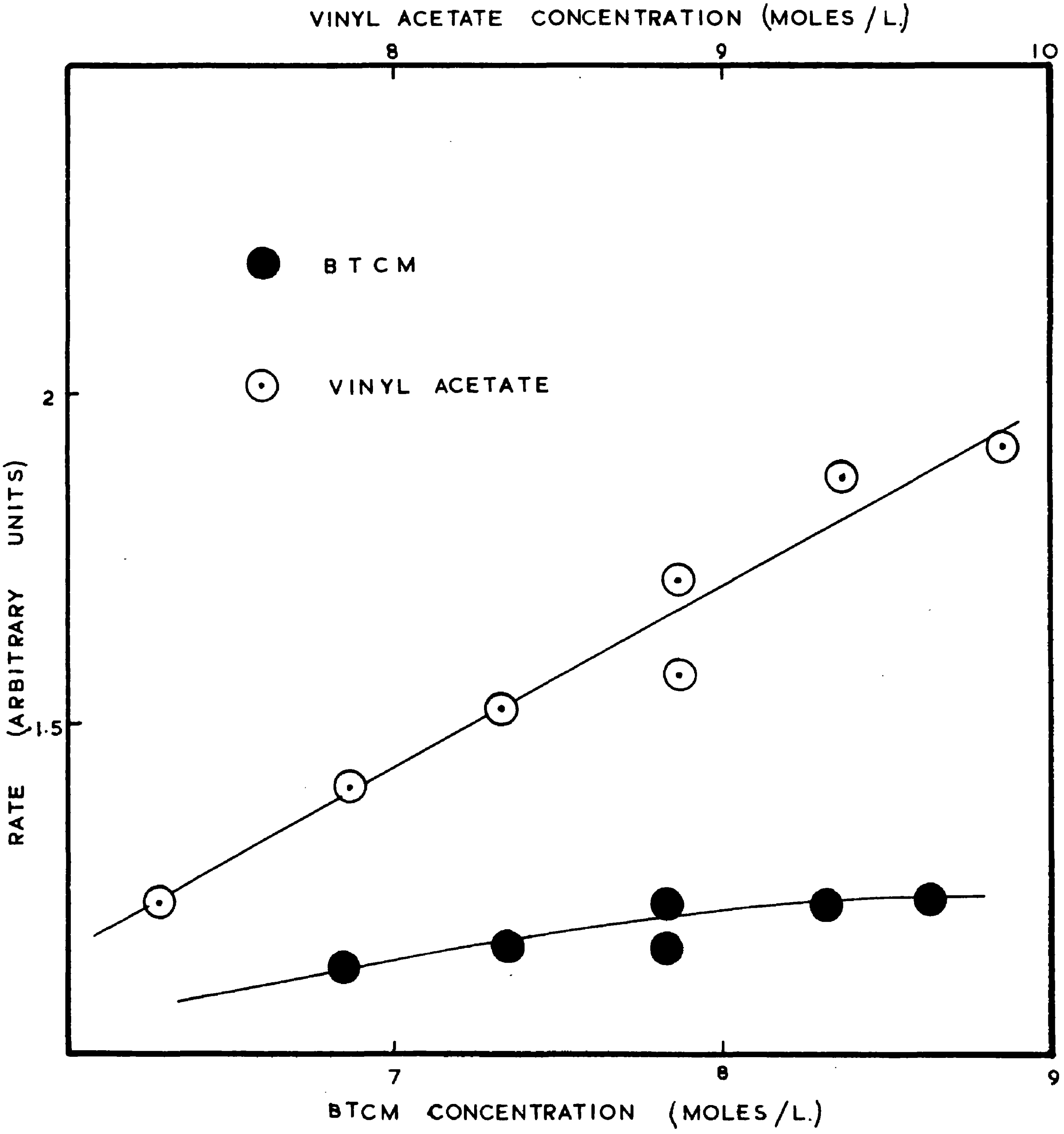


FIGURE 13

RATE - DEPENDENCE ON [BTCM] WHEN IN EXCESS.

BENZENE AS DILUENT

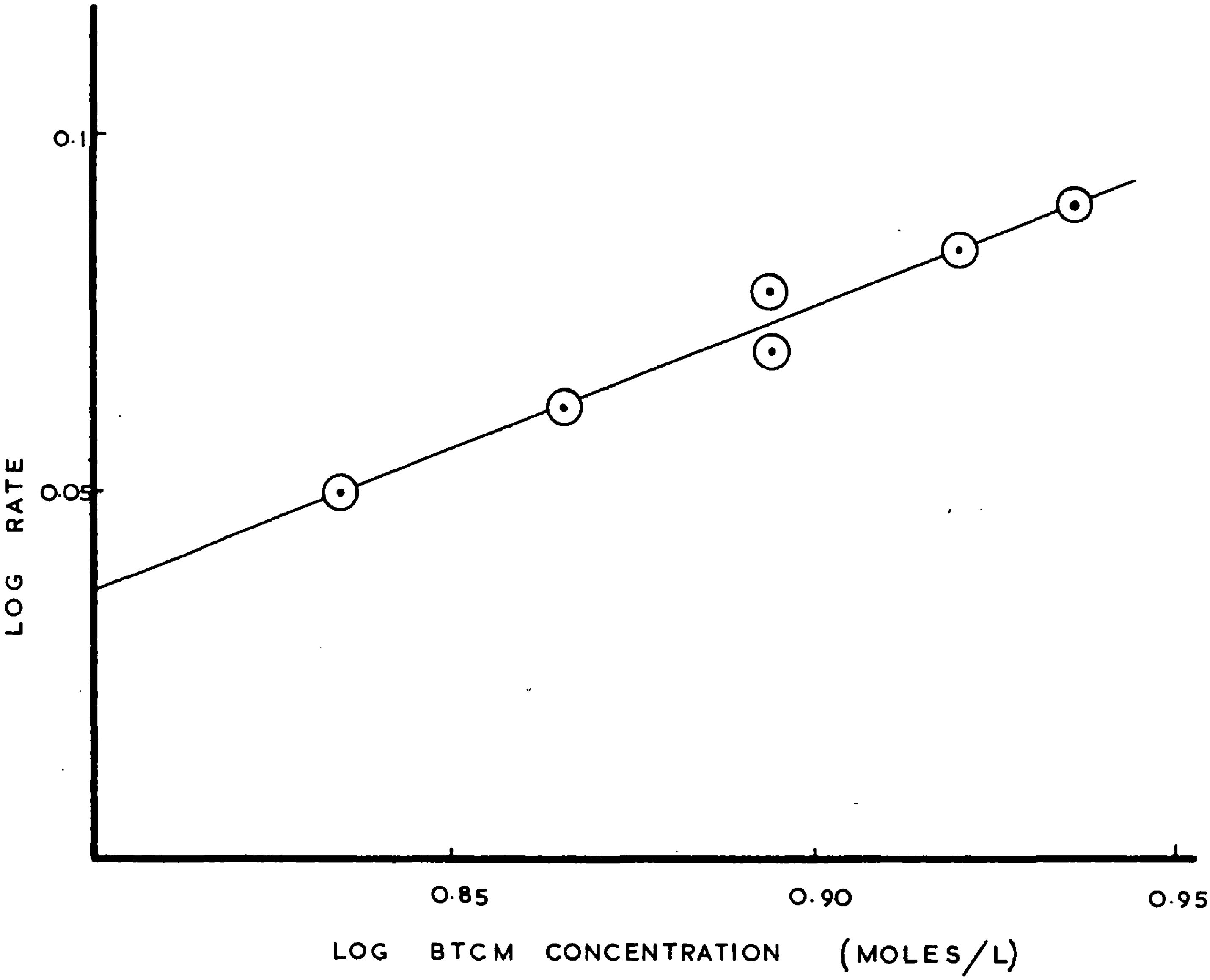


FIGURE 14

RATE - DEPENDENCE ON VINYL ACETATE CONCENTRATION IN EXCESS BTCM BENZENE AS DILUENT.

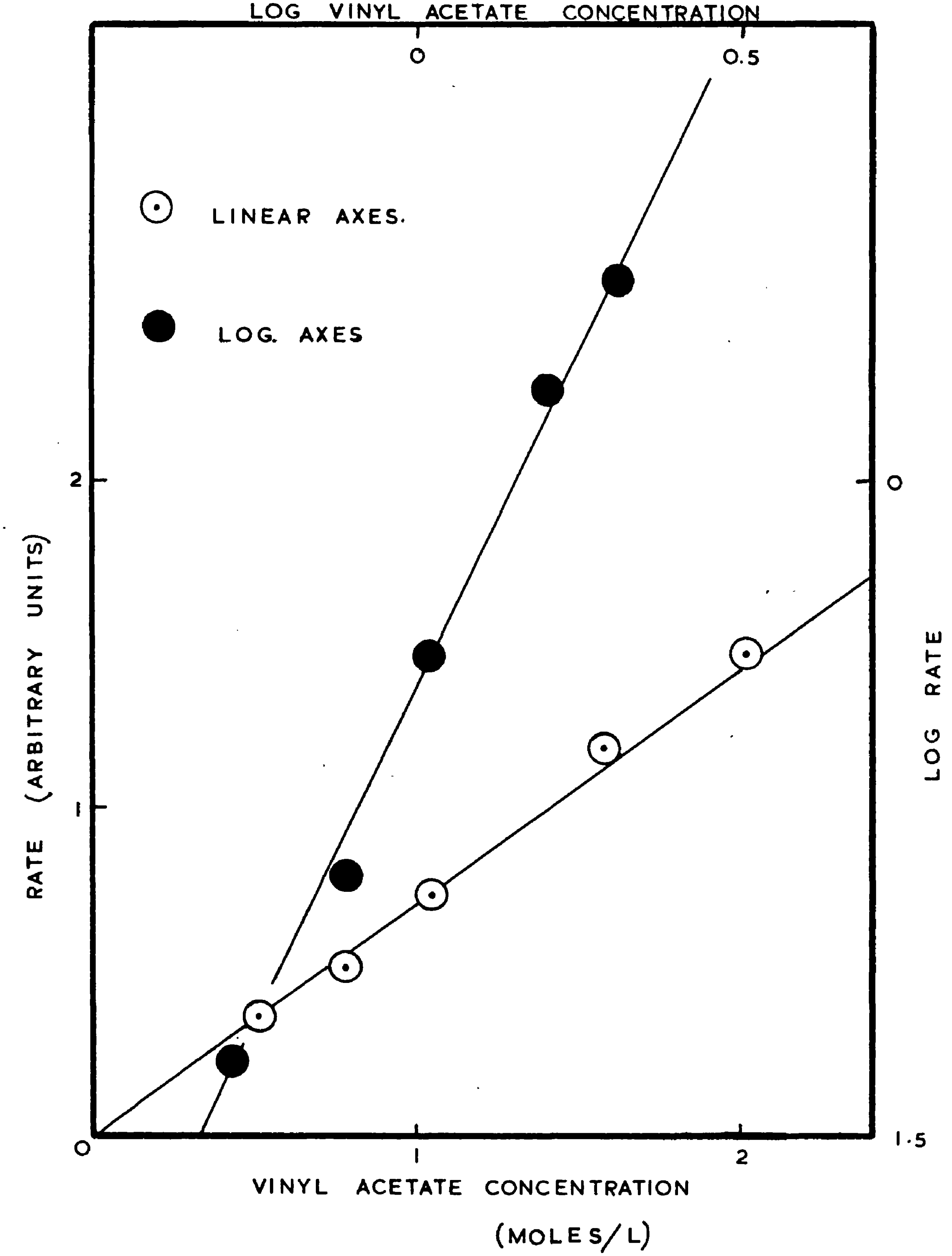


FIGURE 15

RATE - DEPENDENCE ON VINYL ACETATE CONCENTRATION IN EXCESS BTCM

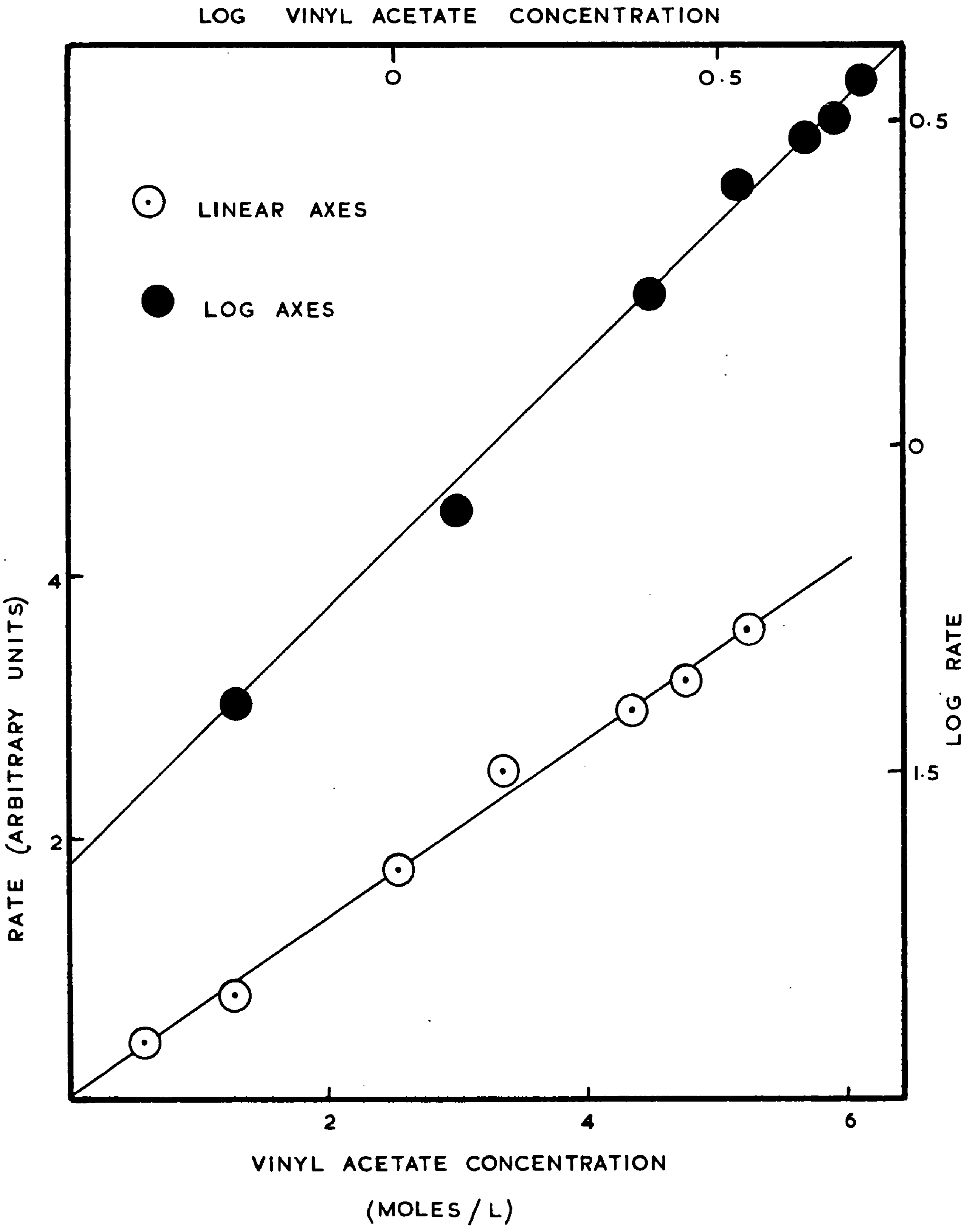


FIGURE 16

RATE-DEPENDENCE ON BTCM CONCENTRATION IN EXCESS VINYL ACETATE

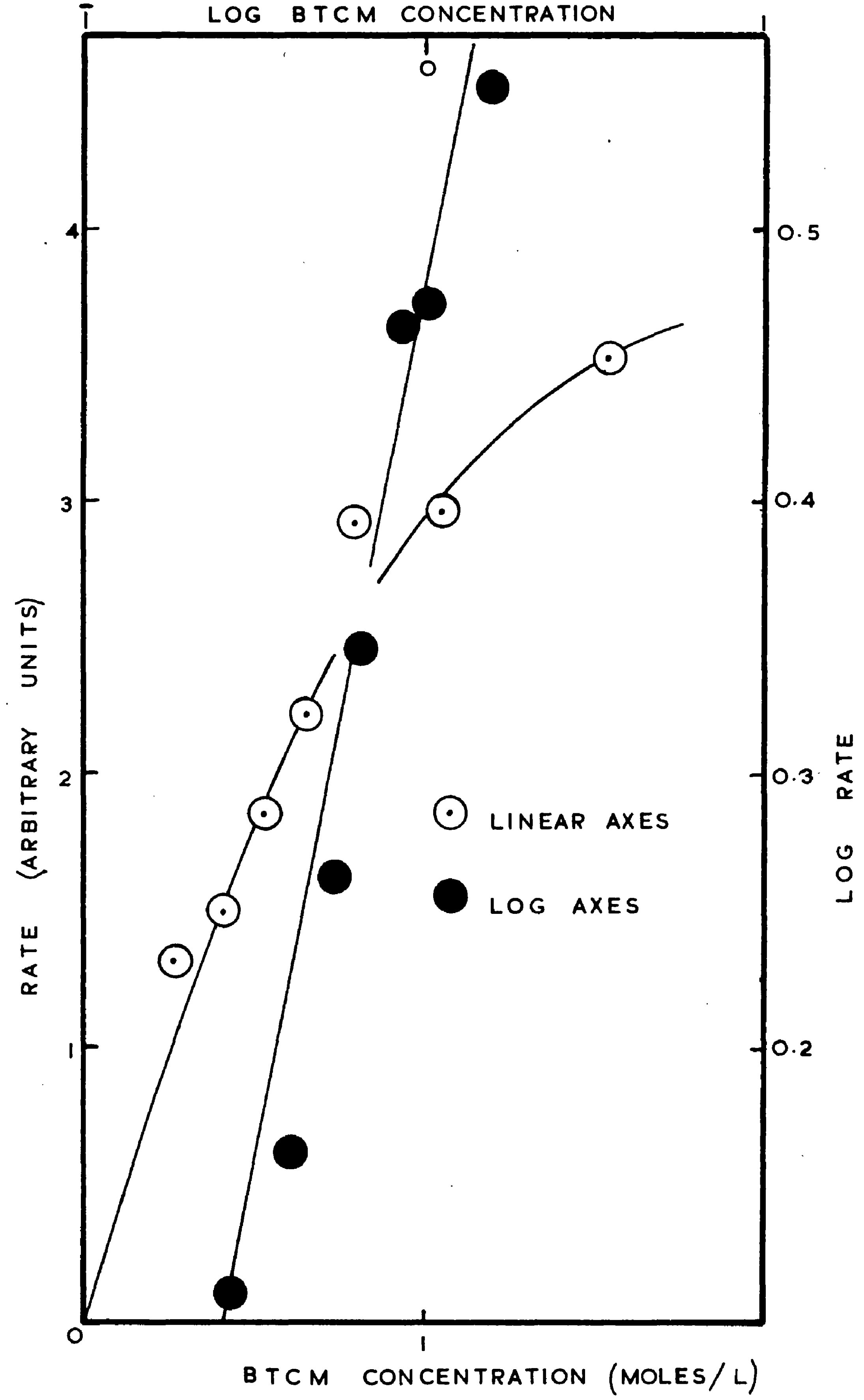


FIGURE 17

RATE-DEPENDENCE ON BTCM IN EXCESS VINYL ACETATE

BENZENE AS DILUENT

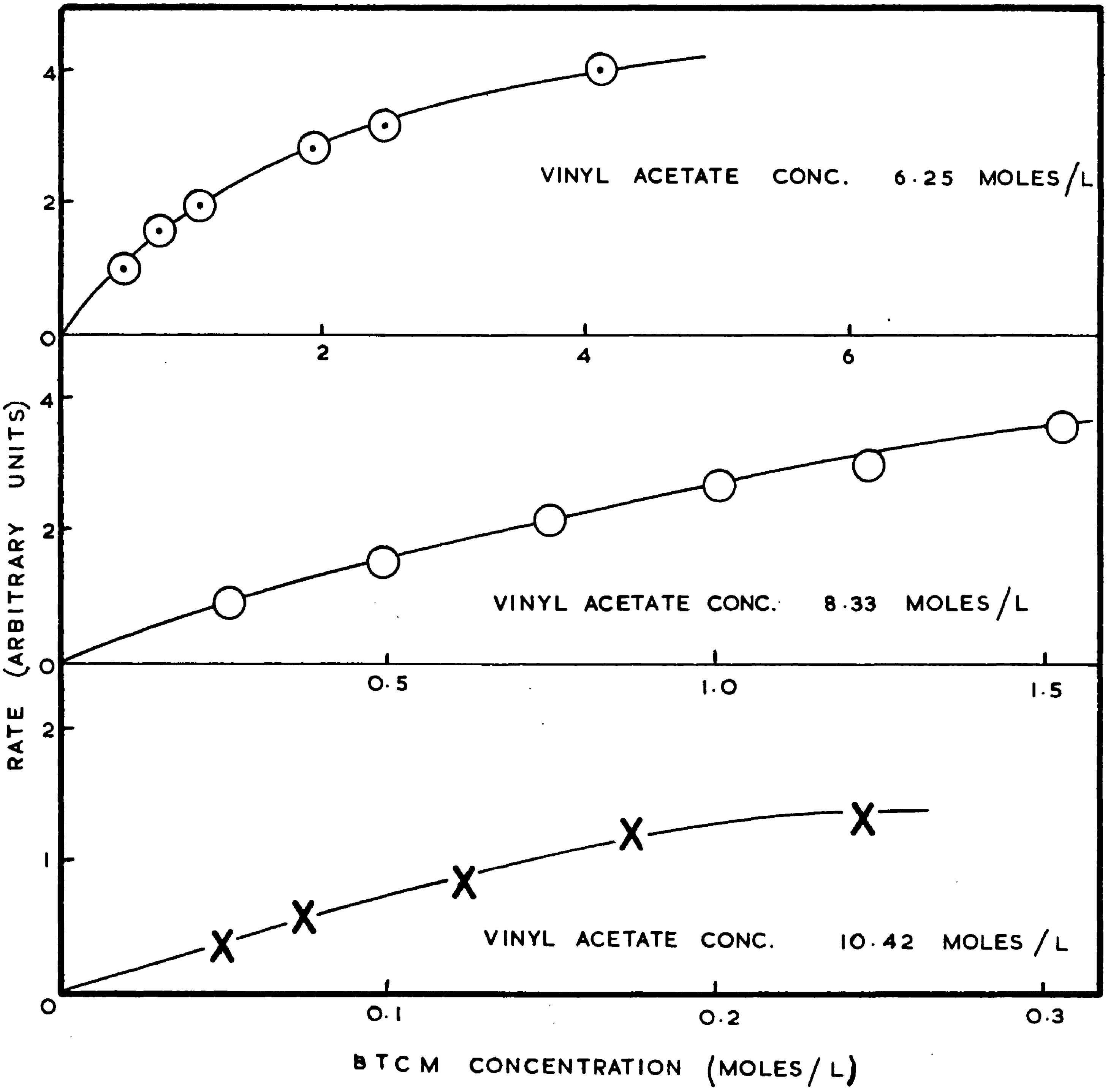


FIGURE 18

RATE - DEPENDENCE ON [BTCM] IN EXCESS VINYL ACETATE

BENZENE AS DILUENT.

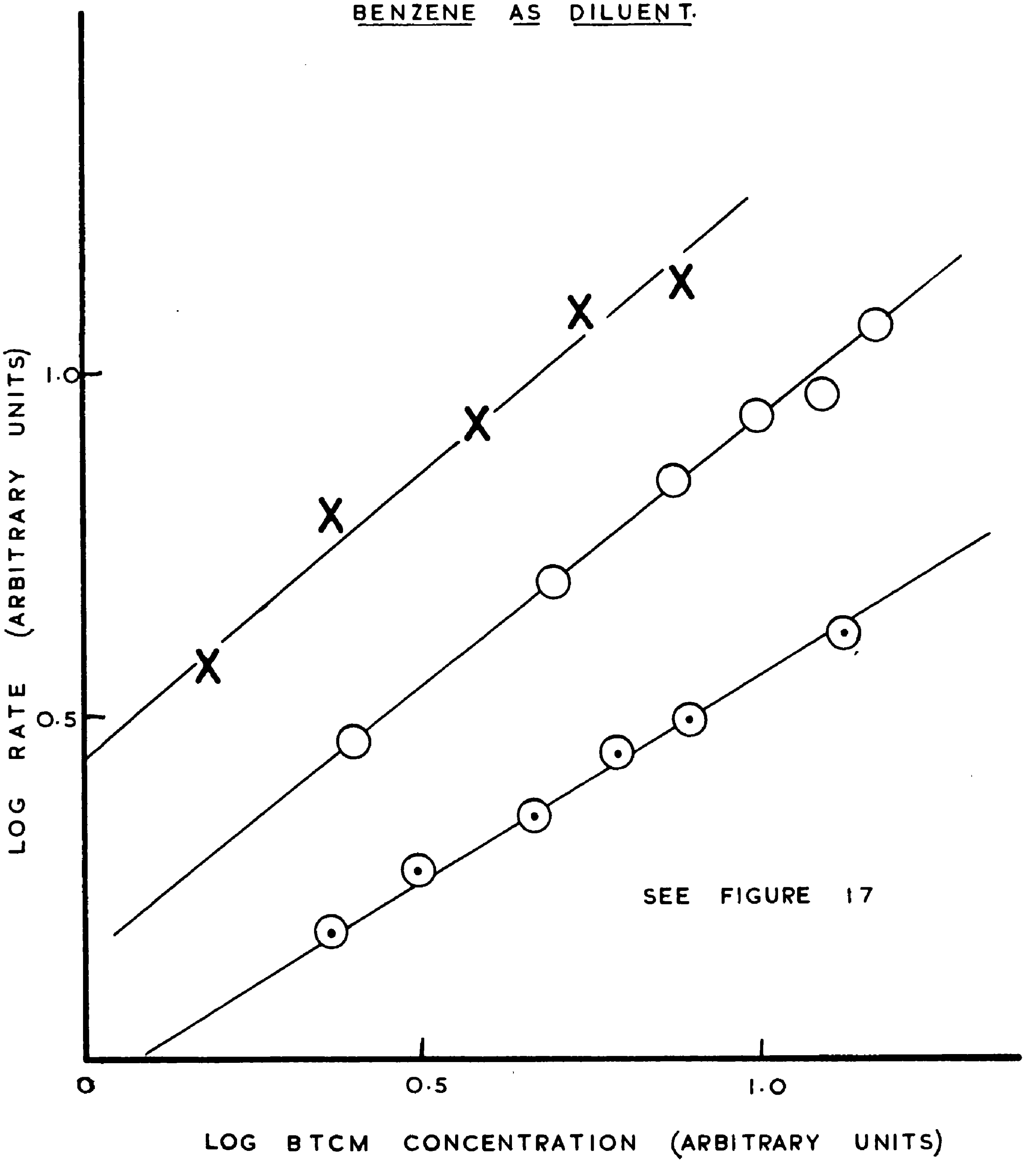


FIGURE 19

RATE-DEPENDENCE ON [BTCM] IN EXCESS VINYL ACETATE

CYCLOHEXANE AS DILUENT

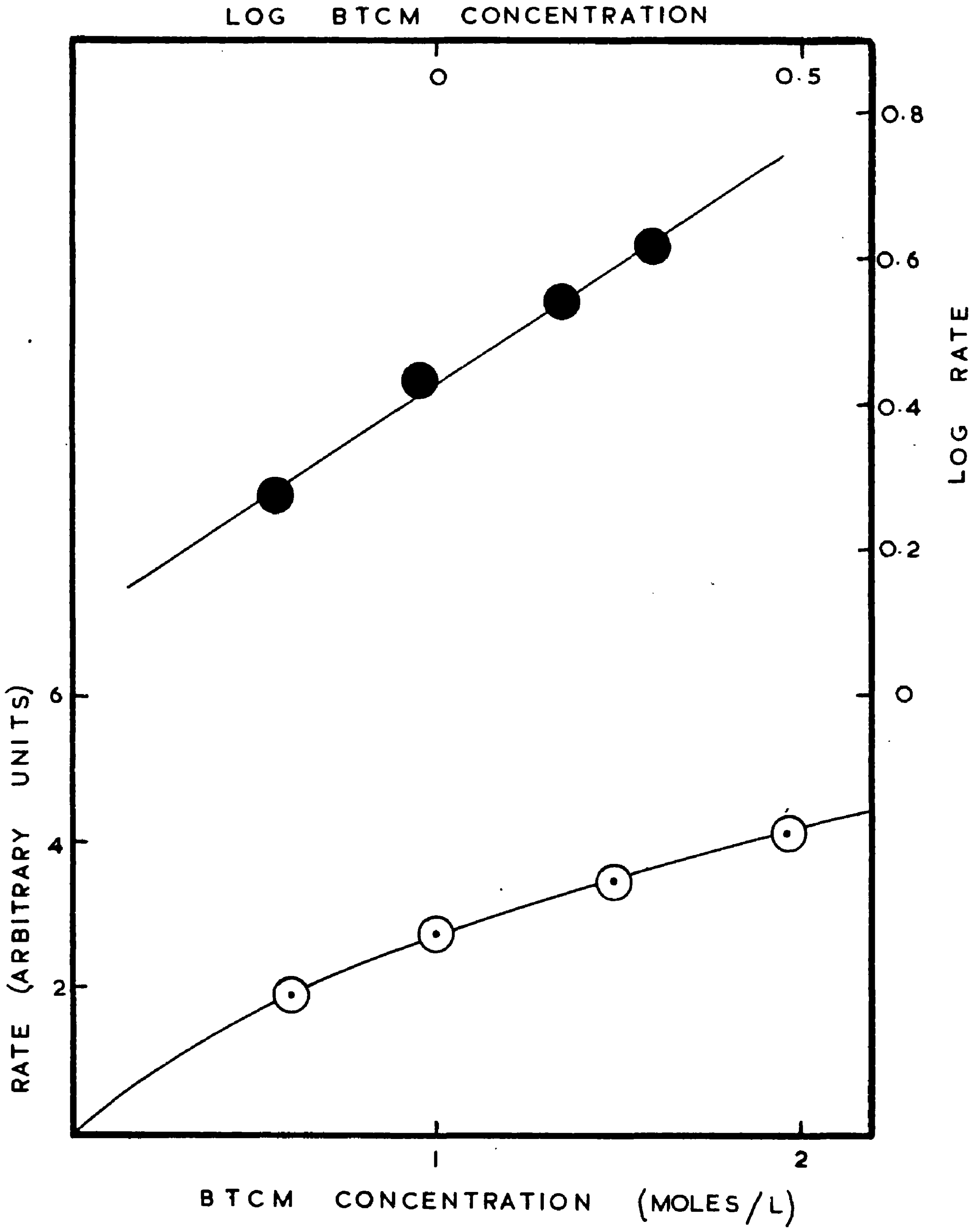


Table 5. **Dependence of the rate of reaction between vinyl acetate and BTCM on the concentration of each of the reactants.**

BTCM Concentration (mole.l^{-1})	Vinyl acetate Concentration (mole.l^{-1})	Rate-dependence.
0.26–1.04	10.50–9.66	$BTCM^{0.65}$
5.20–9.58	5.22–0.55	VA^{1}

Table 5 refers to the experiments carried out in the absence of a diluent.

Table 6. **Dependence of the rate of reaction between vinyl acetate and BTCM on the concentration of each of the reactants in the presence of benzene as a diluent.**

BTCM Concentration (mole.l^{-1})	Vinyl acetate Concentration (mole.l^{-1})	Rate-dependence.
0.048 – 0.245	10.42	$BTCM^{0.79}$
0.245 – 1.467	8.33	$BTCM^{0.77}$
0.489 – 2.450	6.25	$BTCM^{0.73}$
6.840 – 8.640	1.56	$BTCM^{0.5}$
7.820	0.521 – 2.085	VA^{1}
0.488	7.280 – 9.880	VA^{1}

In the presence of *cyclo*hexane as a diluent and in regions of low BTCM concentration, the rate of reaction was proportional to this concentration to the power 0.61 (Figure 19).

5.4.1. Discussion.

From these results, it will be seen that benzene acts as a fairly satisfactory inert diluent. The difficulties involved on measuring the rate-dependence on the reactant which is in excess become increasingly evident. The curves shown in Figure 12 do not pass through the origin. This indicates that the rate-dependence on the concentration of each of the reactants changes at some stage, which is to be expected. It is very doubtful, therefore, if the construction of a log-log curve to evaluate a dependence is justified under these conditions.

Figure 12 shows however, that the rate-dependence on vinyl acetate concentration when in excess, appears to be first order. The shape of the rate-dependence curve for BTCM when in excess (also Figure 12), indicates that a low fractional dependence is obeyed. The log-log plot has a gradient of approximately 0.5 (Figure 13) and the intensity exponent for this concentration range was found to be 0.5 all of which indicate a half-power dependence on BTCM concentration when in excess. It thus seems fairly reasonable to assume that the dependences upon the concentration of each of the reactants when in excess are as quoted in Table 6.

It should also be pointed out that the experimental error under such conditions must be appreciable, since very small percentage changes in concentration and consequently in rate must be measured.

No such difficulties are encountered when the rate-dependence on the reactant in the lower concentration is measured. In this case, the rate-concentration curves inevitably pass through the origin (Figures 14, 15, 16, 17 and 19) so that log-log plots are completely justified (Figures 14, 15, 16, 18 and 19). The experimental error will also be greatly reduced since the percentage difference in concentration, and thus in rate, will be much greater than in the previous case.

It would thus appear that the following relationships are valid:-

In excess BTCM,

$$\text{Rate of reaction} \propto [\text{BTCM}]^{\frac{1}{2}} [\text{VA}]^{1}$$

In excess vinyl acetate,

$$\text{Rate of reaction} \propto [\text{BTCM}]^{\text{ca.}0.7} [\text{VA}]^{1}$$

The results quoted in Table 5 give the composite rate-dependences referred to previously and are therefore less reliable than those given in Table 6.

It follows from the values obtained for these relationships that only in excess BTCM is there a single rate-controlling step. The rate-dependence on BTCM concentration in excess vinyl acetate indicates a tendency for reaction 3 to become rate-controlling. At no concentration range suitable for experimental determination does this reaction become completely rate-controlling, so that a composite dependence is produced by contributions from reactions 2 and 3. This also explains the greater than zero dependence on vinyl acetate concentration when in excess.

It is therefore only in excess BTCM that the velocity coefficients for the reaction can be evaluated. Any attempt to measure those involved under conditions of excess vinyl acetate would give meaningless results.

Chapter 6. Determination of the heat and absolute rate of reaction between BTCM and vinyl acetate.

In a study of any reaction by non-stationary state and modified rotating sector methods it is necessary to know the heat of reaction in order to calculate the overall rate of reaction. As this information was not available for the present reaction, the heat of the photochemical addition of BTCM to vinyl acetate was measured using the dilatometric method described below.[24]

6.1.1. Theory of the method of determining the heat of reaction.

Methods involving adiabatic or isothermal calorimetry are normally employed in the measurement of the heats of such reactions. These methods[25-28] require the measurement of the heat evolved for a certain extent reaction or the measurement of the rate of evolution of heat together with the rate of reaction. The method used in the present work involves the measurement of the rate of reaction during the thermal steady state, i.e., when the rate of self-heating due to reaction is equal to the rate of loss of heat to the surroundings. The latter is easily measured by stopping the reaction abruptly and noting the rate of cooling immediately after. A variation of this method involves measurement of the initial expansion rate on the commencement of irradiation[29,30] as is done in following the non-stationary state of chain reactions. From these measurements can be calculated the heat of most photochemical reactions.

In a chemical reaction of the type under investigation, the total change in volume occurring over a given period is made up of three effects - an expansion produced by self-heating during the reaction, a contraction due to reaction caused by the difference in density between reactants and reaction products and a contraction due to heat losses to the surroundings. Thus, at any particular instant, the overall rate of contraction (C) is given by:-

$$C = Z + Y - \mathcal{E} \qquad \text{............(6.1)}$$

where Z is the rate of contraction due to reaction, Y is the rate of contraction due to heat losses and $\mathcal{E}$ the rate of expansion due to self-heating.

Both Z and $\mathcal{E}$ are obviously directly proportional to the rate of reaction, so that for a reaction proceeding at a rate of X%/sec, they are given by the following equations:-

$$Z = X(\rho' - \rho)/\rho' \qquad \text{.......(6.2)}$$

where ρ and ρ' are the densities of the initial and final materials, and,

$$\mathcal{E} = X.\Delta H.\alpha / S.M \qquad \text{......(6.3)}$$

where ΔH is the heat of reaction (cal/mole), α, S and M are the coefficient of cubical expansion, specific heat and molecular weight of monomer respectively.

Combination of equations (6.2) and (6.3) gives:-

$$\Delta H = \frac{\varepsilon . S . M(\rho' - \rho)}{Z . \alpha . \rho'} \text{ cal/mole } \quad ....(6.4)$$

In other words, the heat of reaction can be calculated from the ratio of ε/Z provided the required physical properties of the system are known.

Now, Z can be measured dilatometrically once the system has attained the thermal steady state, since under these conditions $Y = \varepsilon$ and the overall rate of contraction (C) equals Z. It only remains to evaluate ε and this has been done by two methods.

(a) Under thermal steady state conditions, $Y = \varepsilon$, so that the value of ε may be obtained by measuring Y. A very close approximation to this function is obtained by measuring the rate of contraction due to cooling immediately on the cessation of irradiation.

(b) During the first few seconds of a reaction, the system is approximately adiabatic, i.e., Y = 0, so that $C = Z - \varepsilon$. Now, for most polymerisation reactions, $\varepsilon \gg Z$, so that C is negative during the initial stages. In other words, an expansion occurs on the commencement of irradiation. The value of ε is therefore given by the sum of the initial measured expansion rate (-C) and the steady contraction rate (Z). If both these rates are measured, the value of $\mathcal{E}$ may be calculated.

Equation (6.4) was derived for the evaluation of the heat of a polymerisation reaction, i.e., a one-component system. It can, however, be applied to the two-component system under investigation - a mixture of BTCM and vinyl acetate of various compositions.[30] In this case, the heat capacity (S.M), coefficient of expansion and specific gravity must now refer to the reactants as a whole. For example, consider a reaction mixture of 8 moles of BTCM and 1 mole of vinyl acetate. The heat capacity of the system will be given by:-

$$(8.M_1.S_1 \quad + \quad M_2.S_2) \qquad \ldots\ldots\ldots\ldots(6.5)$$

the coefficient of expansion by:-

$$\left\{\frac{8.M_1.\alpha_1}{\rho_1} + \frac{M_2.\alpha_2}{\rho_2}\right\} \Big/ \left\{\frac{8.M_1}{\rho_1} + \frac{M_2}{\rho_2}\right\} \qquad \ldots\ldots\ldots(6.6)$$

the specific gravity of the system before reaction by:-

$$\left\{8.M_1 + M_2\right\} \Big/ \left\{\frac{8.M_1}{\rho_1} + \frac{M_2}{\rho_2}\right\} \qquad \ldots\ldots\ldots(6.7)$$

and the final system after reaction by:-

$$\{7.M_1 + M_3\} \Big/ \left\{\frac{7.M_1}{\rho_1} + \frac{M_3}{\rho_3}\right\} \quad ....(6.8)$$

where suffixes 1,2 and 3 refer to BTCM, vinyl acetate and the reaction product respectively. These expressions may then be substituted in equation (6.4) to make it applicable to the system under investigation.

Values of the ratio $\mathcal{E}/Z$ were obtained by the methods described in Chapter 2 and are included later in the present chapter.

6.1.2. Evaluation of the physical constants- Theory of the method of measuring the specific heat.

The experimental techniques used for the determination of the physical constants of the reactants and reaction products have been described in Chapter 2. The only case in which the under-lying theory is not self-evident is the determination of specific heats by the method of Newton's cooling curves.[31] It is assumed that for a given volume and surface area of material, the rate of cooling at any given temperature is directly proportional to the reciprocal of the heat capacity of the material (i.e., is inversely proportional to the heat capacity), thus,

$$(W_a.S_a + E)\frac{dT_a}{dt} = (W_b.S_b + E)\frac{dT_b}{dt} \quad ....(6.9)$$

where W is the weight of liquid, S its specific heat, dT/dt the rate of cooling and E the water-equivalent of the calorimeter. Thus, by comparing the rate of cooling of the liquid with that of the standard liquid under the same conditions and at the same temperature, the unknown specific heat may be obtained.

6.2. Results.

6.2.1. Physical properties of the reactants.

Figure 20 depicts liquid volume as a function of temperature for both vinyl acetate and BTCM. A linear relationship was obtained in each case which gave the following results, the value for vinyl acetate being in excellent agreement with the literature.[33]

Table 7. Coefficient of cubical expansion.

Material	Expansion coefficient.
Vinyl acetate	1.402×10^{-3} deg^{-1}
BTCM	1.062×10^{-3} deg^{-1}

FIGURE 20

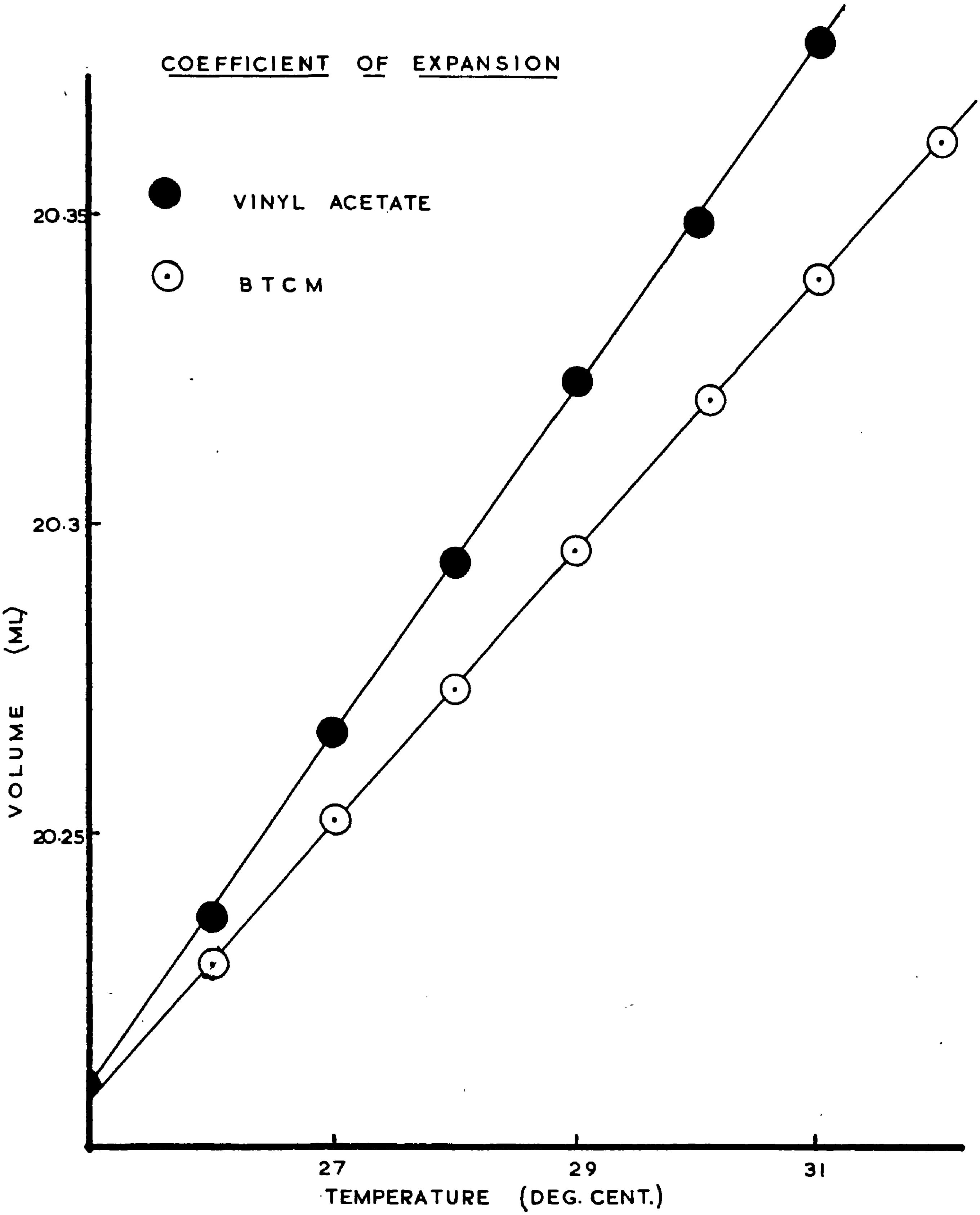
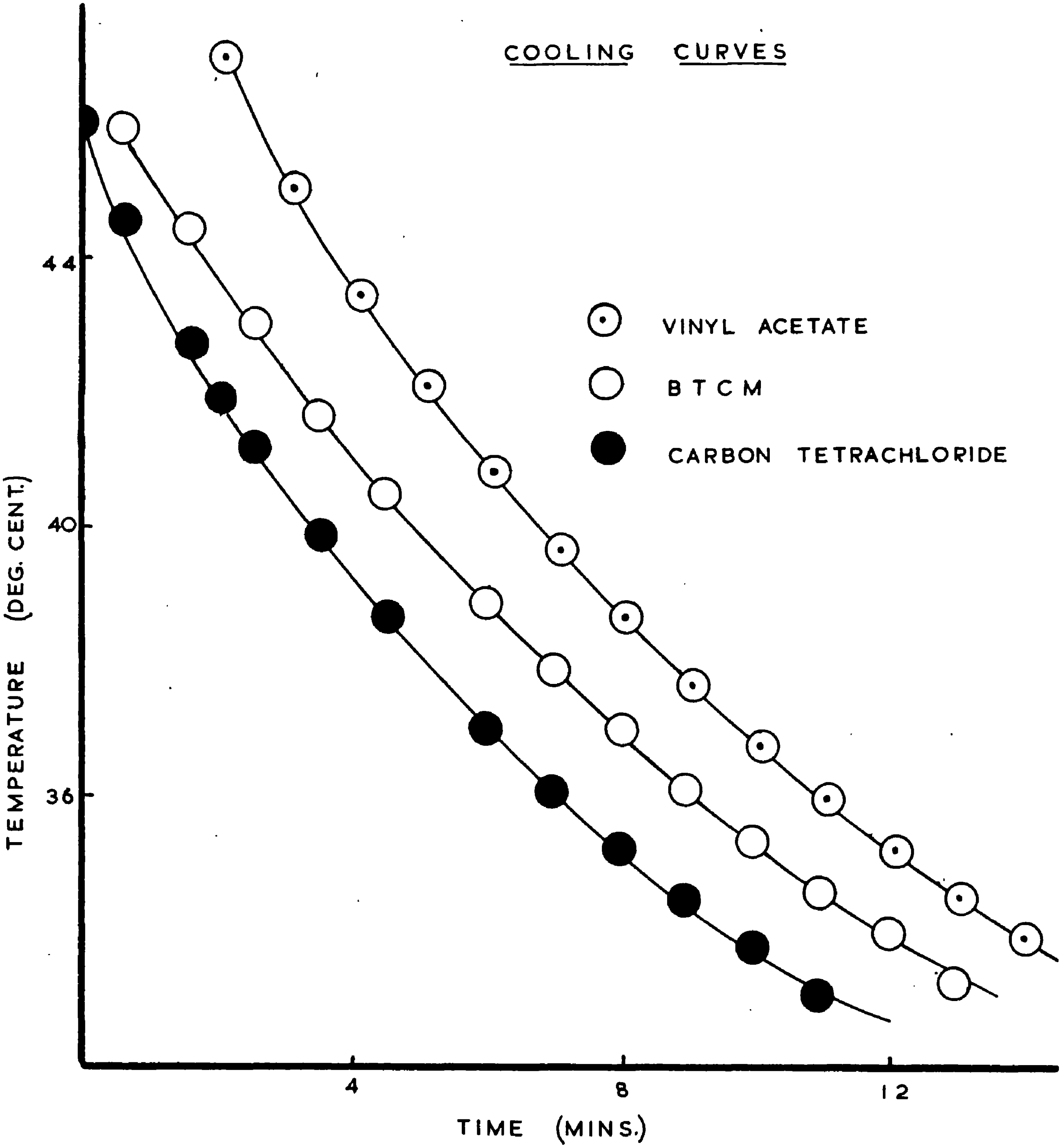

COEFFICIENT OF EXPANSION
● VINYL ACETATE
⊙ BTCM
20.35
20.3
20.25
VOLUME (ML)
27
29
31
TEMPERATURE (DEG. CENT.)

FIGURE 21



COOLING CURVES

In the specific heat determination, carbon tetrachloride, which has a specific heat of 0.201 cal/gm,[32] was used as the standard of reference. Figure 21 shows the actual cooling curves and the results obtained are shown in Table 8.

Table 8. Specific heat of the reactants. (35°C).

Material	Weight (gm)	Relative Cooling Rate	Specific Heat (cal/gm)
BTCM	110.60	3.15	0.18
Vinyl acetate	51.57	2.82	0.47
Carbon tetrachloride	87.65	3.54	0.201

Water-equivalent of copper calorimeter = 2.83 gm

The value obtained for the specific heat of vinyl acetate is in excellent agreement with the literature[24] which indicates that the value obtained for the specific heat of BTCM will also be reasonably accurate.

6.2.2. The ratio of ε/Z was measured for reaction mixtures of mole ratio 8:1 and 0.94:1 BTCM to vinyl acetate. As explained previously, the physical properties involved in the calculation must now refer to the reactants as a whole. For ease of appreciation, the results obtained which are required in this calculation have been re-stated below.

Table 9. Physical properties required for the evaluation of the heat of reaction.

$S_1 = 0.18$ $S_2 = 0.47$ cal/gm

$M_1 = 198$ $M_2 = 86$ $M_3 = 284$

$\rho_1 = 2.006$ $\rho_2 = 0.925$ $\rho_3 = 1.66$ gm/ml (25°C)

$\alpha_1 = 1.062 \times 10^{-3}$ $\alpha_2 = 1.402 \times 10^{-3}$ /deg

From equations (6.5) to (6.8), the following values are obtained for a mixture of mole ratio 8:1 BTCM to vinyl acetate:-

Heat capacity of system = 325.6 cals

Coefficient of expansion of system = 1.095×10^{-3} deg^{-1}

Fractional contraction for complete reaction = $(V - V')/V$

$= (\rho' - \rho)/\rho'$

$= 2.367 \times 10^{-2}$ ml/ml

where V and ρ are the initial volume and density of the system and V' and ρ' are the final volume and density.

Substitution of these values in equation (6.4), page 66, gives,

$$\Delta H = \frac{\varepsilon}{Z} \frac{325.6 \times 2.367 \times 10^{-2}}{1.095 \times 10^{-3}} \text{ cal/mole}$$

$$\text{i.e., } \Delta H = \frac{\varepsilon}{Z} \times 7.052 \text{ Kcal/mole}$$

Similarly, for a mole ratio of 1.06:1 vinyl acetate to BTCM, the relationship is found to be,

$$\Delta H = \frac{\varepsilon}{Z} \times 6.8 \text{ Kcal/mole.}$$

The ratio of ε/Z was determined as has been described. Figure 22 shows a typical determination of rate of contraction due to reaction and rate of contraction due to cooling immediately on the cessation of irradiation. Some typical initial expansions on the commencement of irradiation are shown in Figure 23.

Table 10 shows the results which were obtained in this part of the investigation.

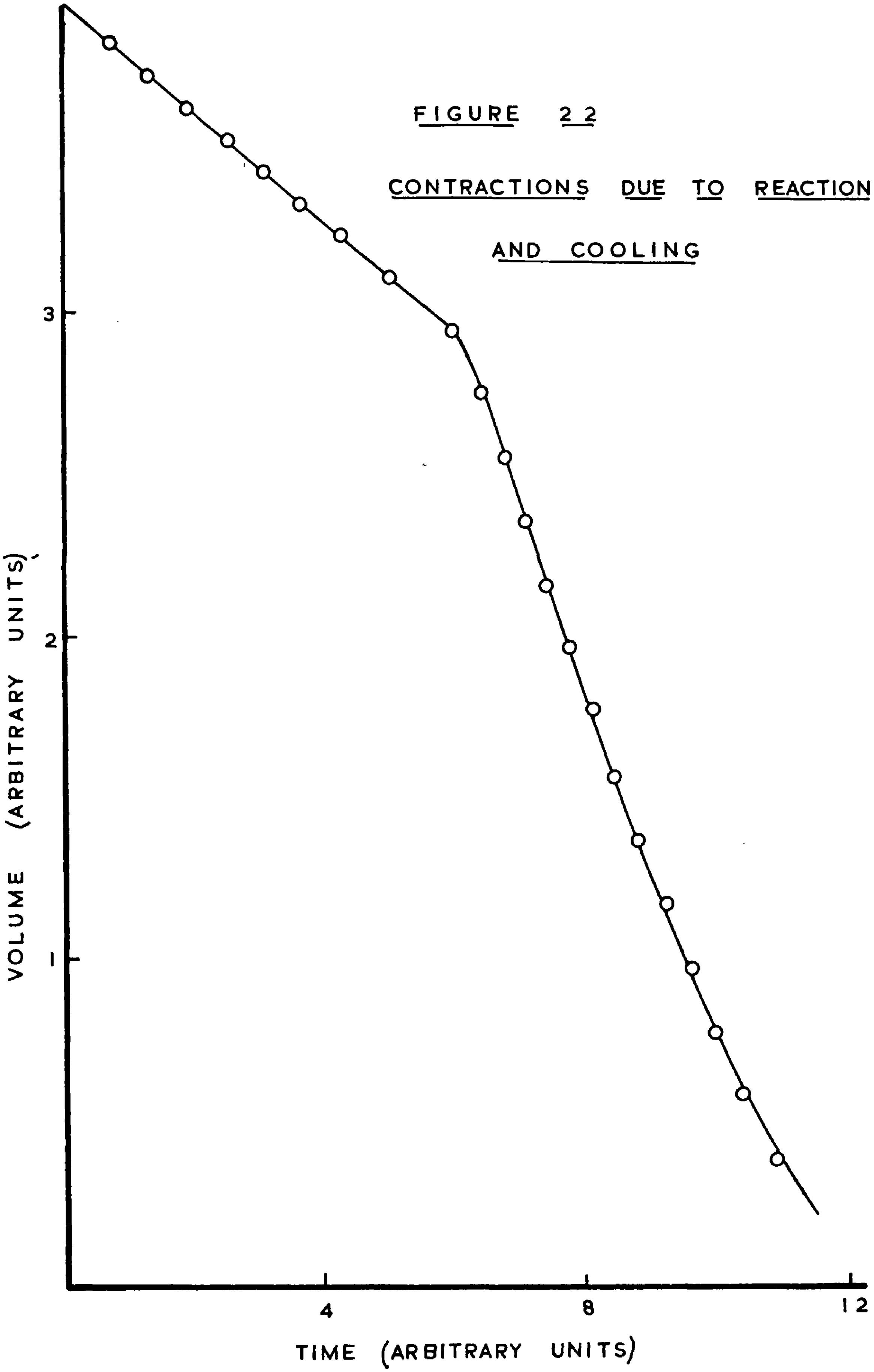


FIGURE 22

CONTRACTIONS DUE TO REACTION AND COOLING

FIGURE 23

TYPICAL INITIAL EXPANSIONS

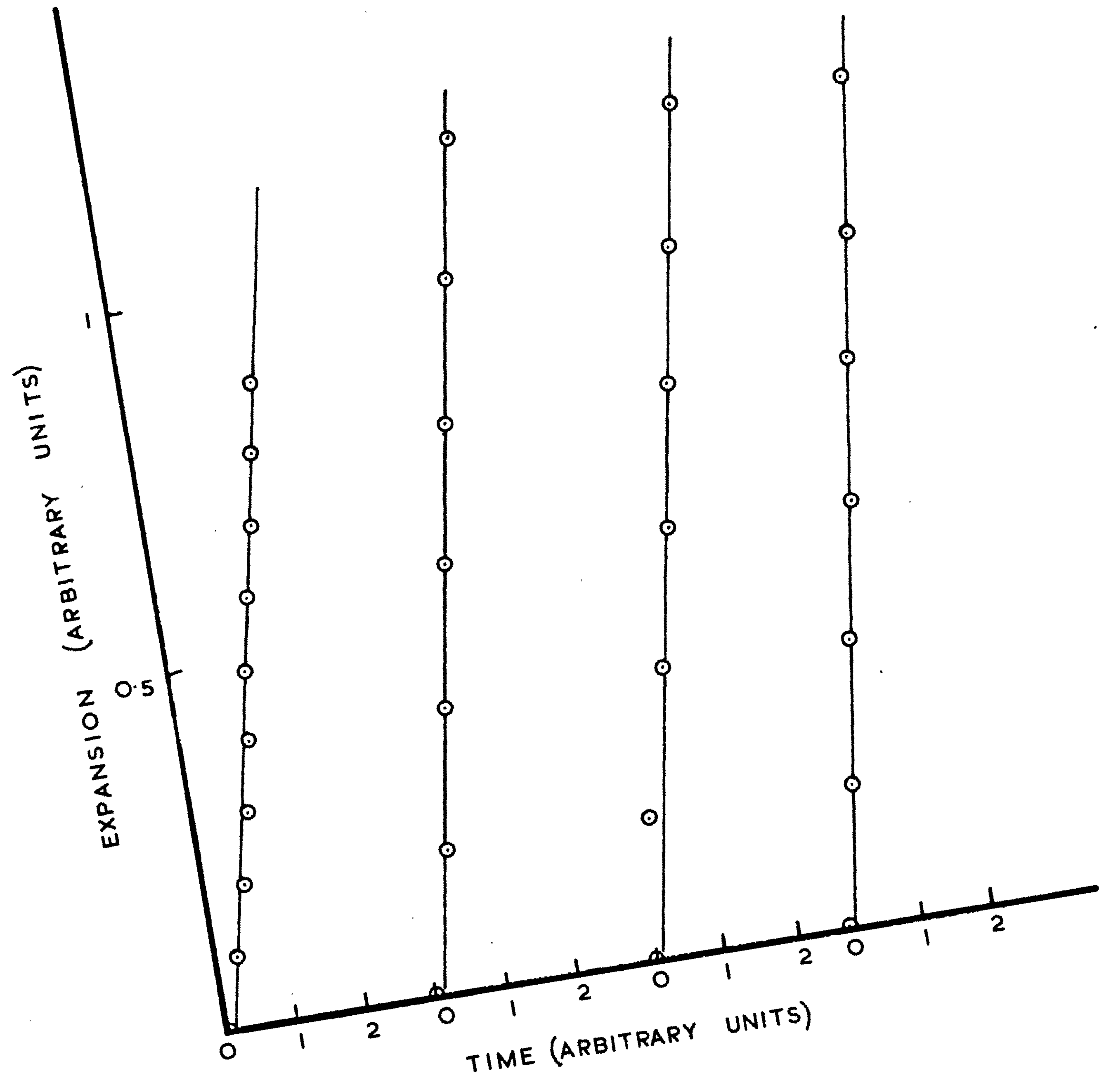


Table 10. **The heat of the photochemical addition of BTCM to vinyl acetate.**

Mole ratio (BTCM/VA)	Reaction Rate*	Initial Expansion Rate*	Cooling Rate*	$\frac{\varepsilon}{Z}$	ΔH (Kcal/mole)
8.0	1.60	-	6.30	3.94	27.8
8.0	1.05	-	4.10	3.91	27.6
8.0	1.63	-	6.40	3.93	27.8
8.0	1.37	-	5.40	3.94	27.8
8.0	2.82	8.20	-	3.92	27.7
8.0	2.82	-	11.10	3.94	27.8
8.0	2.36	7.00	-	3.97	28.0
8.0	2.36	-	8.96	3.80	26.8
0.94	0.85	-	3.55	4.18	28.2
0.94	0.85	-	3.45	4.06	27.3
0.94	0.85	2.90	-	4.41	29.7
0.94	0.85	2.90	-	4.41	29.7
0.94	0.48	-	2.17	4.50	30.3+

* Rates expressed in the same arbitrary units.

\+ This experiment was carried out inside a vacuum-jacket.

6.3.1. Discussion of the values obtained for the heat of reaction.

It will be seen from Table 10 that out of 13 determinations, 8 give values for the heat of reaction which lie between 27.6 and 28.2 Kcal/mole. The average value for the determinations carried out at a mole ratio of BTCM to vinyl acetate of 8 to 1 was 27.7 Kcal/mole and at a mole ratio of 0.94 to 1 was 29.3 Kcal/mole. Together with this, the values obtained from the initial expansion curves agree well with those obtained from the post-irradiation curves. It would also appear that the heat of reaction is virtually independent of the composition of the reactants over an 8-fold range, as would be expected, provided no polymerisation occurs.

6.3.2. Calculation of the rate of reaction.

With a knowledge of the heat of reaction, it is possible to calculate the rate of reaction from the initial expansion curves. An example of this calculation is given below.

It is assumed that the rate of reaction is to be calculated from the initial expansion produced by the irradiation of a mixture of BTCM and vinyl acetate at a mole ratio of 8:1. At this mole ratio, the heat of reaction = 27.7 Kcal/mole.

Actual expansion for complete reaction $= \Delta T \times \alpha$

where ΔT = rise in temperature for 100% conversion

Thus, Actual expansion for complete reaction

$$= \frac{\Delta H \times \alpha}{\text{Heat capacity}}$$

$$= \frac{27.7 \times 10^{3} \times 1.095 \times 10^{-3}}{325.6}$$

$$= \underline{9.35 \times 10}^{-2} \text{ ml/ml}$$

Overall contraction due to reaction

$$= (V - V')/V$$

$$= (\rho' - \rho')/\rho'$$

$$= \underline{2.367 \times 10}^{-2} \text{ ml/ml}$$

Now, the <u>measured expansion rate</u> is a composite effect and is produced by the <u>actual expansion rate</u> minus the <u>contraction rate</u> due to reaction.

Let the reaction proceed at X%/sec.

Then, the initial measured expansion rate (Υ)

$$= (9.35 - 2.367)\text{x}10^{-2}\text{x } X/100 \quad (\%/\text{sec})$$

$$= \underline{6.983 \times 10}^{-2} \,.\, X/100 \quad \%/\text{sec}.$$

Rate of contraction due to reaction (Z) $= \underline{2.367 \times 10^{-2}} \times X/100$ %/sec.

Thus,

$$\frac{\text{Initial measured expansion rate}}{\text{Contraction rate due to reaction}} = \frac{6.983 \times 10^{-2}}{2.367 \times 10^{-2}}$$

i.e.,

$$\underline{\text{Reaction rate} = \text{Initial measured expansion rate} \times 0.339} \quad \ldots\ldots\ldots\ldots\ldots(6.12)$$

This conversion factor, of course, only applies at the reactant concentration in the feed for which it has been calculated.

6.3.3. Calculation of reaction rate in absolute units.

If, as was the case in this investigation, the initial expansion rate is measured in terms of percentage volume change/second, then the reaction rate calculated from this will be in the same units. Before the latter can be applied to the evaluation of the velocity coefficients for a reaction, it must be converted to absolute units (mole.$1.^{-1}$sec.$^{-1}$). On the assumption that no polymer is produced by the reaction, and that the product consists entirely of the 1:1 adduct of vinyl acetate and BTCM (which is very reasonable in view of the results quoted in Chapter 3), a method of calculating the absolute rate was devised as follows.

The photochemical addition of BTCM to vinyl acetate may be represented by the following general equation:-

	$Cl_3C\ Br$	+	VA	→	$Cl_3C(VA)Br$
Molecular weight	198		86		284
Density (25°C) (gm/ml)	2.006		0.925		1.660
Volume/mole (ml)	99		93		171

In other words, the photochemical addition of 1 mole of BTCM to 1 mole of vinyl acetate to form 1 mole of the 1:1 adduct produces a contraction of (192 - 171) = 21 ml. This will be the case so long as exactly 1 mole of the reactant which is in the lower concentration is present. The total contraction will be independent of the quantity of the reactant which is in excess. For example, in a reaction mixture consisting of 8 moles of BTCM and 1 mole of vinyl acetate, only 2 moles of the reactants (one of each) will undergo conversion. Similarly, in a mixture consisting of 2 moles of BTCM and 1 of monomer, 2 moles will undergo conversion to the adduct once more. In both cases, however, the total contraction on complete reaction will amount to 21 ml. and 1 mole of product will have been formed.

If the actual contraction observed when a volume (V) of any BTCM-vinyl acetate mixture reacts is given by $(c \times A)$, then, the rate of contraction due to reaction will be given by:-

$$\text{Rate of contraction} = \frac{c \times A}{t \times 60} \quad \text{ml.sec}^{-1}$$

where c is the contraction (cm) at time t (mins), and A is the cross-sectional area of the dilatometer stem (cm^2)

Now, for the production of 1 mole of 1:1 adduct, the theoretical contraction is 21 ml. In other words,

$$\begin{array}{l}\text{Theoretical volume contraction}\\ \text{on production of adduct.}\end{array} = 21 \text{ ml.mole}^{-1}$$

Thus,

$$\begin{array}{l}\text{Rate of production of adduct}\\ \text{for a reaction mixture of}\\ \text{volume V ml.}\end{array} = \frac{c \times A}{t \times 60 \times 21} \text{mole.sec}^{-1}$$

Thus,

$$\text{Rate of reaction}^{*} = \frac{c \times A \times 1000}{t \times V \times 21 \times 60} \text{ mole.l.}^{-1}\text{sec}^{-1}$$

...............(6.13)

where c is the contraction (cm) at time t (mins), A is the cross-sectional area of the dilatometer stem (cm^2) and V is the volume (ml) of the dilatometer.

It is now possible to evaluate several of the velocity coefficients involved in the reaction and this has been described in the next chapter.

---

[*] When the 1:1 adduct is produced in the reaction between vinyl acetate and BTCM, rate-calculations are simplified to some extent in that the rate of formation of adduct, the rate of removal of monomer and the rate of removal of BTCM are numerically equal, so that it is perfectly justifiable to speak of the rate of reaction without being more explicit.

Chapter 7. The evaluation of the velocity coefficients for the photochemical addition of BTCM to vinyl acetate.

7.1.1. Parameters required for the evaluation of the velocity coefficients involved in a photochemical reaction.

Experiments designed to measure the rate-dependence on reactant concentration as described in Chapter 5 have shown that only with excess BTCM is there a single rate-controlling step. Thus, only in this region can the velocity coefficients be evaluated.

The rate equation deduced under these conditions was:-

$$-\frac{d[M]}{dt} = \frac{k_2 . I^{\frac{1}{2}}[M]}{k_4^{\frac{1}{2}}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(5.5)$$

From equation (5.3), page 52,

$$I = k_4 [Cl_3C^{\bullet}]^2$$

$$\text{i.e.,} \quad [Cl_3C^{\bullet}] = I^{\frac{1}{2}}/k_4^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(7.1)$$

Now, τ, the life-time of the kinetic chain $= [Cl_3C^{\bullet}]/I$

$\ldots\ldots\ldots(7.2)$

so that,

$$[Cl_3C^{\bullet}] = I . \tau$$

Thus,

$$I \times \tau = I^{\frac{1}{2}}/k_4^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(7.3)$$

Therefore,

$$I^{\frac{1}{2}} = (\tau . k_4^{\frac{1}{2}})^{-1} \qquad \ldots\ldots\ldots\ldots\ldots(7.4)$$

Substitution of equation (7.4) in (5.5) gives,

$$-\frac{d[M]}{dt} = \frac{k_2 [M]}{k_4 . \tau} \qquad \ldots\ldots\ldots\ldots\ldots(7.5)$$

Thus, $$\frac{k_2}{k_4} = \frac{-\frac{d[M]}{dt} \times \tau}{[M]} \qquad \ldots\ldots\ldots\ldots(7.6)$$

Re-arrangement of equation (5,5) gives,

$$\frac{k_2}{k_4^{\frac{1}{2}}} = \frac{-\frac{d[M]}{dt}}{I^{\frac{1}{2}}.[M]} \qquad \ldots\ldots\ldots\ldots(7.7)$$

It is obvious therefore that if the rate of removal of monomer (which in the case of the production of 1:1 adduct is numerically equal to the rate of formation of product), the rate of formation of trichloromethyl radicals, and the life-time of the kinetic chain are evaluated under these conditions, two separate ratios of k_2 and k_4 will be obtained (k_2/k_4 and $k_2/k_4^{\frac{1}{2}}$). From these values it is easy to calculate the individual velocity coefficients.

7.1.2. Order of termination.

The above kinetic analysis is based on the assumption that termination occurs through the mutual interaction of pairs of radicals. At the steady radical concentration ($[R]_s$), equation (7.10) (page 89) gives,

$$[R]_s = I/k_t^{\frac{1}{2}}$$

where k_t is the velocity coefficient for termination. It follows therefore that

$$I^{\frac{1}{2}} \propto [R]_s$$

Now, the rate of initiation (I) should be proportional to the intensity of illumination (f(i)),

i.e.,

$$I \propto f(i)$$

Since the rate of removal of monomer ('rate of reaction') is given by:- (for the general case)

$$-\frac{d[M]}{dt} = k_p [R]_s [M] \quad \text{............(7.8)}$$

where k_p is the velocity coefficient for propagation, it follows that,

$$\text{rate of reaction} \propto [R]_s$$

Thus,

$$\text{Rate of reaction} \propto I^{\frac{1}{2}} \propto f(i)^{\frac{1}{2}}$$

Thus, if the rate of a photochemical reaction is proportional to the square root of the intensity of irradiation, second order termination is taking place. Another way of expressing this is to say that the reaction has an intensity exponent of 0.5.

7.2.1. The rate of formation of trichloromethyl radicals.

Because of the lack of relevant experimental data, an initiator efficiency of 100% has been tacitly assumed for the photochemical reaction under investigation. Although discussed more fully later, this fact has been mentioned here to indicate the equivalence in the present work of the terms 'rate of formation of trichloromethyl radicals' and 'rate of initiation'. Strictly speaking, each term has its own meaning, but for convenience, the latter term will be used where possible.

Two principal methods are available for measuring the rate of initiation of chain growth. These are:-

(a) Calculation from measured kinetic quantities- rate of reaction, degree of polymerisation, etc.

(b) Inhibition or retardation measurements.

An inhibitor is a material, which, added to a system reacting by a free radical mechanism, completely suppresses the reaction for a period proportional to the quantity added. Ideally, when all the inhibitor has been used up, the reaction should attain the rate which is operative when no inhibitor has been added. Retarders merely reduce the reaction rate by an amount proportional to the quantity present, so that as it is removed, the reaction will gradually assume its normal rate.

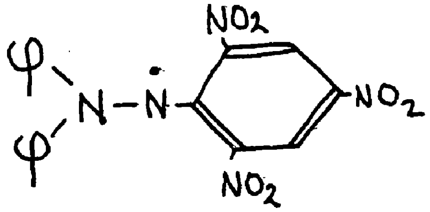
The difference between inhibitors and retarders is of degree rather than kind. It is generally accepted that inhibitors react with initial radicals to produce materials which are incapable of further propagation. Retarders, being less reactive than inhibitors, do not entirely prevent the propagation reaction. A sufficiently high concentration of retarder will, however, act as an inhibitor. Similarly, a sufficiently low concentration of inhibitor will act as a retarder.

Since chain transfer processes prevent the determination of the rate of initiation from $\overline{DP}$ measurements, and since retardation studies are even more dubious than inhibition measurements, the last-mentioned was used for the determination of the rate of initiation.

7.2.2. The use of DPPH as an inhibitor.

In this investigation, the stable free radical, 1:1'-diphenyl-2-picrylhydrazyl (DPPH) has been used.

This has the structure:-



Bawn and Mellish[34] have suggested that each DPPH radical will react with one other free radical by a sharing of their unpaired electrons to give a stable, neutral molecule. Several workers have suggested that other complications are involved. It has been pointed out that one DPPH radical may react with several initiator radicals through the re-generation of DPPH by subsequent reactions.[35]

Other factors which favour the use of DPPH for the determination of the rate of initiation are as follows, however. The optical density at 5240 Å of the product of inhibition is much lower than that of DPPH itself, so that its rate of removal is easily followed. The product of inhibition appears to be of low reactivity, so that there should be little secondary break-down. All in all, it may be said that DPPH is no better and certainly no worse than a number of other possible inhibitors.

It has been postulated that in the present reaction, each DPPH radical reacts with one trichloromethyl radical.

Thus, the rate of removal of DPPH will be numerically equal to the rate of formation of trichloromethyl radicals. The rate of removal may be measured by observing the inhibition periods produced in the reaction by known concentrations of DPPH. Two methods have been used for this purpose - dilatometric measurements, and measurement of the time required for the complete removal of the colour due to the inhibitor, using a photometer. In each case, the rate of removal of DPPH (and thus the rate of initiation) is obtained from the following expression:-

$$I = \frac{\text{DPPH concentration initially present (mole.l}^{-1}\text{)}}{\text{period of inhibition (sec)}}$$

7.3. Measurement of the life-time of the kinetic chain.

As stated previously, the life-time of the kinetic chain was measured by two methods:-

(a) The non-stationary state method.[36]

(b) A modification of the rotating sector method.[37,38]

Before dealing with the actual results obtained, the underlying theory of each method will be examined - the procedure which has been adopted throughout this dissertation.

7.3.1. The non-stationary state method.

The non-stationary state method,[38] by its name, obviously involves the measurement of some function of the initial build-up of radical concentration at the beginning of a reaction. It is an essential of this method of measuring kinetic chain life-times that the following are available:-

(a) A method of starting the reaction abruptly, such as polymerisation by some form of irradiation, e.g., light, γ - or X-radiation.

(b) A method of determining the extent of reaction which is sufficiently sensitive to detect the small changes which occur.

(c) Pure reagents, so that no inhibition periods are produced.

Techniques which have been employed include measurement of the dielectric constant as a function of time,[39,40] interferometry,[41] measurement of the rise in temperature due to reaction by means of a thermocouple[42,43] and by a thermistor.[44]

The method used in the present investigation has been a dilatometric technique of measuring the expansion produced immediately on the commencement of irradiation and during the adiabatic period.[45]

From the theory due to Burnett,[36] when the stationary state radical concentration has been attained,

$$\frac{d[R]}{dt} = I - k_t[R]_s^2 = 0 \quad \ldots\ldots\ldots(7.9)$$

Thus,

$$[R]_s = (I/k_t)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.10)$$

where I = rate of initiation, k_t is the velocity coefficient for the mutual termination of two radicals, [R] the radical concentration at time t secs and $[R]_s$ the radical concentration at the steady state.

Before the attainment of the steady state,

$$\frac{d[R]}{dt} = I - k_t[R]^2 \quad \ldots\ldots\ldots\ldots(7.11)$$

which on integration gives,

$$\frac{1}{2}\ (k_tI)^{\frac{1}{2}}\ \ln\left\{\frac{1 + (kt/I)^{\frac{1}{2}}\ [R]}{1 - (k_t/I)^{\frac{1}{2}}\ [R]}\right\} = t + c \ \ldots(7.12)$$

$$\tanh^{-1}\left\{[R]/[R]_s\right\} = (k_tI)^{\frac{1}{2}}.\ t$$

$$= t/\gamma \quad \ldots\ldots\ldots\ldots(7.13)$$

$c = 0$, since $[R] = 0$ when $t = 0$, and τ is the life-time of the kinetic chain, which is given by equation (7.4) page 81, on re-arrangement.

Thus,

$$[R] = [R]_s \tanh(t/\tau) \quad \text{............(7.14)}$$

The rate of removal of monomer at any instant will thus be given by:-

$$-\frac{d[M]}{dt} = k_p.[R]_s.[M].\tanh(t/\tau) \quad \text{......(7.15)}$$

which on integration gives,

$$-\ln\frac{[M]}{[M]_o} = \frac{k_p}{k_t}.\ln\cosh(t/\tau) \quad \text{....(7.16)}$$

where k_p is the velocity coefficient for propagation, $[M]$ the monomer concentration at any particular instant and $[M]_o$ the initial monomer concentration.

If F is the fraction of monomer which has been converted, then:-

$$[M]_o/[M] = 1 - F \quad \text{............(7.17)}$$

$$-\ln(1 - F) = \frac{k_p}{k_t}.\ln\cosh(t/\tau) \quad \text{...(7.18)}$$

If $F \ll 1$, as will be the case if the extent of reaction is low,

$$- \ln (1 - F) \doteqdot F \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.19)$$

so that,

$$F = \frac{k_p}{k_t} . \ln \cosh (t/\tau) \quad \ldots\ldots\ldots(7.20)$$

When $t \gg \tau$, i.e., when the stationary state has been attained,

$$F = \frac{k_p}{k_t} . \left\{ \frac{t}{\tau} - \ln 2 \right\} \quad \ldots\ldots\ldots(7.21)$$

Thus, if the fraction of monomer converted is plotted as a function of time, a straight line should be obtained, whose time-axis intercept will be $\tau . \ln 2$ and whose slope will be $k_p/k_t . \tau$.

$$\text{i.e.,} \quad \frac{F}{t} = \frac{k_p}{k_t . \tau} \quad \text{or,} \quad \frac{k_p}{k_t} = \frac{F \times \tau}{t}$$

$$\text{i.e.,} \quad \frac{k_p}{k_t} = \frac{F \times [M] \times \tau}{t \times [M]}$$

$$= \frac{- \frac{d[M]}{dt} \times \tau}{[M]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.22)$$

It is noticeable that equation (7.22) is identical in form to equation (7.6), (page 82) which was derived by the normal kinetic analysis.

7.3.2. The modified rotating sector method.

The theory of the normal rotating sector method for the kinetic chain life-time determination is in effect a variation of the above (para. 7.3.1.). The idea of using intermittent illumination to determine velocity coefficients was first introduced by Briers et al[37] in 1926. The method was first successfully applied to the liquid phase polymerisation in 1945 through the study of the velocity coefficients for the polymerisation of vinyl acetate.[46–49]

Consider a system exposed to intermittent illumination. If the light and dark periods are comparatively long with respect to Υ , the total radiation incident on the system for equal light and dark periods will be 1/2 of that under steady illumination. The average rate of reaction will be reduced by the same factor. If the flash-times are short compared with Υ , only a small fraction of the radical chain-carriers present in a given light period will terminate during the following dark period so that the rate of reaction during the dark period will not differ appreciably from that during the light period. The reaction may thus be considered to be continuous, with the rate of initiation being 1/2 that under steady illumination. If the rate of reaction varies as $I^{0.5}$ as is the case in the present reaction with excess BTCM (see page 62), the rate of reaction will be 1/2 and $(1/2)^{\frac{1}{2}}$ times its value under steady illumination for low and high flash-frequencies respectively.

Figure 24 illustrates the principle more clearly. The ordinate represents the ratio of the radical concentration at time t secs to the radical concentration at the steady state (i.e., $[R]/[R]_s$). The abcissa is the ratio of t to τ, the life-time of the kinetic chain at the steady state and under constant illumination. In curve C, the flash-time is long compared with the life-time. In this case, the radical concentration has almost reached its stationary state level at the end of the light period. When the light is cut off, the concentration decreases along FG and by the end of the first dark period has fallen almost to zero. At G, the light is turned on again and the same thing occurs once more as it does in subsequent cycles.

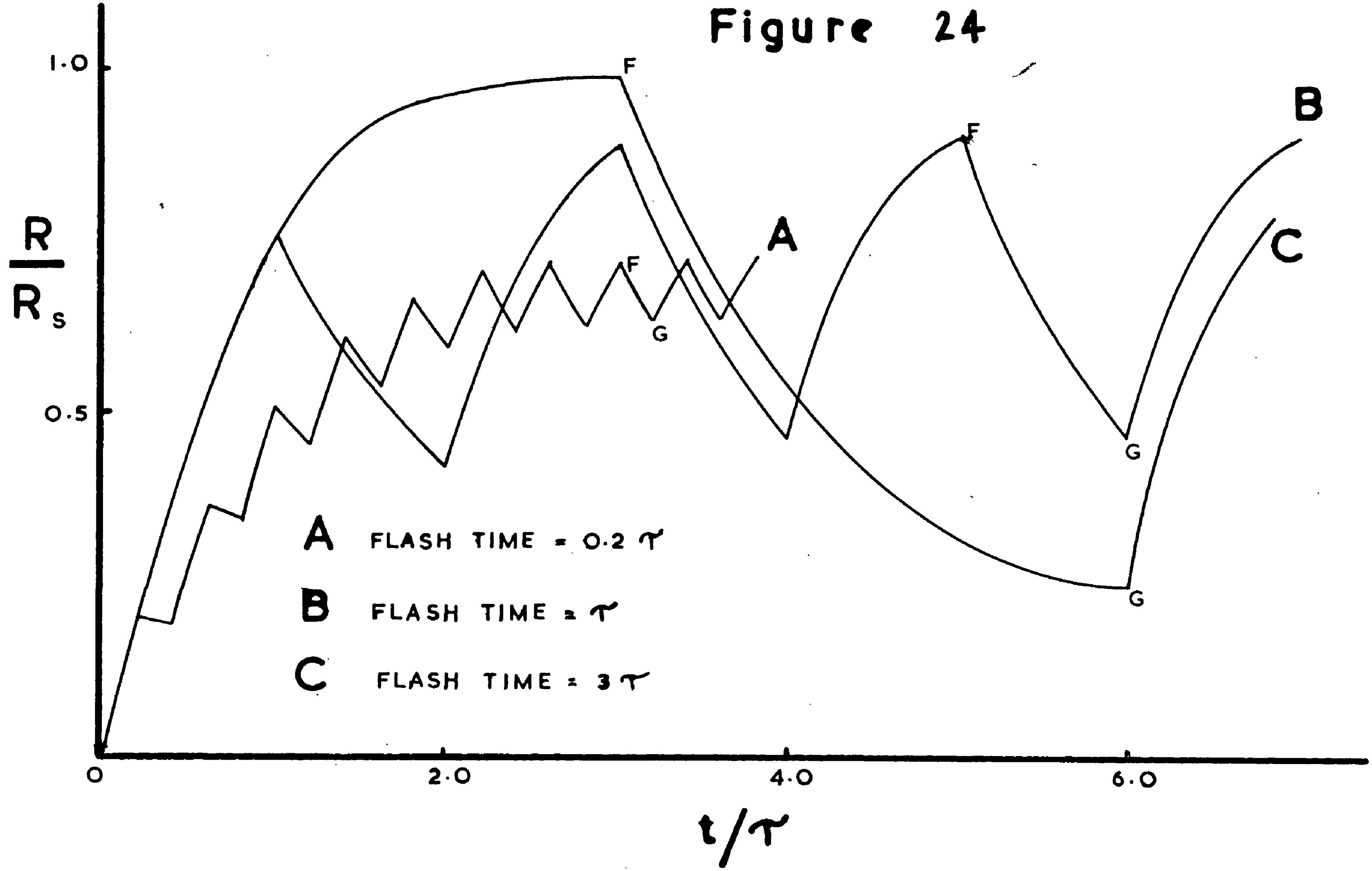


Figure 24

1·0
0·5
R/R_s
0
2·0
4·0
6·0
t/τ
F
G
F
G
F
G
A
B
C
A FLASH TIME = 0·2 τ
B FLASH TIME = τ
C FLASH TIME = 3 τ

Consider now curve A, in which the flash-time is short compared with the life-time. Initially, the radical concentration at the end of consecutive dark periods increases steadily, since the increase in R during one light period is always slightly greater than the decrease during the following dark period. The difference gradually decreases until a pseudo-stationary state is reached in which the radical concentration at the end of the light and dark periods attains fixed values. Curve B depicts an intermediate range where the flash-time is equal to the life-time.

If second order termination and the absence of a dark rate are assumed, it is possible to derive an expression for the kinetic chain life-time.

Consider first the build-up of radical concentration on irradiation.

For the light period,

$$\frac{d[R]}{dt} = I - k_t[R]^2 \qquad \text{............(7.11)}$$

which, when treated as on page 89 gives,

$$\frac{[R]}{[R]_s} = \tanh\,(t/\tau) \qquad \text{...........(7.14)}$$

By choosing arbitrary values for (t/τ), equation (7.14) was graphed as the radical build-up curve (Figure 25A).

Consider now the decay of the radical concentration during the dark period. The rate of decay in concentration will be given by:-

$$-\frac{d[R]}{dt} = k_t[R]^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(7.23)$$

which on integration gives,

$$\frac{1}{[R]} = k_t . t + c' \qquad \ldots\ldots\ldots\ldots(7.24)$$

where c' is a constant of integration and will normally be zero, thus,

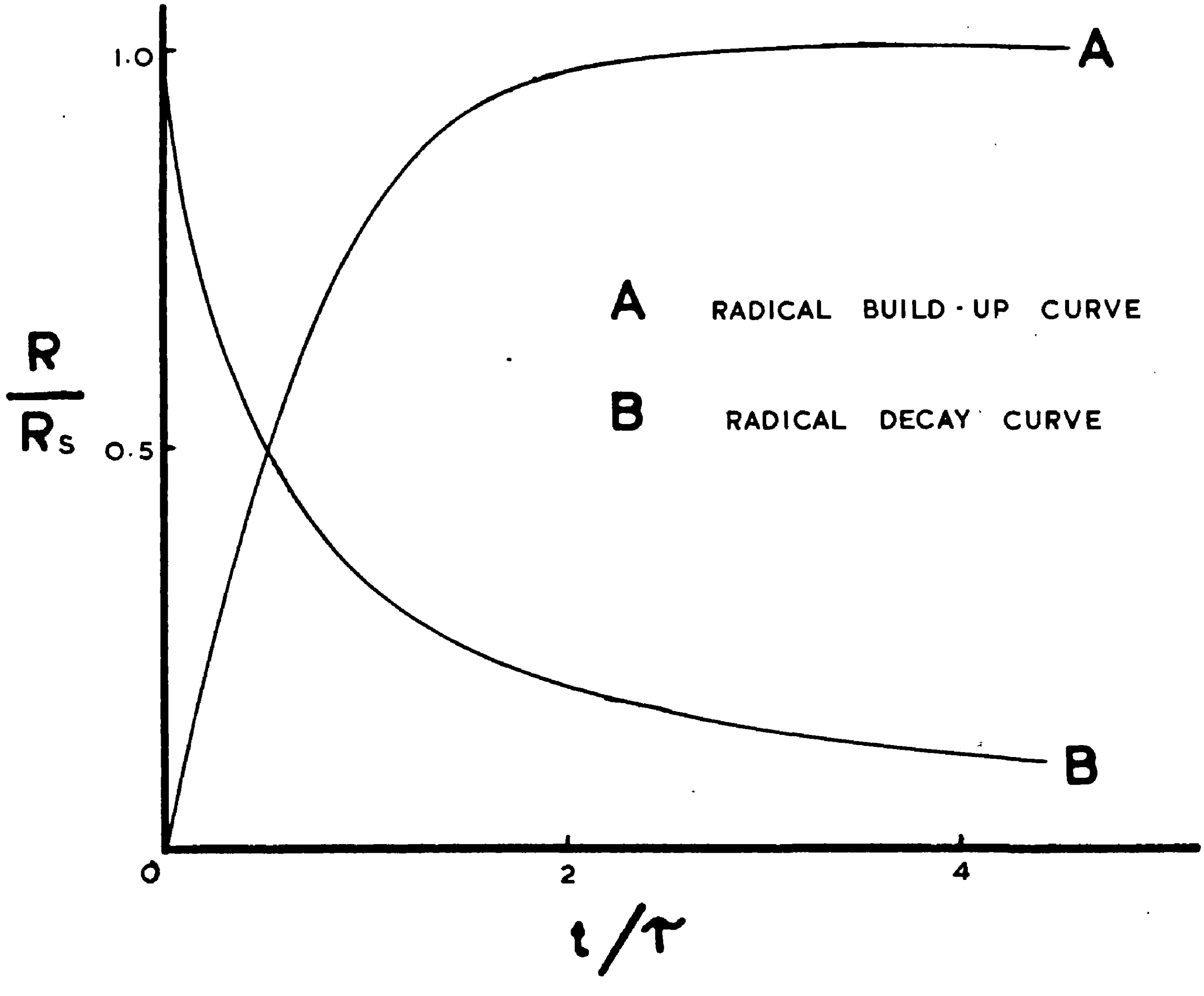
$$\frac{1}{[R]/[R]_s} = k_t . [R]_s . t \qquad \ldots\ldots\ldots\ldots\ldots(7.25)$$

Now, $\tau = [R]_s / I$ and $k_t = I/[R]_s^2$, so that

$$k_t . [R]_s = I/[R]_s = 1/\tau$$

Therefore,
$$\frac{1}{[R]/[R]_s} = (t/\tau) \qquad \ldots\ldots\ldots\ldots(7.26)$$

FIGURE 25


1.0
0.5
R/Rs
0
2
4
t/τ
A
B
A RADICAL BUILD-UP CURVE
B RADICAL DECAY CURVE

By once more choosing arbitrary values for (t/τ), equation (7.26) was graphed as the radical decay curve (Figure 25B).

In the present work, the sector used was such that the light and dark periods were of the same length, so, for convenience, this and not the general case will be considered.

Let t secs represent the length of the light and dark periods. Equations (7.14) and (7.26) give the instantaneous value of the ratio of the radical concentration to that of the steady state during the light and dark periods respectively. The average radical concentration during the light period will thus be given by:-

$$[R]_L = \frac{1}{t} \int_{\substack{\text{light} \\ \text{period}}} [R] \, dt \qquad \ldots\ldots\ldots\ldots(7.27)$$

Equation (7.13) may be re-written,

$$\frac{1}{[R]_s} \cdot \tanh^{-1} \frac{[R]}{[R]_s} = k_t . t + c'' \qquad \ldots.(7.28)$$

so that,

$$[R]_L = \frac{[R]_s}{t} \int_{T_2}^{T_1} \tanh \left\{ [R]_s \; (k_t . t + c'') \right\} . dt$$

$$= \frac{1}{2 \, k_t . t} \, . \, \ln \left\{ \frac{1 - \left\{ [R]_g / [R]_s \right\}^2}{1 - \left\{ [R]_f / [R]_s \right\}^2} \right\} \quad ...(7.29)$$

Similarly, the average concentration of radicals during the dark period will be given by integration of equation (7.24), to give,

$$[R]_D = \frac{1}{2 \, k_t . t} \, . \, \ln \left\{ \frac{[R]_f^{\;2}}{[R]_g^{\;2}} \right\} \quad ....(7.30)$$

where $[R]_f$ = radical concentration at the end of light period.

$[R]_g$ = radical concentration at end of dark period

$[R]_L$ = Mean radical concentration during light period.

$[R]_D$ = Mean radical concentration during dark period.

The mean concentration ($[R]_o$) of radicals during one complete(light + dark) cycle will be

$$[R]_o = \tfrac{1}{2} \left\{ [R]_L + [R]_D \right\} \quad ....(7.31)$$

Substitution of equations (7.29) and (7.30) in equation (7.31) gives,

$$2[R]_o = \frac{1}{2\,k_t.t} \cdot \left\{ \ln \left[\frac{1 - ([R]_g/[R]_s)^2}{1 - ([R]_f/[R]_s)^2} \right] + \ln \frac{([R]_f)^2}{([R]_g)^2} \right\} \quad \ldots\ldots\ldots\ldots\ldots(7.32)$$

Application of equation (7.28) to points F and G gives,

$$\tanh^{-1}\left\{\frac{[R]_f}{[R]_g}\right\} - \tanh^{-1}\left\{\frac{[R]_g}{[R]_s}\right\} = k_t.t.[R]_s$$

$$= (t/\tau)$$

$$= m \quad \ldots\ldots\ldots(7.33)$$

Application of equation (7.24) to points F and G gives,

$$\frac{1}{[R]_g} - \frac{1}{[R]_f} = k_t.t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.34)$$

Equation (7.33) may be written in the logarithmic form:-

$$2\left\{m + \ln\frac{(1 + [R]_g/[R]_s)}{(1 + [R]_f/[R]_s)}\right\} = \ln\left\{\frac{1 - ([R]_g/[R]_s)^2}{1 - ([R]_f/[R]_s)^2}\right\}$$

$$\ldots\ldots\ldots\ldots\ldots(7.35)$$

Substitution in equation (7.32) gives,

$$2\,[R]_o = \frac{1}{k_t.t}\left\{m + \ln\left[\frac{(1 + [R]_g/[R]_s)}{(1 + [R]_f/[R]_s)}\right] + \ln\frac{[R]_f}{[R]_g}\right\}$$

$$\ldots\ldots\ldots\ldots\ldots(7.36)$$

Also, from considerations noted on page 95,

$$k_t.t.[R]_s = t/\tau = m \quad \ldots\ldots\ldots(7.37)$$

Thus, by substituting the value of $[R]_g$ from equation (7.34) the following expression is obtained:-

$$2\,[R]_o = \frac{m}{k_t.t}\left\{1 + \frac{1}{m}\ln\left[1 + \frac{m}{1 + [R]_s/[R]_f}\right]\right\}$$

$$\ldots\ldots\ldots\ldots(7.38)$$

and by further substitution of equation (7.37)

$$2\,\frac{[R]_o}{[R]_s} = 1 + \frac{1}{m}\cdot \ln\left\{1 + \frac{m}{1 + [R]_s/[R]_f}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(7.39)$$

Figures 21A and 21B were drawn from equations (7.14) and (7.26). From these two curves, Figure 24 was drawn. By drawing a series of such curves the ratio of $[R]_f/[R]_s$ was obtained for several values of $\underline{m}$ and the results of such calculations are shown in Figure 26. By substitution of a number of values of the ratio of $[R]_f/[R]_s$ together with the corresponding value of $\underline{m}$ obtained from Figure 26 in equation (7.39), a curve was plotted of $[R]_o/[R]_s$ as a function of log $\underline{m}$ (Figure 27).

From equation (7.8) it will be seen that the reaction rate is directly proportional to the steady radical concentration. This should apply to the pseudo- as well as the normal stationary state. The ratio of the rate of reaction under intermittent illumination to that under steady illumination will thus be numerically equal to the ratio of the average radical concentration over the light and dark periods of intermittent illumination of the same frequency to the steady state radical concentration at constant illumination of the same intensity.

FIGURE 26

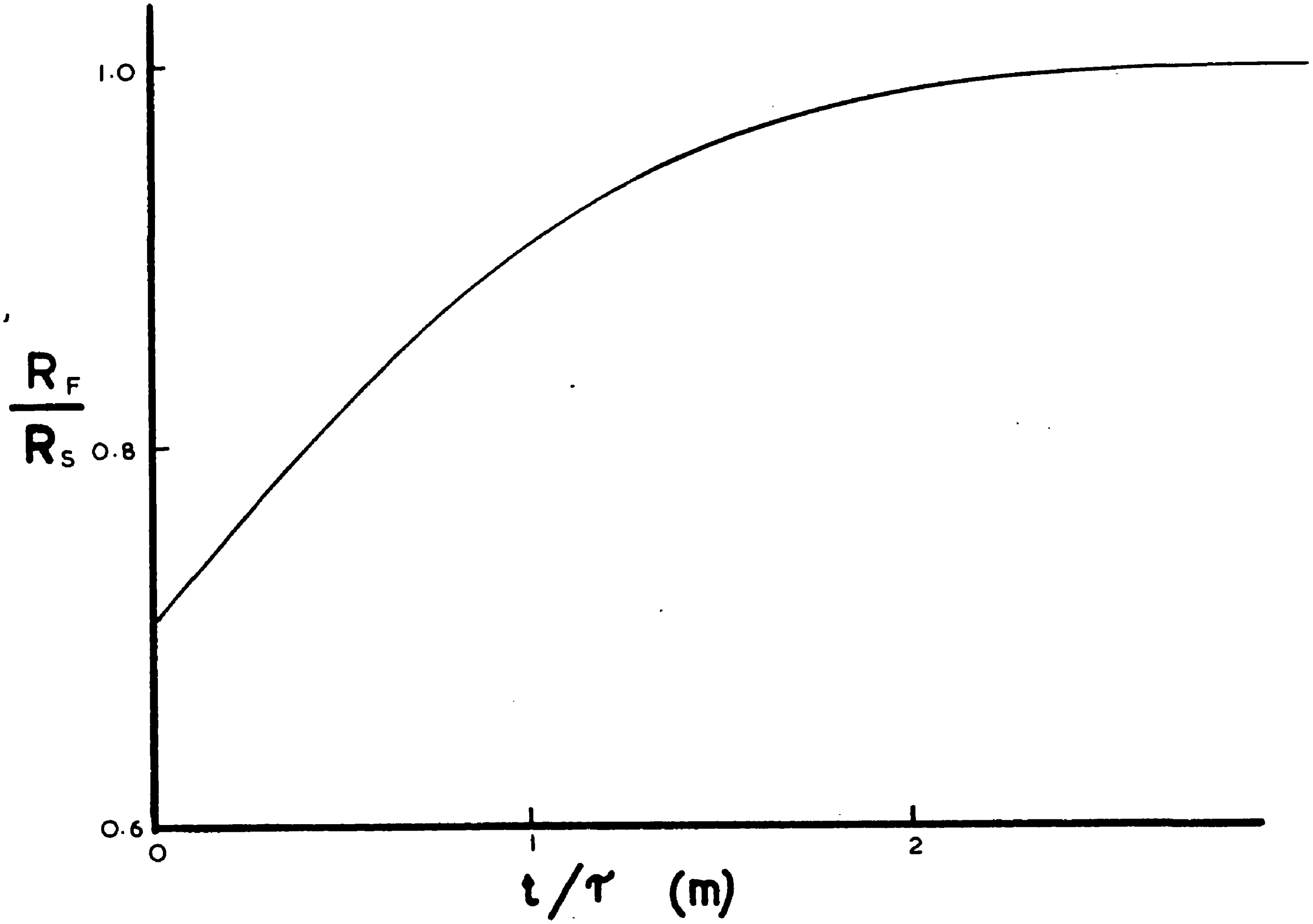
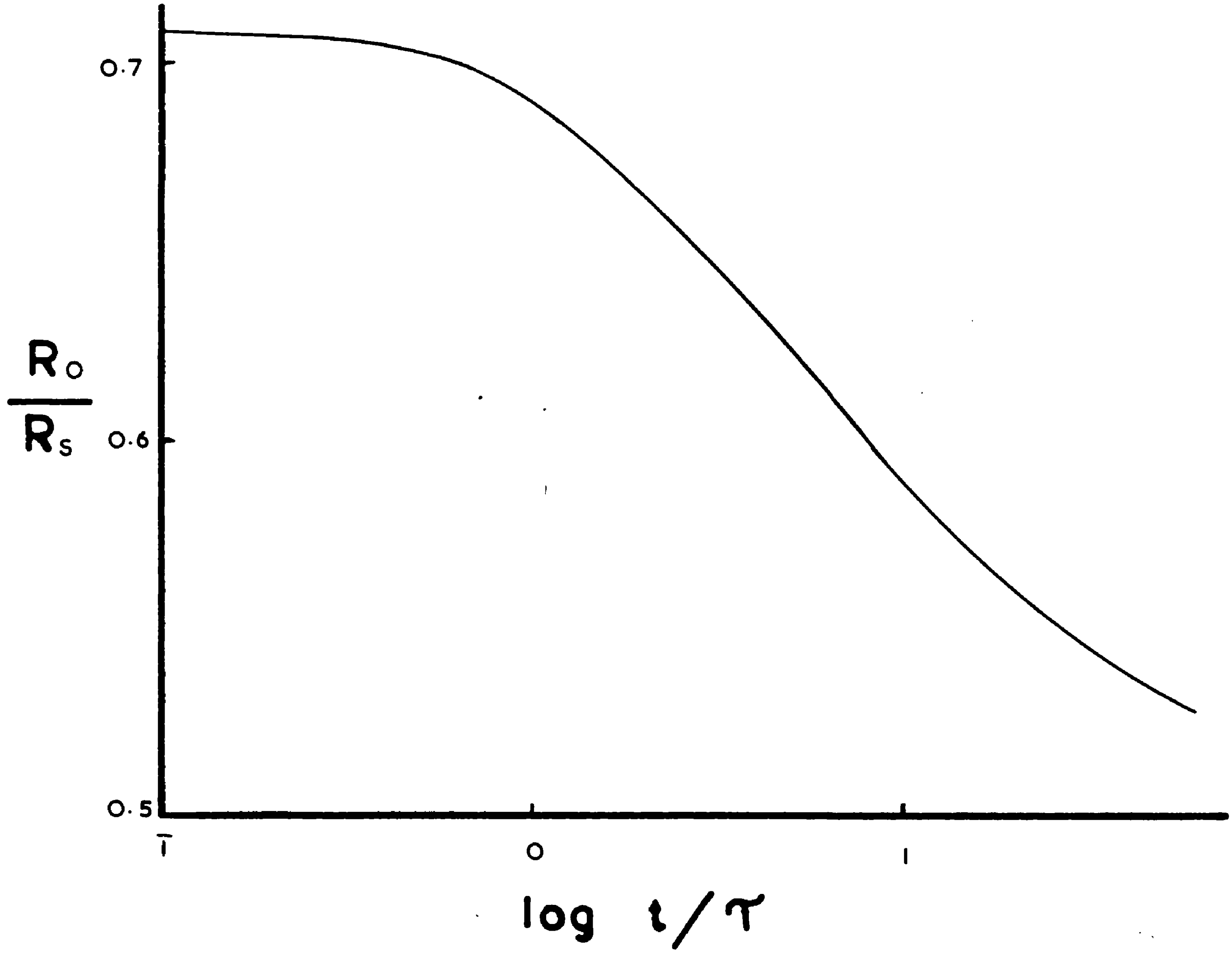


FIGURE 27

THEORETICAL CURVE



Thus, graphing rate(sectored)/rate(unsectored) as a function of log (flash-time) is equivalent to plotting $[R]_o/[R]_s$ as a function of log $\underline{m}$.

By substitution of the required parameters in equation (7.39), it is found that when $t = \Upsilon$, (i.e., when $\underline{m} = 1$), $[R]_o/[R]_s = 0.694$. In other words, the life-time of the kinetic chain is equal to the flash-time when the ratio of the sectored to the unsectored rate is 0.694. In practise, the experimental points are fitted to the theoretical curve (Figure 27) from which Υ is usually obtained by interpolation.

Figure 25A also shows that the steady state radical concentration is rapidly attained. Now, Chapter 6 shows that the initial expansion rate on the attainment of the steady state radical concentration and during the adiabatic period is directly proportional to the rate of reaction of a specific reactant mixture (see, for example, equation (6.12), page 76). The normal rotating sector technique has been modified in the present work by measuring, not the rate of contraction due to reaction, but the initial expansion rate during steady and intermittent illumination of various frequencies.[50] The curve obtained by graphing expansion rate (sectored)/expansion rate (unsectored) as a function of log (flash-time) should be identical with the curve obtained by the normal method. Using the present technique, it is possible to measure both the life-time of the kinetic chain and the overall rate of reaction under the same conditions.

7.4. Results.

7.4.1. Order of termination in the photochemical reaction between vinyl acetate and BTCM.

Table 11. Intensity exponents for the reaction.

BTCM/VA (mole ratio)	$\left\{ \text{Light Intensity} \right\}^{\frac{1}{2}}$ (relative)	Rate (relative)	Intensity Exponent
6 : 1	1 0.56	1 0.57	0.49
1 : 5	1 0.56	1 0.56	0.5

7.4.2. Rate of initiation measurements.

The rate of formation of trichloromethyl radicals was determined in the presence of vinyl acetate, vinyl chloride, benzene and chloroform. Figure 28 shows the optical density at 5240 Å of the DPPH-BTCM-solvent (or monomer) mixture as a function of time of irradiation for a typical experiment in each medium. Figure 29 shows the rate of formation of trichloromethyl radicals (calculated as described previously) as a function of the BTCM concentration for several media. Figure 30 is a plot of inhibition period as a function of DPPH concentration and Figure30A shows the actual results which were obtained in these measurements.

7.4.3. Measurement of kinetic chain life-time.

This was measured for conditions of excess BTCM. Figures 31 and 32 show the results obtained in typical non-stationary state and rotating sector experiments respectively. In the latter, the experimental points have been fitted to the theoretical curve (Figure 27).

FIGURE 28

RATE OF REMOVAL OF D.P.P.H. IN SEVERAL MEDIA

(VARIOUS CONCENTRATIONS)

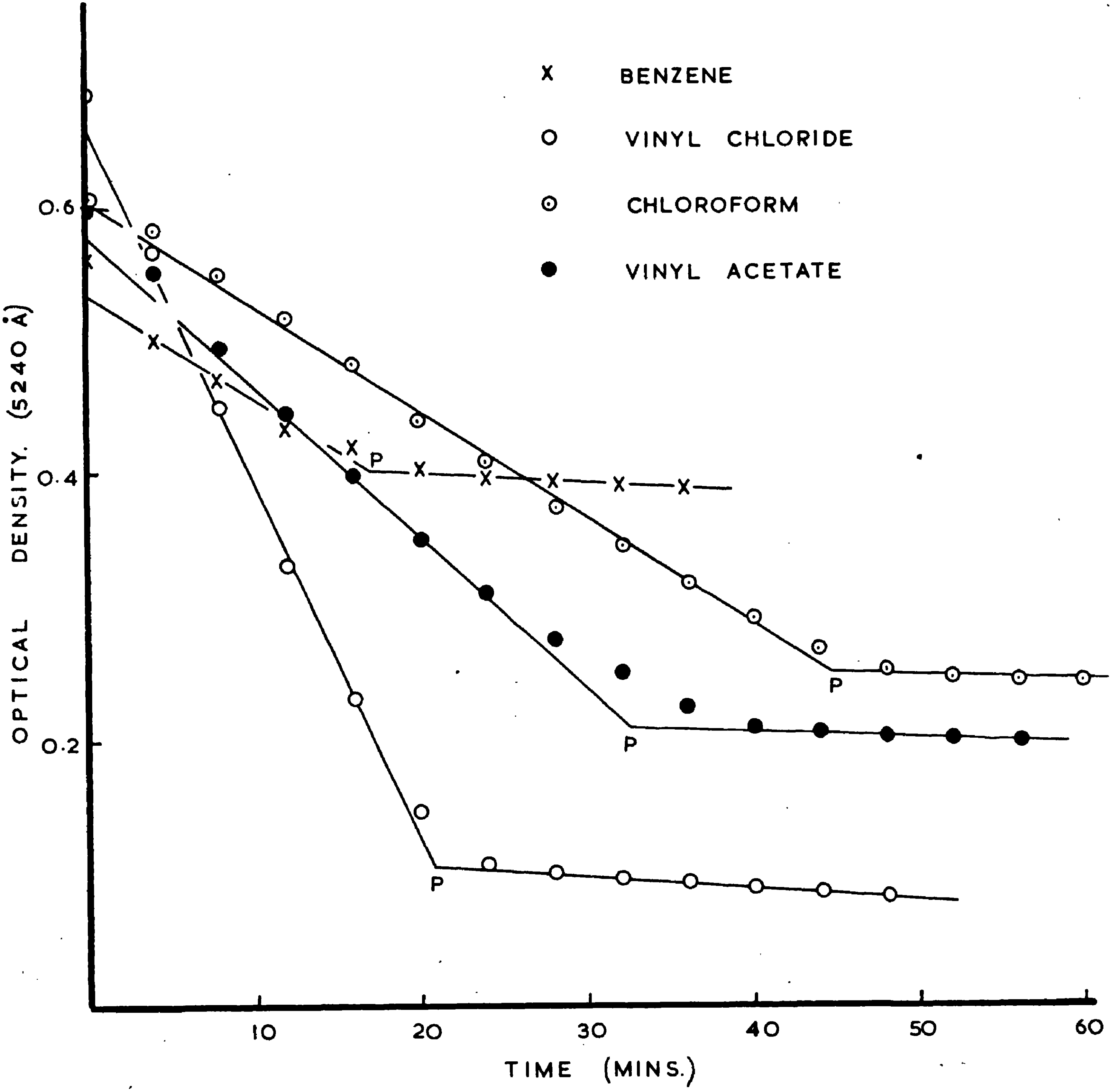


FIGURE 29

DEPENDENCE OF I ON BTCM CONCENTRATION IN SEVERAL MEDIA.

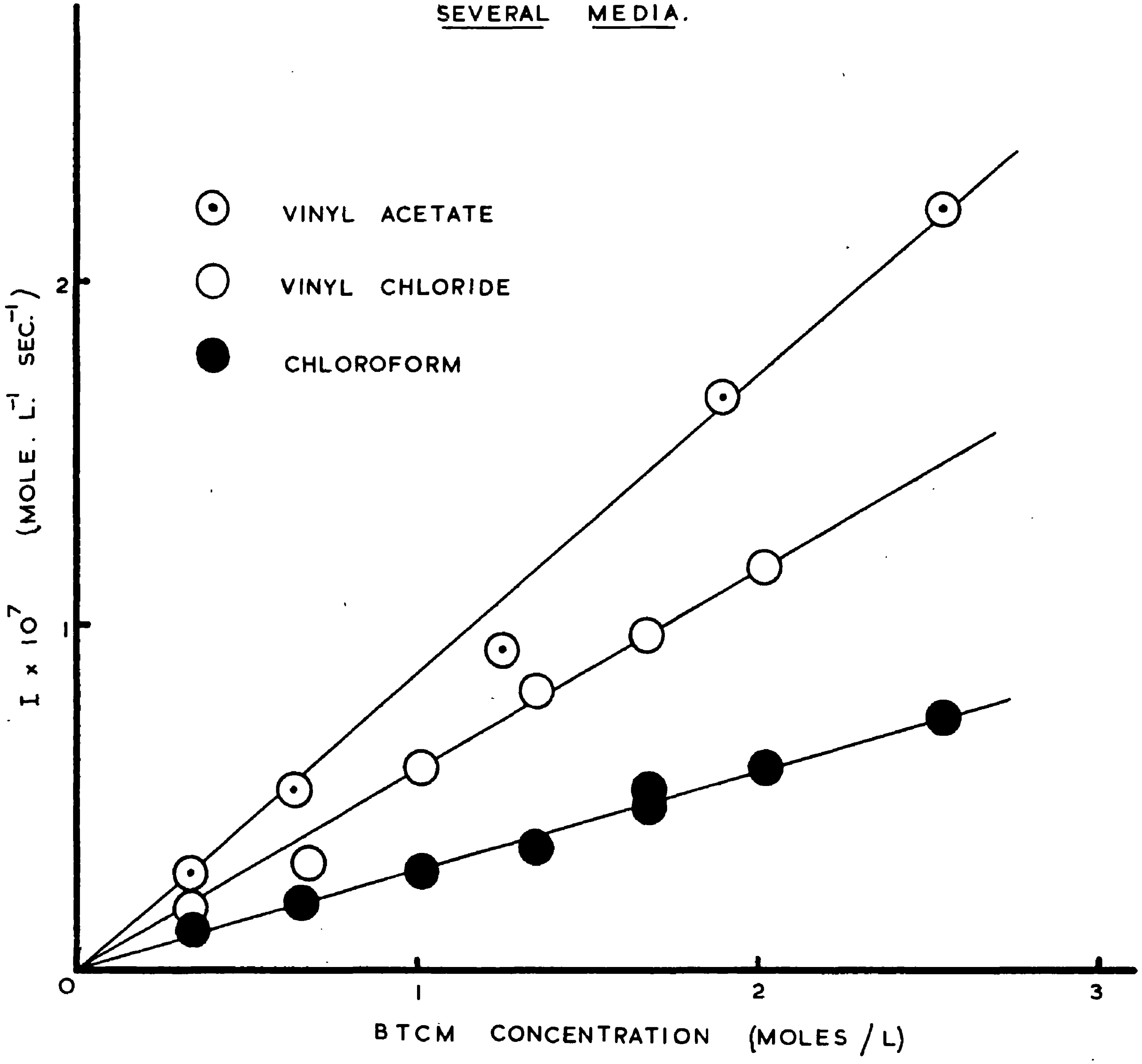


FIGURE 30

INHIBITION PERIODS PRODUCED BY D.P.P.H.

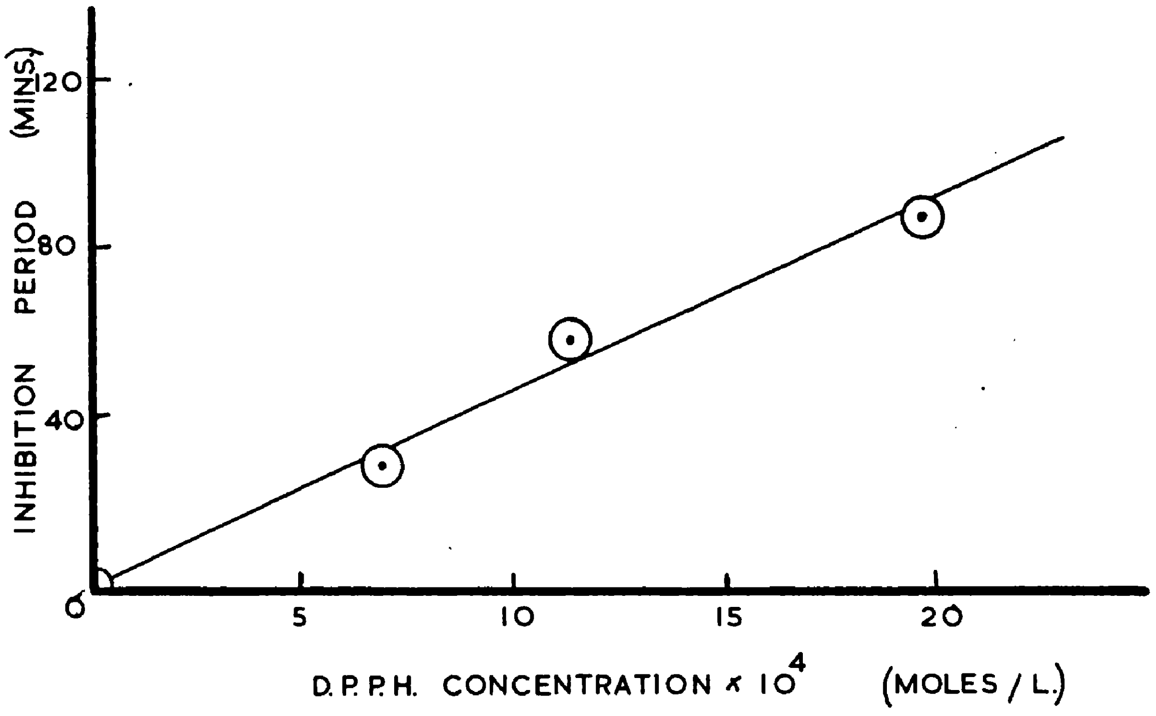
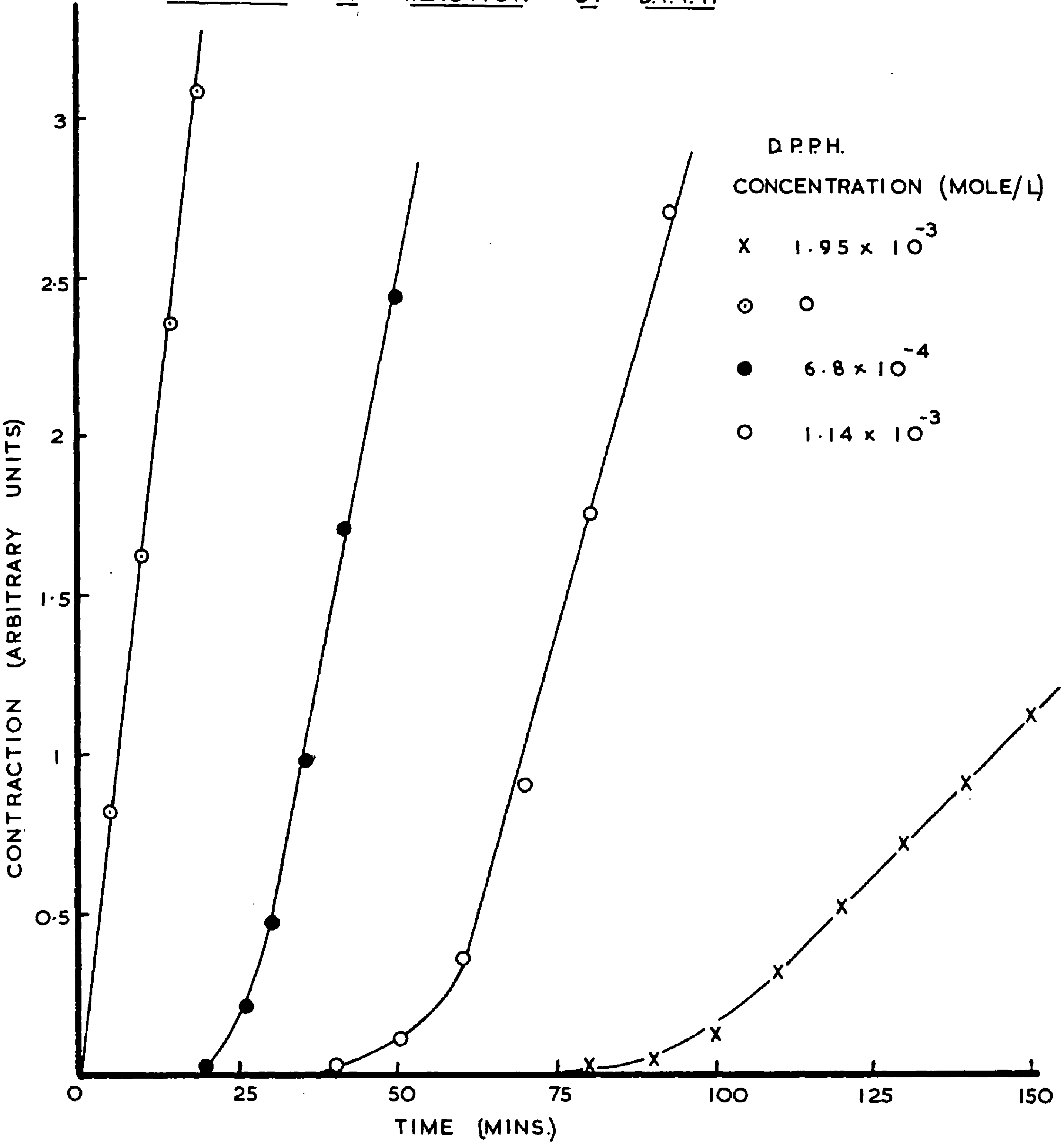


FIGURE 30A

INHIBITION OF REACTION BY D.P.P.H



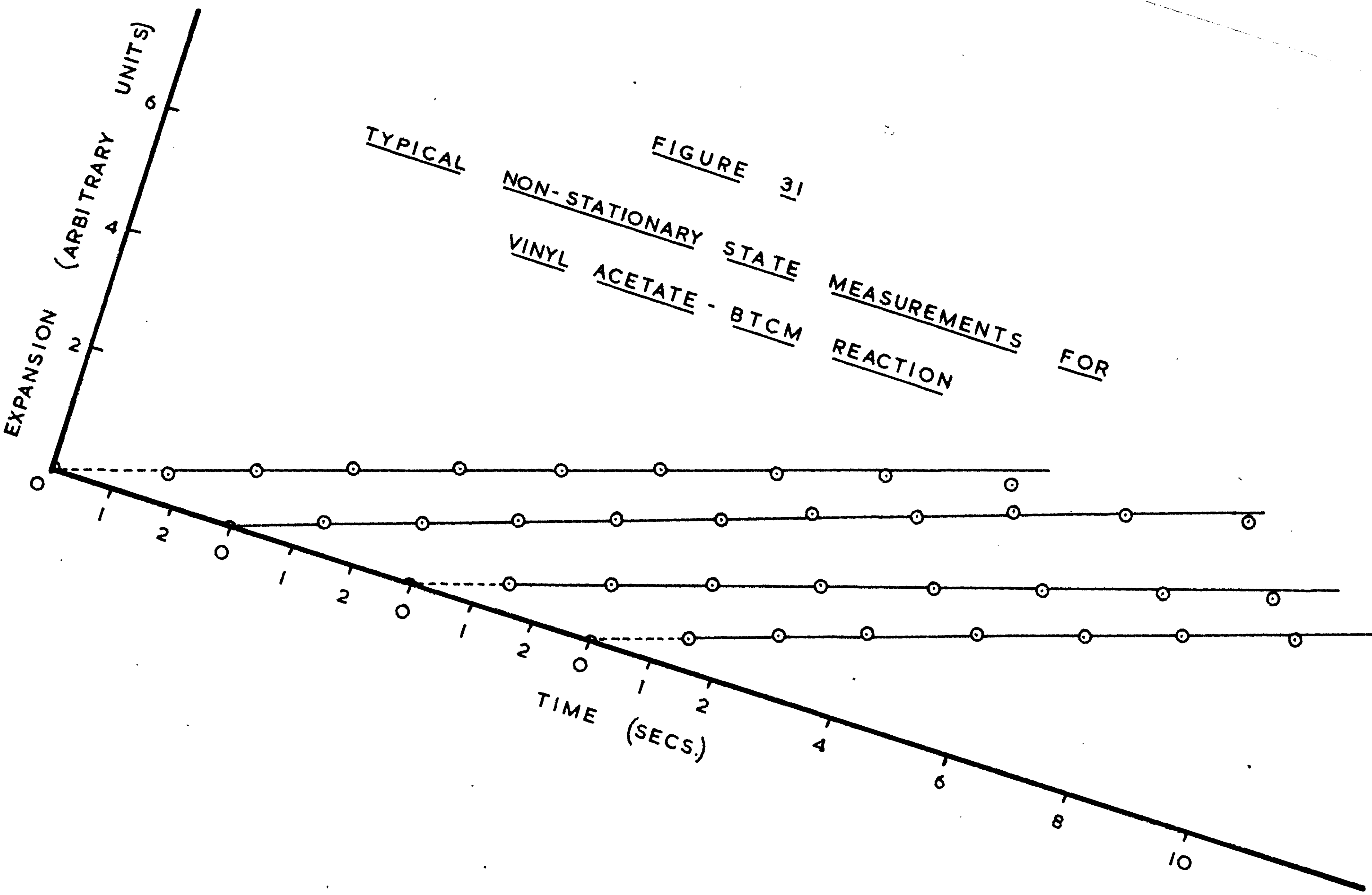
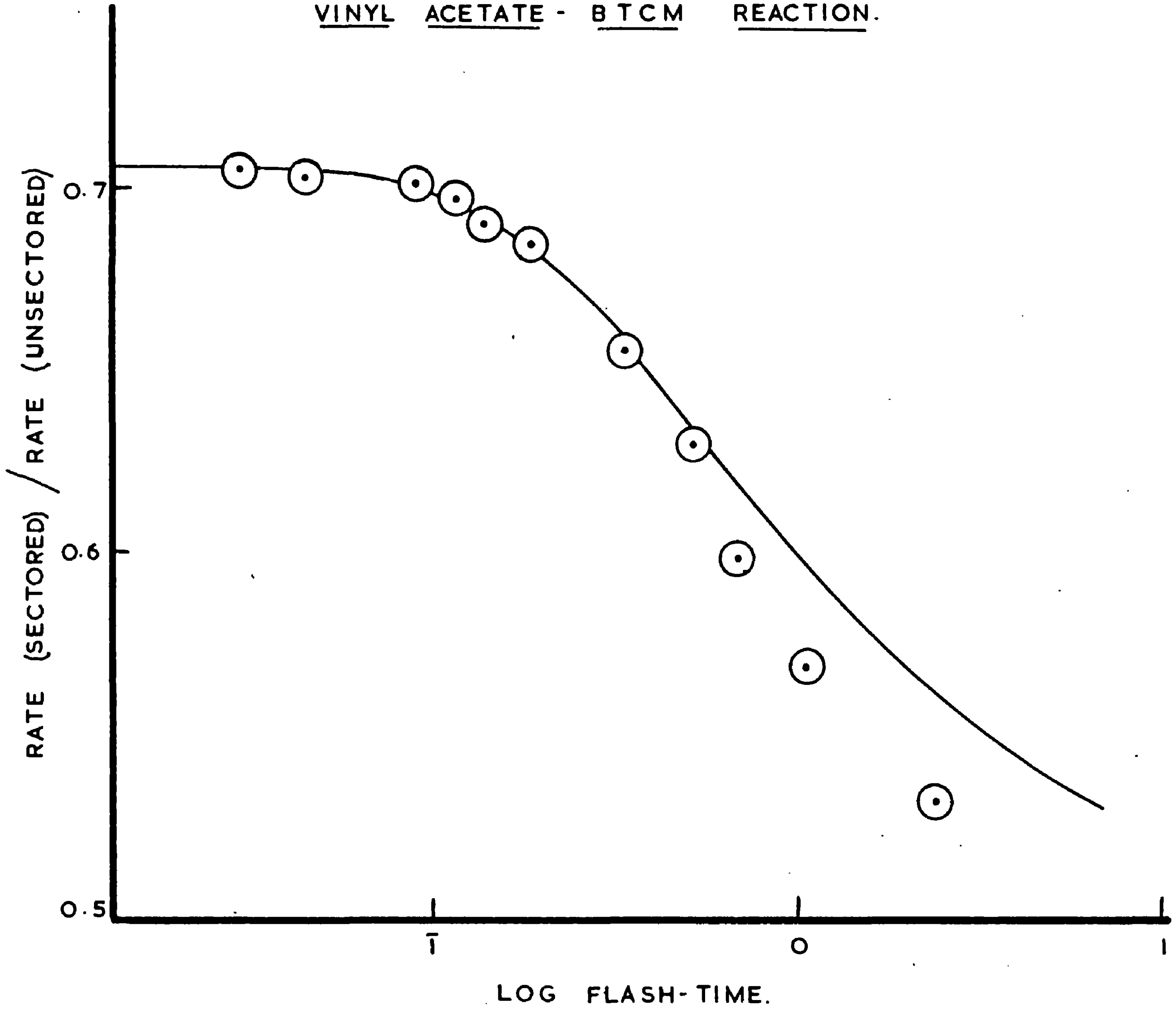


FIGURE 31

TYPICAL NON-STATIONARY STATE MEASUREMENTS FOR VINYL ACETATE - BTCM REACTION

FIGURE 32

TYPICAL ROTATING SECTOR CURVE FOR VINYL ACETATE - BTCM REACTION.



7.5. Calculation of velocity coefficients.

7.5.1. Evaluation of $k_2/k_4^{\frac{1}{2}}$ from rate of initiation data.

From Figure 29 it will be seen that the rate of initiation (I) is directly proportional to the BTCM concentration. By extrapolation it is thus possible to calculate the rate of initiation at any BTCM concentration. It will be explained later why it is impossible to measure this rate at very high BTCM concentrations.

The velocity coefficients were measured in excess BTCM, for a mixture of 9.05 mole.l^{-1} BTCM and 1.13 mole.l^{-1} vinyl acetate. As stated previously, the rate of initiation was determined both absorptiometrically and dilatometrically. The value for the rate of initiation at a BTCM concentration of 9.05 mole.l^{-1} was obtained by extrapolation in both cases. By substitution in equation (7.7) (page 82) of this value together with that of the overall rate of reaction (obtained from equation (6.13), page 79) and the monomer concentration, the ratio of $k_2/k_4^{\frac{1}{2}}$ was obtained.

Table 12. The evaluation of $k_2/k_4^{\frac{1}{2}}$ (with vinyl acetate as medium in the rate of initiation determination.

	Absorptiometric Method	Dilatometric Method
Rate of initiation ($mole.l.^{-1}sec^{-1}$)	7.90×10^{-7}	5.02×10^{-7}
Rate of reaction ($mole.l.^{-1}sec^{-1}$)	0.99×10^{-4}	1.13×10^{-4}
Monomer concentration ($mole.l^{-1}$)	1.13	1.13
$k_2/k_4^{\frac{1}{2}}$ $(mole^{-1}.l.\ sec^{-1})^{\frac{1}{2}}$	9.9×10^{-2}	13.9×10^{-2}

Thus, the average value for the ratio of $k_2/k_4^{\frac{1}{2}}$ was found to be <u>11.9 x 10</u>$^{-2}$ $(mole^{-1}.l.\ sec^{-1})^{\frac{1}{2}}$ when the rate of initiation is determined in the presence of vinyl acetate.

Replacement of vinyl acetate by chloroform gives the following results:-

Table 13. The evaluation of $k_2/k_4^{\frac{1}{2}}$ (with chloroform as medium in the rate of initiation determination).

Rate of initiation ($mole.l.^{-1}sec^{-1}$)	2.6×10^{-7}
Rate of reaction ($mole.l.^{-1}sec^{-1}$)	0.99×10^{-4}
Monomer concentration ($mole.l^{-1}$)	1.13
$k_2/k_4^{\frac{1}{2}}$ ($(mole.l.^{-1} sec^{-1})^{\frac{1}{2}}$)	17.3×10^{-2}

Thus the value of the ratio of $k_2/k_4^{\frac{1}{2}}$ was found to be 17.3×10^{-2} $(mole^{-1}.l. \ sec^{-1})^{\frac{1}{2}}$ in the presence of chloroform for the rate of initiation determination.

7.5.2. Evaluation of the ratio of k_2/k_4 from kinetic chain life-time data.

Kinetic chain life-time determinations were carried out on reaction mixtures consisting of 9.05 $mole.l.^{-1}$ BTCM and 1.13 $mole.l.^{-1}$ vinyl acetate. By substituting the value obtained together with the overall rate of reaction and monomer concentration in equation (7.6), page 82, the ratio of k_2/k_4 was obtained.

Table 14. Evaluation of the ratio of k_2/k_4 by the non-stationary state and rotating sector techniques.

	Non-stationary state	Rotating sector.
Rate of reaction (mole.l.$^{-1}$sec^{-1})	9.33×10^{-5}	$9,70 \times 10^{-5}$
Monomer concentration (mole.l.$^{-1}$)	1.13	1.13
Kinetic chain life-time (secs)	0.2	0.15
k_2/k_4	1.64×10^{-5}	1.34×10^{-5}

It will be seen that very good agreement was obtained between the two methods and that the average value for the ratio of k_2/k_4 was $\underline{1.5 \times 10^{-5}}$.

7.5.3. Calculation of the individual velocity coefficients.

Combination of the values obtained for the ratios of $k_2/k_4^{\frac{1}{2}}$ and k_2/k_4 gives the following results:-

Table 15. The velocity coefficients for the photochemical addition of BTCM to vinyl acetate.

	Vinyl acetate* medium	Chloroform* medium
k_2 (25^0C) ($l.mole^{-1}sec^{-1}$)	950	1950
k_4 (25^oC) ($l.mole^{-1}sec^{-1}$)	0.63×10^8	1.3×10^8

* Refers to the medium which was used in the rate of initiation determination.

7.6. Discussion.

7.6.1. Order of termination.

Table 11 shows that over the concentration range employed for these experiments, second order termination occurs. The kinetics derived earlier are thus applicable to the system and from this point of view, the velocity coefficients may be evaluated.

7.6.2. Inhibition measurements.

As stated previously, the rate of removal of DPPH was determined in benzene, chloroform, vinyl acetate and vinyl chloride. In the three latter cases, as will be seen from Figure 28, the DPPH concentration (measured by its optical density at 5240 Å) decreased rapidly at first. A fairly abrupt change in rate of removal then occurred around point P, when it was considered that all the DPPH had been removed. Ideally, after point P had been reached, the optical density would remain steady. Since however, it usually continued to decrease at a very slow rate, it would appear that a certain amount of secondary reaction was taking place.

In practise, the end-point, P, was obtained by extrapolating the two parts of each curve, since the rate did not change instantaneously.

Figure 30a shows that following the period of complete inhibition, the reaction rate gradually increases until it attains a steady value. This indicates that DPPH in sufficiently low concentration acts as a retarder rather than an inhibitor, which would be expected from the theory of inhibition.

Attempts to measure the rate of formation of trichloromethyl radicals in benzene solution proved very unsatisfactory. The optical density at the apparent end-point was very similar to that of the initial reactants. It may be that the benzene contained an impurity which acted as a much more reactive inhibitor than DPPH. Since the former was fairly rigorously purified, however, this would appear unlikely. Alternatively, the optical density at 5240 Å of the normal inhibition product may be quite high in the presence of benzene due to interaction between the various species available.

Due to the uncertainty of the measurements carried out in benzene, and to the inapplicability to the present reaction of the measurements made in vinyl chloride, values of k_2 and k_4 were calculated from measurements of the rate of formation of trichloromethyl radicals in vinyl acetate and chloroform.

To be of use for inhibition measurements, an inhibitor must completely suppress reaction for periods proportional to the quantity present. Figure 30 shows that DPPH is very suitable in this respect. Besides indicating this important property, Figure 30 gives an alternative method of calculating the rate of initiation. It will be seen from Table 12 (page 105) that the two methods give reasonably good agreement.

From Figure 29 it will be seen that the rate of initiation is directly proportional to the BTCM concentration. For reasonable experimental accuracy, the period of inhibition should be around 30-120 minutes. To avoid the "skin effects" referred to previously (page 32), the inhibitor concentration must be fairly low, thus the BTCM concentration must also be low to produce the inhibition periods quoted above. It follows that the rate of initiation at high BTCM concentrations must be calculated by extrapolation from Figure 29.

It will also be seen from Figure 29 that the value obtained for this rate is dependent on the medium in which it is measured. The apparent rate is greater in monomer than in chloroform. This phenomonen is probably due to the various interactions which take place between the several species present in the reacting mixtures and has been discussed in Chapter 9.

7.6.3. Techniques used for the measurement of the kinetic chain life-time.

The modified rotating sector method[50] was devised because of the inherent difficulties and errors which are introduced when measuring very short life-times by the non-stationary state and the normal rotating sector methods. In the former, instrument lags and personal response factors involve considerable errors in the measurement of life-times of less than 0.5 seconds. Another not inconsiderable source of error lies in the difficulty of accurate extrapolation.

The normal rotating sector technique is somewhat laborious and reaction will have proceeded to a considerable extent during a life-time determination, rendering the results suspect. Difficulty in reproducing feed-composition will introduce a further error if an attempt is made to measure the life-time at as low an extent conversion as possible (i.e., by using a freshly filled dilatometer at each sector speed).

The modified rotating sector method described in the present work combines both the above methods and obtains the advantages of each. Errors due to personal response, etc are considerably reduced as are extrapolation difficulties. A rate measurement can be made in about 10 seconds, so that a typical life-time determination (allowing 25 minutes between rate measurements for the system to attain thermal equilibrium) will take under 6 hours. The actual period of irradiation will be a few minutes, so that the life-time may be measured over a very low extent reaction. One disadvantage compared with the normal rotating sector method is that for flash-times approaching 1 second or more, cooling effects become increasingly evident. Thus, in practise, the method is ideally suited for measuring kinetic chain life-times in the region of 0.1-0.5 seconds.

Good agreement was obtained for the value of the kinetic chain life-time as measured by both methods. (Table 14, page 107). It would appear, nevertheless, that for kinetic chain life-times of this order, the modified rotating sector method is much more reliable.

7.6.4. Efficiency of initiation.

In the calculation of the velocity coefficients, the initiator efficiency has been neglected. There are two reasons for this omission. Firstly, its value for the present reaction is unknown. Secondly, no attempt was made to evaluate it since the magnitude of the rate of formation of trichloromethyl radicals varies depending on the medium in which it is measured. In the presence of such uncertainty, it was considered unjustifiable to apply a doubtful correction factor. It has thus been assumed that the rate of formation of trichloromethyl radicals is numerically equal to the rate of chain initiation.

The significance of the individual values obtained for the velocity coefficients has been discussed in Chapter 9.

Chapter 8. The photochemical reaction between vinyl chloride and BTCM.

As mentioned in Chapter 1, by comparing the velocity coefficients governing the reaction between various monomers and BTCM it should be possible to obtain a general picture of monomer reactivities towards the same radical. More specifically, by comparing the velocity coefficients for the reaction between BTCM and vinyl acetate with those for the reaction between BTCM and vinyl chloride, it was hoped to compare the reactivities of the two monomers towards the trichloromethyl radical. The photochemical polymerisation of vinyl chloride sensitised with AIBN was also investigated to determine if, under conditions of large excess vinyl chloride, BTCM acted as a normal initiator.

8.1.1. Outline of method used for evaluating the velocity coefficients.

The underlying principles involved in the evaluation of the velocity coefficients for the photochemical reaction between vinyl chloride and BTCM are identical to those applied to the study of the reaction between vinyl acetate and BTCM.

The reaction products were isolated by the distillation technique and examined as in the previous reaction. It was impossible to measure the specific heat of vinyl chloride by the calorimeter method, so this factor was obtained using Kopp's Rule.[51]

The dependence of rate of reaction on reactant concentration was measured over a wide range as was the intensity exponent for the reaction.

The kinetic chain life-time, rate of initiation and rate of reaction were determined as before under suitable conditions for the evaluation of the velocity coefficients.

8.2. Theory.

8.2.1. Evaluation of the velocity coefficients.

8.2.1a. BTCM in excess.

Consideration of equation (5.5), page 52,

$$-\frac{d[M]}{dt} = \frac{k_2 . I^{\frac{1}{2}} . [M]}{k_4^{\frac{1}{2}}} \qquad \text{...........(5.5)}$$

will show that if, in excess BTCM, reaction 2*is rate-controlling, then the rate of reaction will be directly proportional to the monomer concentration and proportional to the square root of the BTCM concentration.

8.2.1b. Monomer in excess.

Equation (5.13), page 54, gives,

$$-\frac{d[M]}{dt} = \frac{k_3 . I^{\frac{1}{2}} . [BTCM]}{k_6^{\frac{1}{2}}} \qquad \text{..........(5.13)}$$

Thus, if in this case, step 3* is rate-controlling, the rate of reaction will be proportional to the three-halves power of the BTCM concentration and independent of monomer concentration.

---

* Refers to reaction scheme on page 6

8.2.1c. Monomer in large excess.

If, under these conditions, polymerisation occurs, then from equation (5.18), page 56,

$$-\frac{d[M]}{dt} = \frac{k_p . I^{\frac{1}{2}} . [M]}{k_t^{\frac{1}{2}}} \qquad \ldots\ldots\ldots\ldots(5.18)$$

Thus, if the polymerisation follows the normal kinetics, the rate should be proportional to the monomer concentration and to the square root of the BTCM concentration.

Under conditions where the predicted dependences are obtained therefore, the velocity coefficients may be evaluated as in Chapter 7.

8.2.2. Kopp's rule for the estimation of specific heats.[51]

By summing the values of the atomic heats of the constituent atoms, the specific heat of a molecule may be estimated. The values given for the atomic heats are as follows:-

C - 2.8, H - 4.3, Cl - 8 cal/gm atom.

Thus, the specific heat of vinyl chloride (C_2H_3Cl) $= \dfrac{26.5}{62.5}$ cal/gm

$= 0.43$ cal/gm.

8.3. Results.

8.3.1. Reactants and reaction products.

Table 16 shows the results of experiments to measure the physical properties which are necessary for further evaluations.

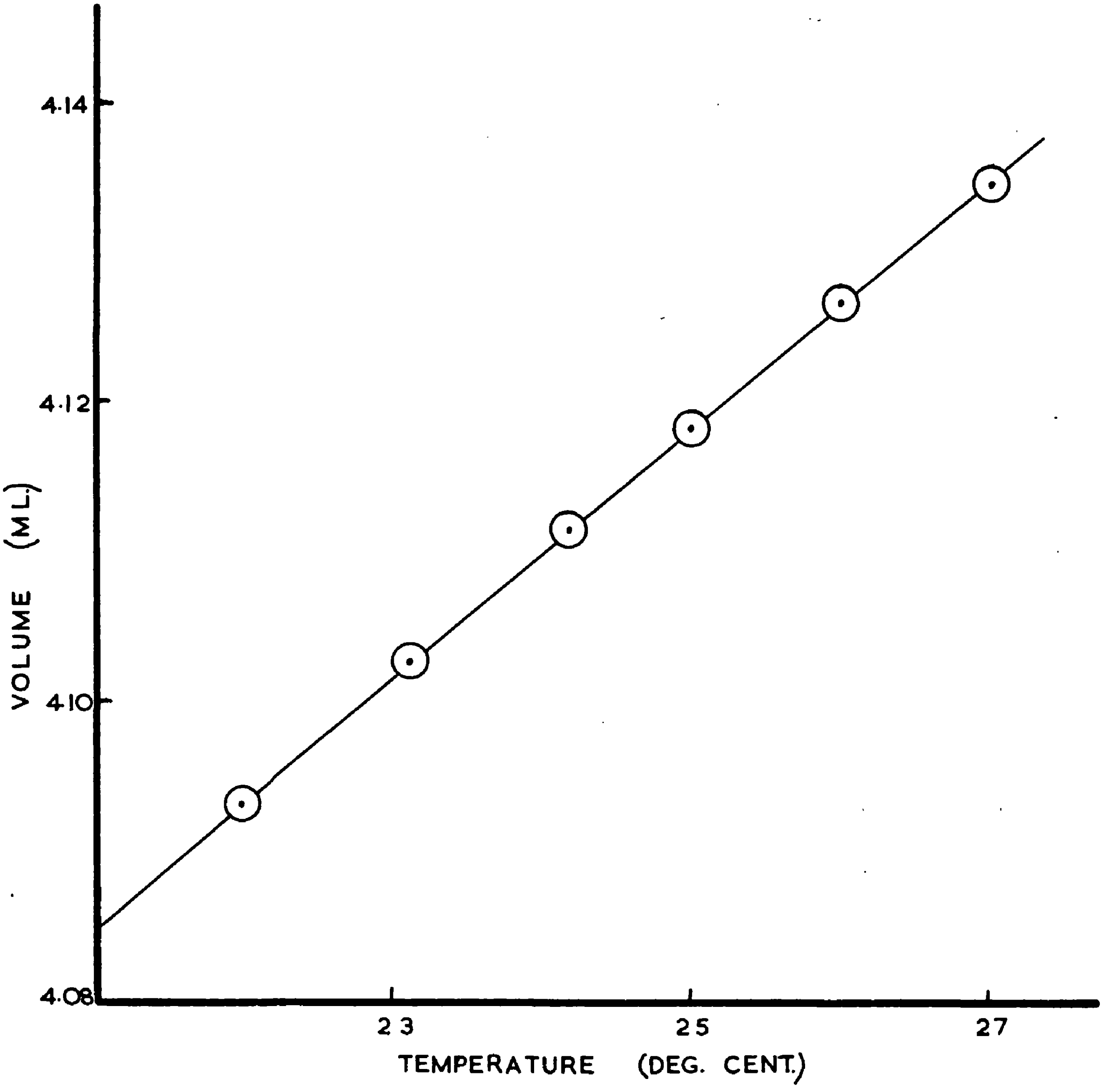
Table 16. Physical properties of the reactants.

	BTCM	Vinyl chloride (liquid)
Specific heat ($cal.gm^{-1}$)	0.18	0.43
Expansion coefficient (deg^{-1})	1.062×10^{-3}	2.0×10^{-3}
Density (25°C) ($gm.ml^{-1}$)	2.006	0.905
Molecular weight	198	62.5

The value of the expansion coefficient of vinyl

FIGURE 33

EXPANSION COEFFICIENT OF VINYL CHLORIDE



chloride was calculated from Figure 33, which shows its volume as a function of temperature. The liquid density of vinyl chloride was also obtained from the data collected in this determination.

The products of the reaction between vinyl chloride and BTCM were isolated by the distillation technique and several of their properties are detailed in Table 17.

Table 17. Products of the reaction between vinyl chloride and BTCM.

Mole ratio (VCl/BTCM)	Degree of polymerisation	Density (25°C) ($gm.ml^{-1}$)
200:1	polymer precipitates	ca. 1.4[52]
14:1	1.76	1.77
1.5:1	1.0	1.825

8.3.2. Heat of reaction between vinyl chloride and BTCM.

Figure 34 shows initial expansion as a function of time. Figure 35 shows rate of contraction due to reaction followed by rate of contraction due to cooling on the

FIGURE 3 4

TYPICAL INITIAL EXPANSIONS.

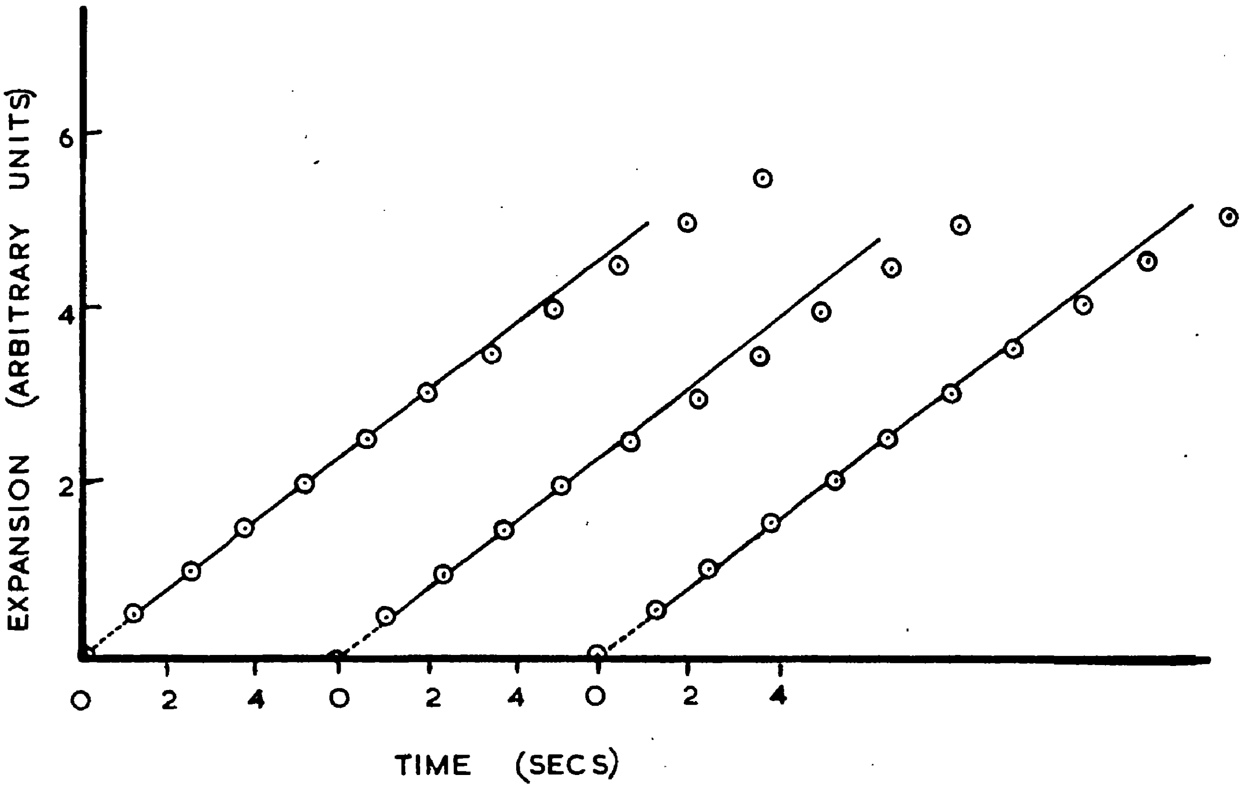
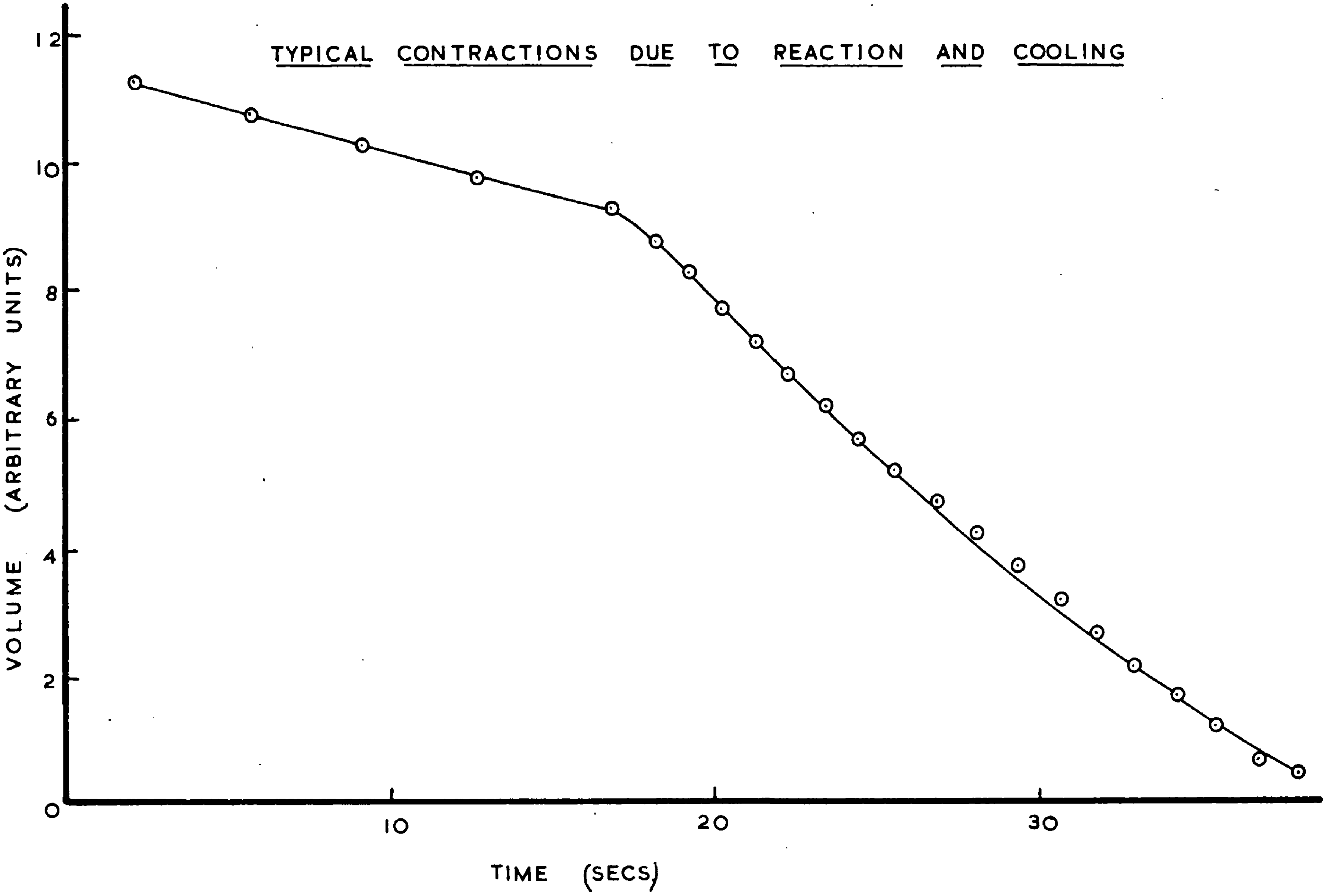


FIGURE 35

TYPICAL CONTRACTIONS DUE TO REACTION AND COOLING



cessation of irradiation. From such curves was obtained the ratio of $\mathcal{E}/Z$ and by a similar treatment to that described in Chapter 6, the following values were obtained for the heat of the reaction at various concentrations of the reactants. (The average values from a number of experiments have been taken).

Table 18. The heat of the photochemical reaction between vinyl chloride and BTCM.

Mole ratio (VCl/BTCM)	$\frac{\Upsilon + Z}{Z}$	$\frac{\text{Cooling rate}}{\text{Reaction rate}}$	Average ratio (ξ/Z)	ΔH (Kcal/mole)
3.87×10^{-3} mole.l^{-1} AIBN	4.49	4.32	4.40	20.9
ca 200:1	4.04	4.61	4.32	20.5
ca 1:1	3.73	3.73	3.73	22.5
ca 1:6	3.37	3.29	3.33	26.5

8.3.3. Dependence of rate of reaction on reactant concentration.

Figures 36 to 41 show the actual curves which were obtained in this part of the work. The results are quoted in Table 19.

FIGURE 36

RATE-DEPENDENCE ON REACTANT CONCENTRATION IN EXCESS BTCM

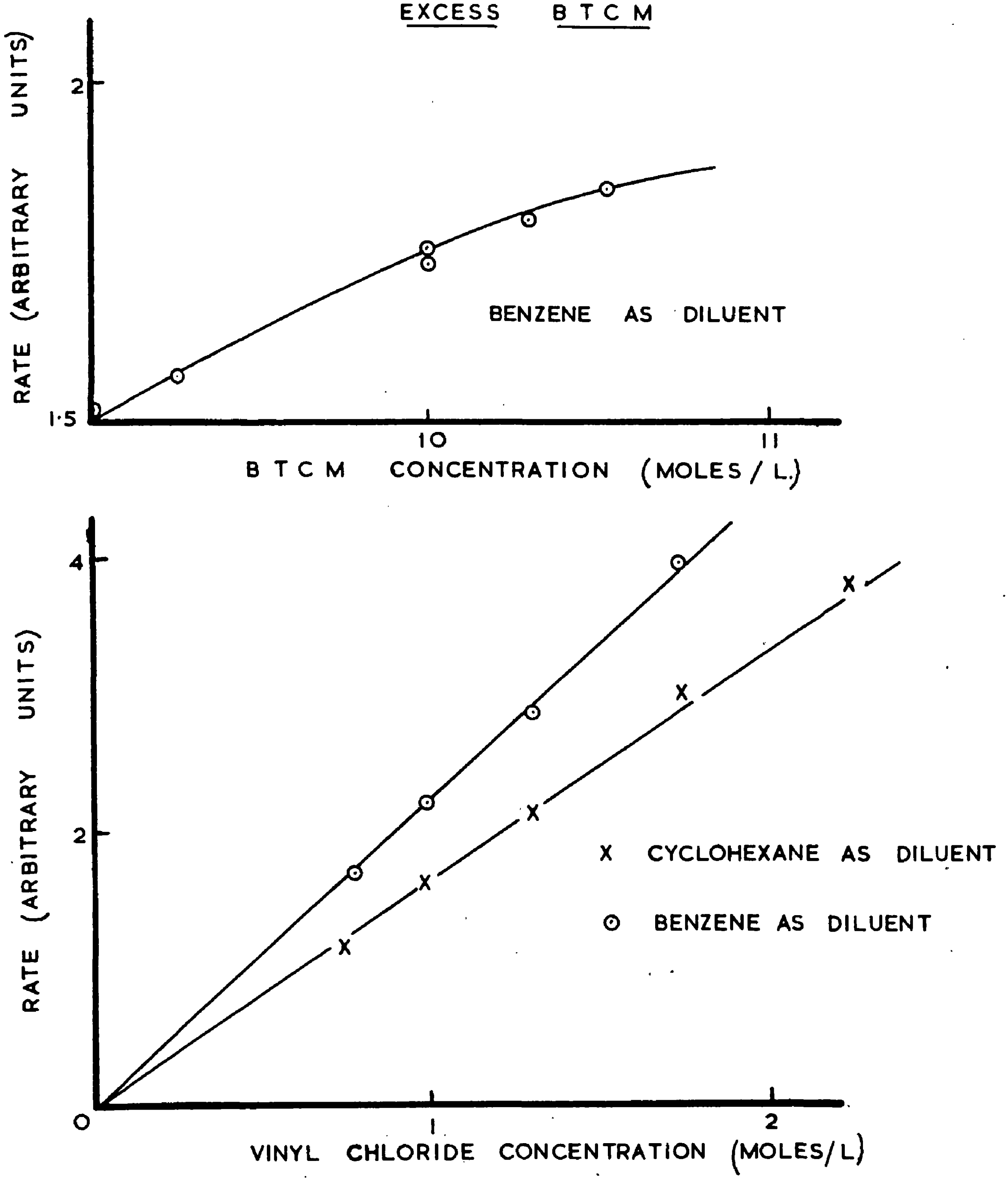


FIGURE 37

RATE - DEPENDENCE ON VINYL CHLORIDE CONCENTRATION IN EXCESS B T C M.

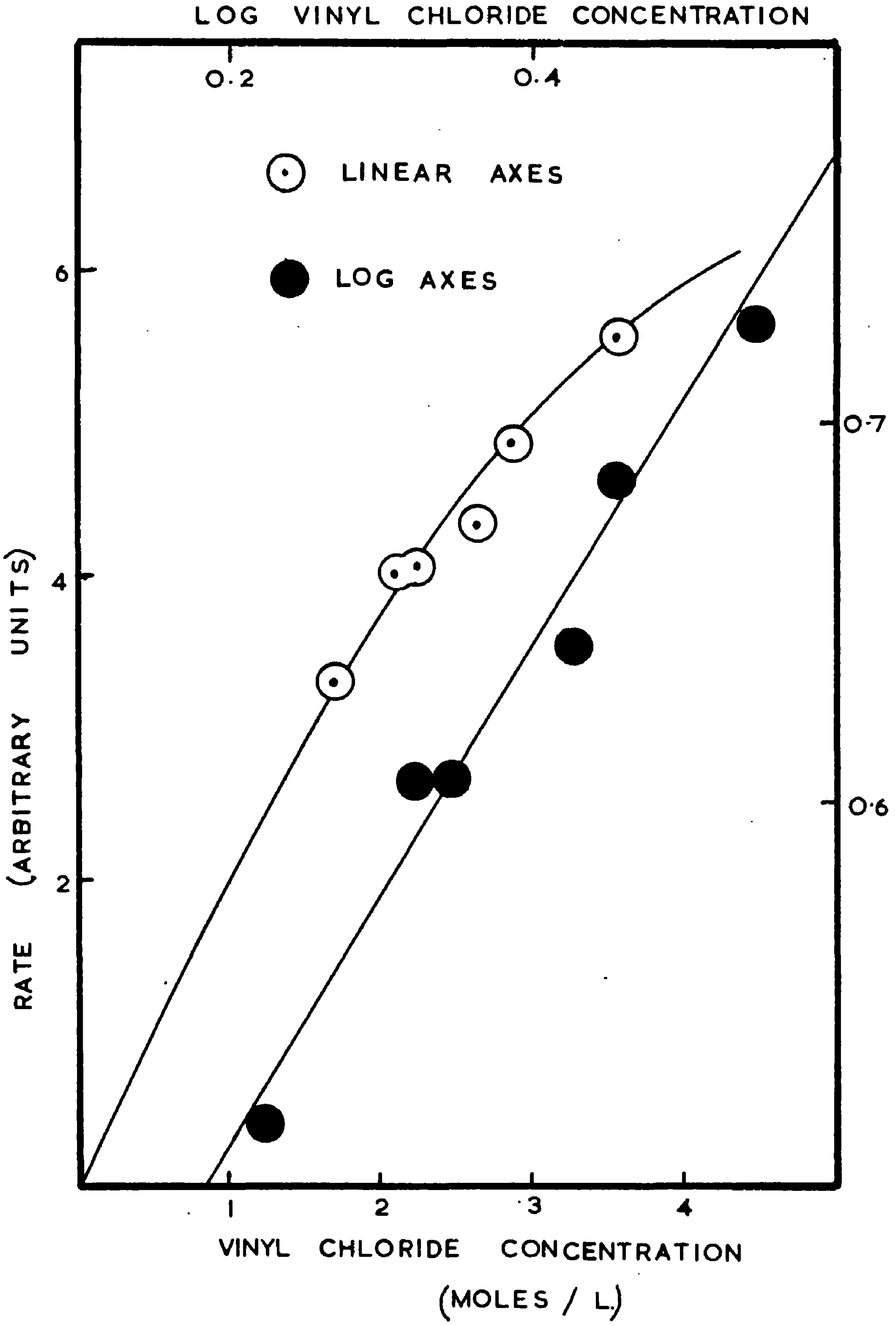


FIGURE 38

RATE - DEPENDENCE ON VINYL CHLORIDE WHEN IN EXCESS BENZENE AS DILUENT.

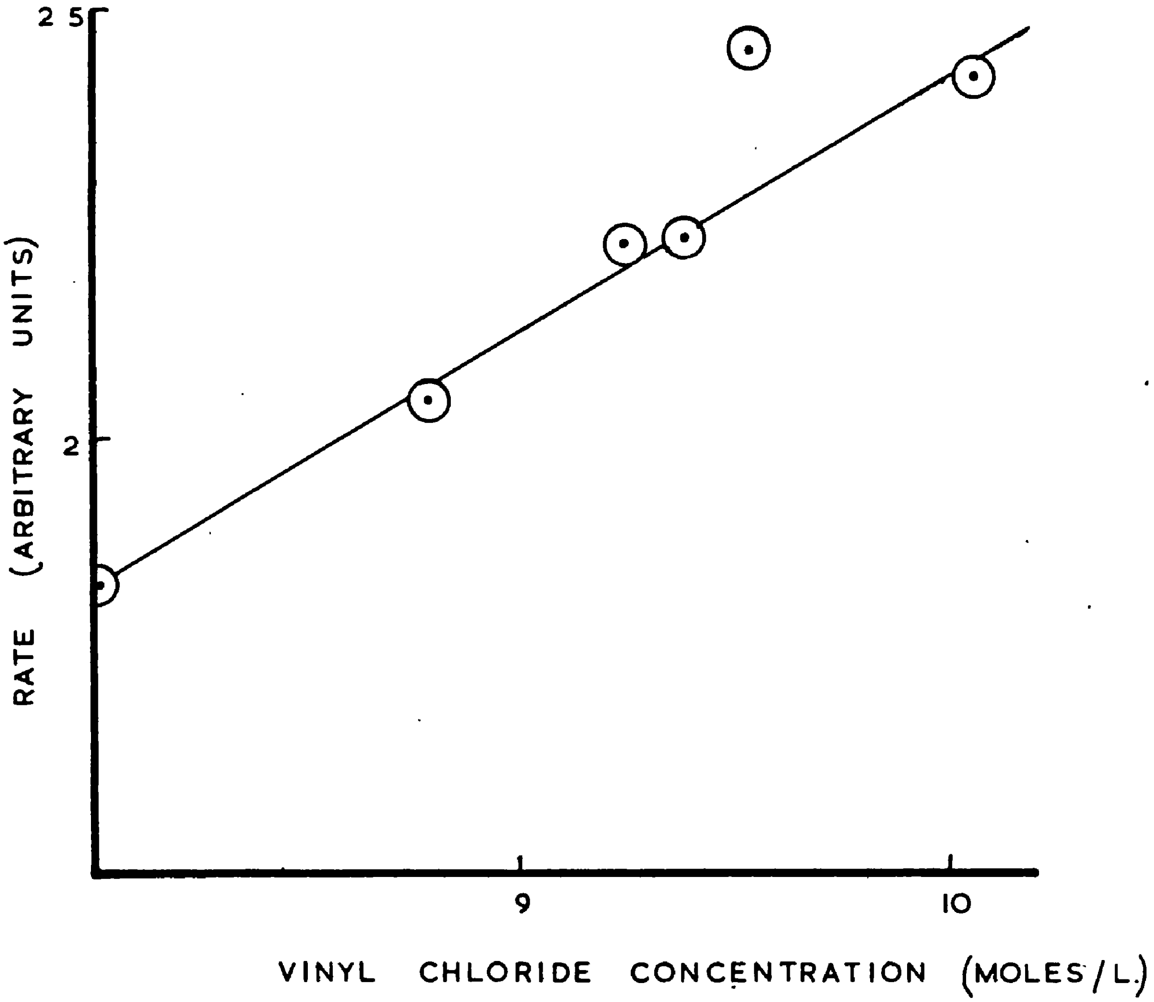


FIGURE 39

RATE - DEPENDENCE ON B T C M CONCENTRATION IN EXCESS VINYL CHLORIDE BENZENE AS DILUENT

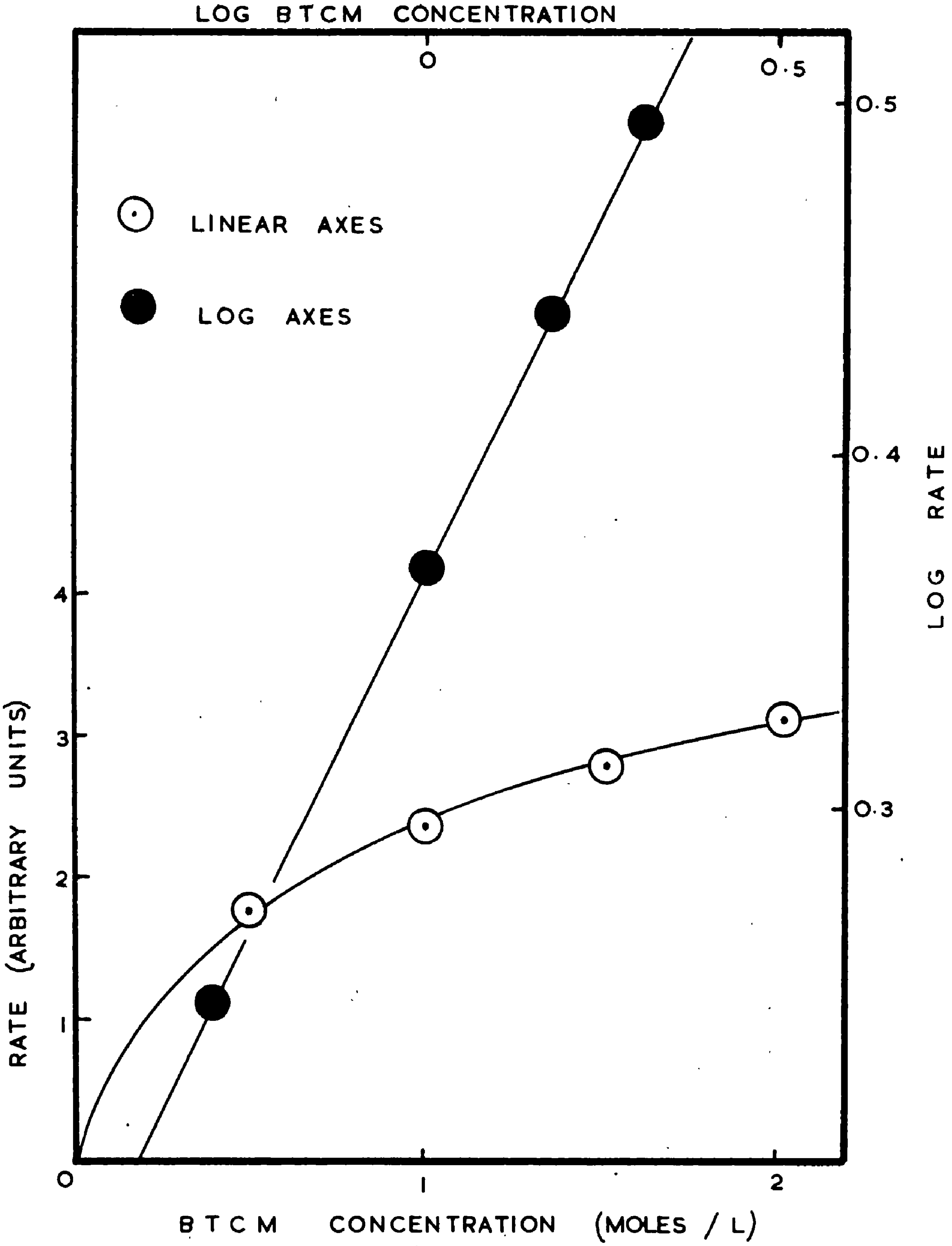


FIGURE 40

RATE - DEPENDENCE ON BTCM CONCENTRATION IN VERY LARGE EXCESS VINYL CHLORIDE.

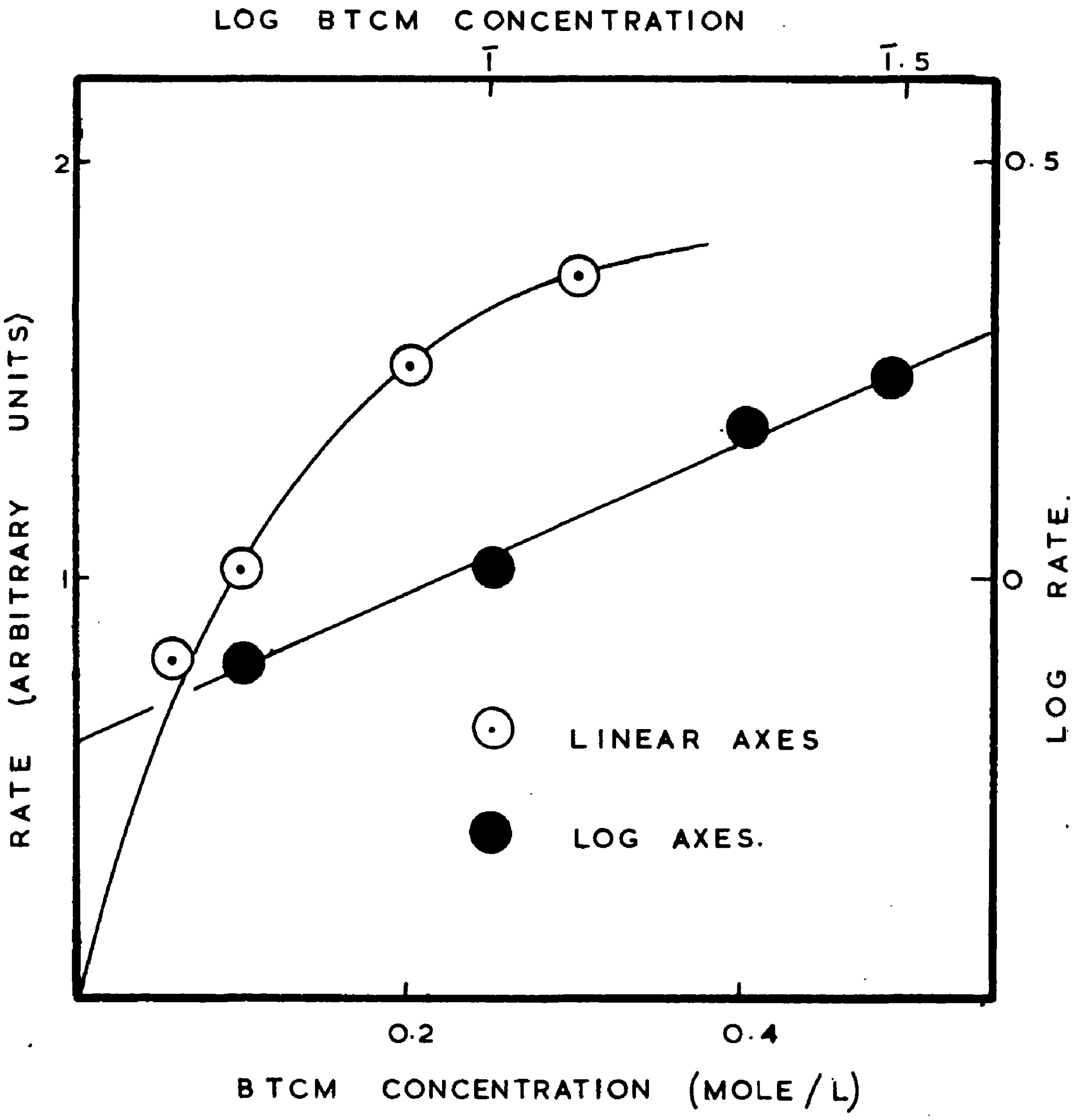


FIGURE 41

RATE - DEPENDENCE ON BTCM CONCENTRATION OVER A WIDE RANGE BENZENE AS DILUENT

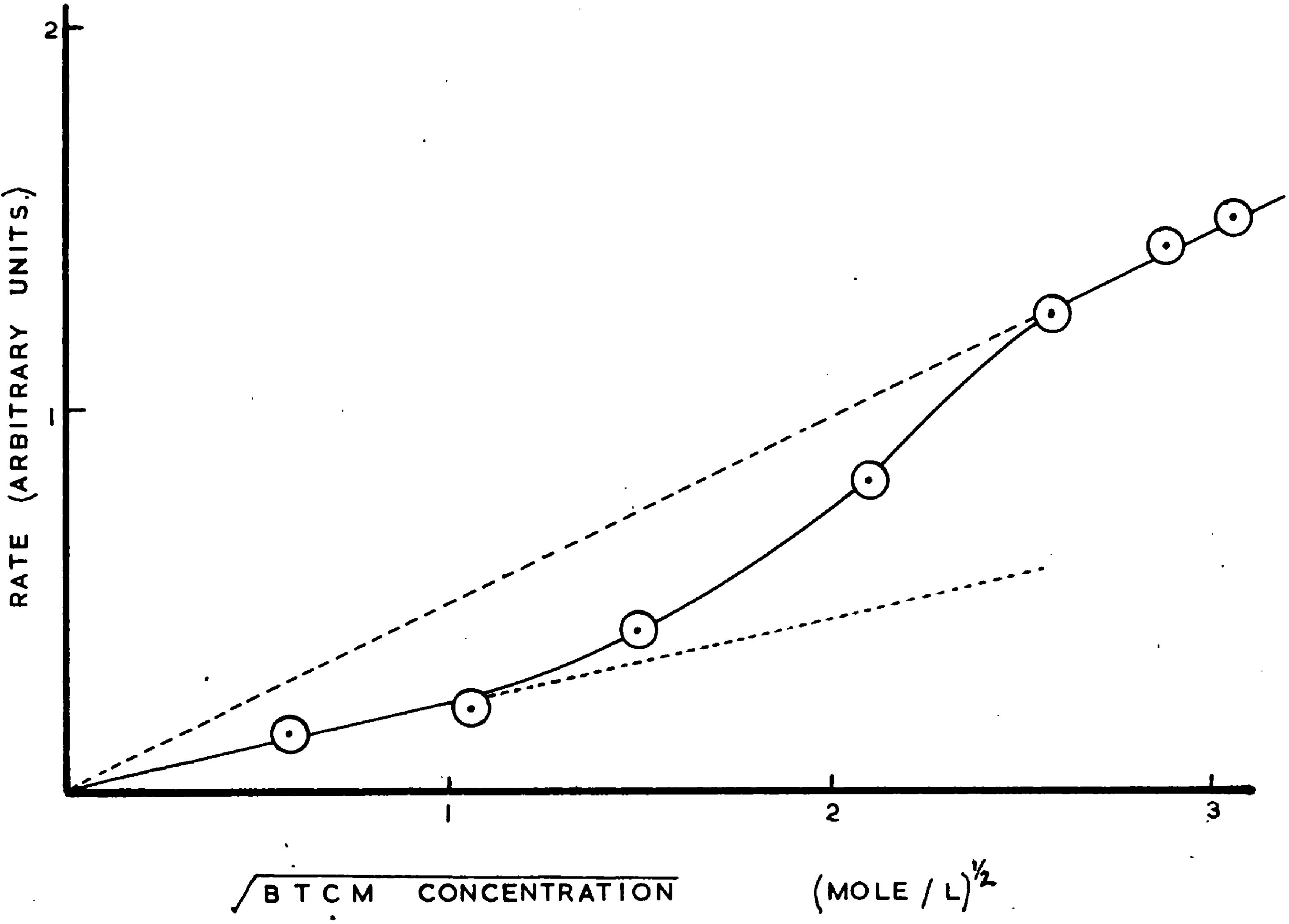


Table 19. Dependence of rate of reaction on reactant concentration.

Excess Reagent	Concentration range (mole ratio)	Diluent	Varying reactant	Rate-dependence
BTCM	10:1 to 8:1	benzene	BTCM	0.5
BTCM	9:1 to 4:1	benzene	VCl	1.1
BTCM	9:1 to 3:1	cyclohexane	VCl	1.1
VCL	26:1 to 7:1	benzene	BTCM	0.5
VCl	15:1 to 11:1	benzene	VCl	1.0
VCl	160:1 to 50:1	-	BTCM	0.5
BTCM	7:1 to 2:1	-	VCl	0.66

It would appear from Table 19 that the following dependences are obeyed:-

BTCM in excess,

$$\text{Rate} \propto [\text{BTCM}]^{0.5} . [\text{VCl}]^{1.1}$$

Vinyl chloride in excess,

$$\text{Rate} \propto [\text{BTCM}]^{0.5} [\text{VCl}]^{1.1}$$

Vinyl chloride in very large excess,

$$\text{Rate} \propto [\text{BTCM}]^{0.5} [\text{VCl}]^{?}$$

the dependence on vinyl chloride concentration could not be measured under these circumstances.

Figure 41 is similar in nature to Figures 36 to 40, but in this case, the rate-dependence has been measured over a much wider concentration range. From this curve it will be seen that a discrepancy from the above results arises in the middle of the range. This point has been discussed later.

8.3.4. Order of termination.

Table 20 shows the results of intensity exponent determinations which were carried out at various mole ratios of BTCM to vinyl chloride.

Table 20. Intensity exponent for the photochemical reaction between vinyl chloride and BTCM.

Mole ratio (VCl/BTCM)	$\left\{\begin{array}{c}\text{Light}\\ \text{Intensity}\end{array}\right\}^{\frac{1}{2}}$ (relative)	Rate (relative)	Intensity exponent.
10:1	1	1	0.51
	0.56	0.55	
4:1	1	1	0.53
	0.56	0.54	
1:8	1	1	0.50
	0.56	0.56	

8.3.5. Evaluation of the ratio of $k_p/k_t^{\frac{1}{2}}$.*

Results of the rate of initiation measurements have been detailed in Chapter 7 (see Figure 29). The rate of reaction, measured dilatometrically and calculated as in Chapter 6, together with the resulting values of $k_p/k_t^{\frac{1}{2}}$ obtained by equations (5.5) and (5.18) (pp. 117, 118) are shown in Tables 21, 22 and 23.

Table 21. Evaluation of the ratio of $k_p/k_t^{\frac{1}{2}}$* from inhibition measurements (vinyl chloride as medium).

[BTCM] (mole.l^{-1})	[VCl] (mole.l^{-1})	Reaction** rate x 10^5	I x 10^8 **	$\frac{k_p}{k_t^{\frac{1}{2}}}$ x 10^2 +
9.24	1.26	6.0	53.0	6.57
0.087	14.40	3.6	0.5	3.55

---

* Numerical subscripts have not at this stage been assigned to the velocity coefficients, since these will be different under the various conditions. In general terms, k_p is the velocity coefficient for propagation and k_t the velocity coefficient for termination by the mutual combination of pairs of

radicals.

** In units of mole.l.$^{-1}$ sec^{-1}

+ In units of (l.mole^{-1} sec^{-1})$^{\frac{1}{2}}$

Table 22. Evaluation of the ratio of $k_p/k_t^{\frac{1}{2}}$ from inhibition measurements (chloroform as medium).

[BTCM] (mole,l^{-1})	[VCl] (mole.l^{-1})	Reaction** rate x 10^5	I x 10^{8}**	$\frac{k_p}{k_t^{\frac{1}{2}}}$ x 10^2 +
9.24	1.26	6.0	26.0	9.4
0.087	14.40	3.6	0.25	5.1

** mole.l^{-1} sec^{-1} + (l.mole.$^{-1}$ sec^{-1})$^{\frac{1}{2}}$

Table 23. Evaluation of the ratio of $k_p/k_t^{\frac{1}{2}}$ for the polymerisation of vinyl chloride sensitised with 3.87 x 10^{-3} mole.l^{-1} AIBN.

Medium ++	VCl (mole.l.$^{-1}$)	Reaction** rate x10^4	I x 10^{8}**	$k_p/k_t^{\frac{1}{2}}$ x 10^2 +
Chloroform	14.50	1.52	2.56	6.56
Benzene			11.3	3.11

** $mole.l.^{-1}sec^{-1}$

\+ $(l.mole.^{-1}sec^{-1})$

++ Refers to the medium in which the rate of initiation experiments were carried out.

The rate of initiation data appearing in Table 23 was kindly supplied by Mr S.A. McIntosh.[53]

8.3.6. Evaluation of the ratio of k_p/k_t.

Figure 42 shows initial expansion on the commencement of irradiation as a function of time from which was obtained the kinetic chain life-time. Figure 43 is a typical modified rotating sector determination of the same parameter. By a similar treatment to that described previously, the following results were obtained.

FIGURE 42

TYPICAL NON-STATIONARY STATE MEASUREMENTS FOR VINYL CHLORIDE - BTCM REACTION

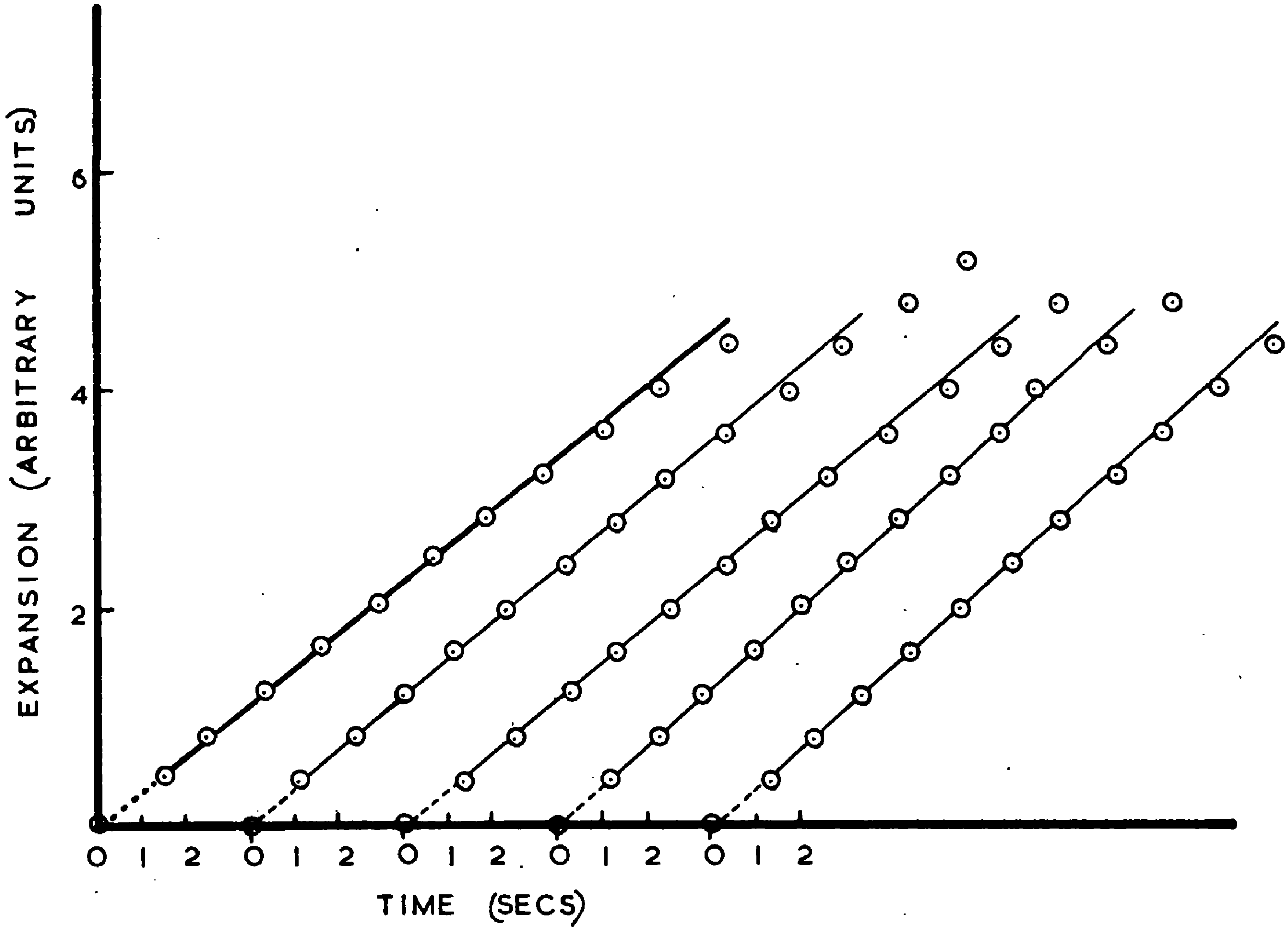


FIGURE 43

TYPICAL ROTATING SECTOR CURVE FOR VINYL CHLORIDE - BTCM REACTION.

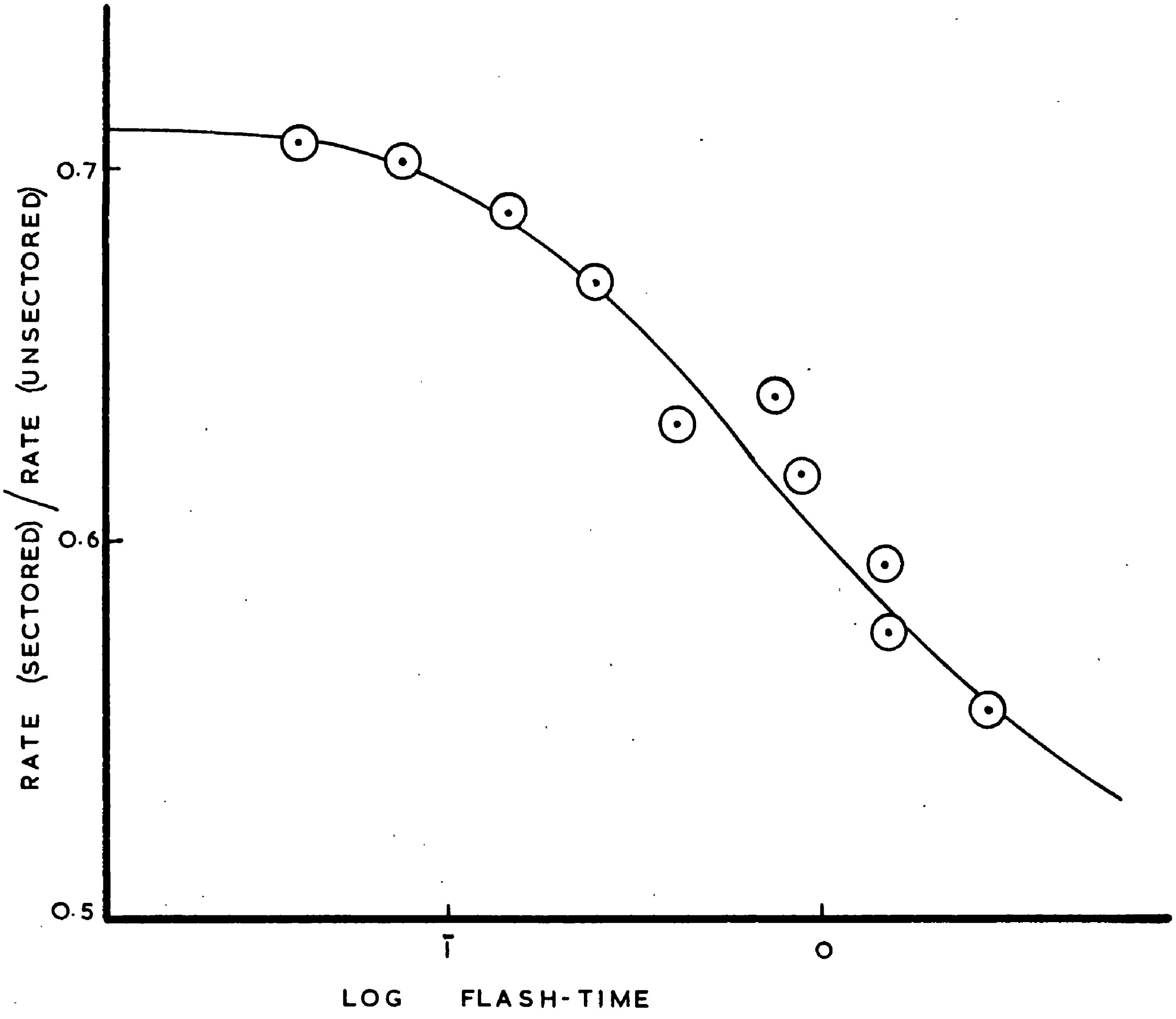


Table 24. Evaluation of the ratio of k_p/k_t from kinetic chain life-time measurements.

[BTCM] (mole.l^{-1})	[VCl] (mole. l^{-1})	Reaction** rate x 10^5	τ (sec)		k_p/k_t x 10^6
			Sector*	N.S.S.*+	
9.24	1.26	9.42	0.06	-	4.50
0.087	14.40	6.45	0.16	0.17	0.74
***-	14.50	15.2	0.13	0.13	1.36

** In units of mole.$l.^{-1}$ sec^{-1}

* Refers to the modified rotating sector technique.

*+ Refers to the non-stationary state technique.

*** Initiated with 3.87 x 10^{-3} mole.l^{-1} AIBN

It should be mentioned that allthe measurements carried out for the evaluation of the velocity coefficients were at 25°C.

8.3.7. Calculation of the individual velocity coefficients for the reaction.

From the two separate ratios of the velocity coefficients (i.e., k_p/k_t and $k_p/k_t^{\frac{1}{2}}$), the individual values are easily obtained. This was done to give the following results.

Table 25. The velocity coefficients involved in the photochemical reaction between vinyl chloride and BTCM at 25°C.

Feed-composition (VCl/BTCM)		Chloroform* as medium	Vinyl chloride* as medium
1:7.35	k_p^+	1950	990
	k_t^+	4.3×10^8	2.2×10^8
165:1	k_p^+	3510	1700
	k_t^+	4.8×10^9	2.3×10^9

* Refers to medium in which the rate of initiation determination was carried out.

\+ Velocity coefficients in units of l.mole^{-1}sec^{-1}

Table 26. The velocity coefficients for the photochemical polymerisation of vinyl chloride at 25°C sensitised with 3.87×10^{-3} mole.l^{-1} AIBN.

Velocity coefficient (l.mole.$^{-1}$sec^{-1})	Chloroform* as medium	Benzene* as medium
k_p	3130	710
k_t	2.3×10^9	0.52×10^9

* Refers to medium in which the rate of initiation experiments were carried out.

8.4. Discussion.

In Table 16 (page 119) are quoted the physical properties of the reactants which are required for the evaluation of the heat of reaction. The value obtained for the liquid density of vinyl chloride is in good agreement with the value found in the literature,[54] and the coefficient of expansion and specific heat both seem of a reasonable magnitude for this type of compound.

Table 17 (page 120) shows that the molecular weight of the reaction product increases with increase in mole ratio of vinyl chloride to BTCM in the feed. This, of course is to be expected from polymerisation theory. Since at a feed mole ratio of approximately 1:1 vinyl chloride to BTCM a 1:1 adduct is produced (ie, T(VCl)Br) it is obvious that in excess BTCM, product of a higher molecular weight is unlikely. This was not checked experimentally as extremely large quantities of BTCM would be required to give a measurable yield of product under these circumstances. It also appears that the density of the various reaction products increases with decreasing molecular weight as would be expected.

Table 18 (page 121) shows the values obtained for the heat of reaction at various feed-compositions. The values for the AIBN and BTCM-initiated polymerisations are in close agreement. This indicates that at very high mole ratios of vinyl chloride to BTCM the normal polymerisation reaction takes place. The values obtained over this range are in good agreement with those normally found for the heats of polymerisation of similar monomers.[55]

A knowledge of the value of the heat of reaction also enables overall reaction rates to be calculated from subsequent non-stationary state and modified rotating sector experiments.

The interpretation of the results of the rate-dependence experiments is subject to the same difficulties as have been described in Chapter 5 (pp. 57-8, 60-1). It does appear, however, from the results shown in Table 19 (page 122), from Figures 36 to 41 and from intensity exponent considerations (Table 20, page 123) that in the presence of excess BTCM, the rate-controlling step is the addition of a trichloromethyl radical to a vinyl chloride molecule (step 2, page 6) and that termination is governed by reaction 4 (page 6). The change in slope displayed by Figure 41 might indicate that as the vinyl chloride concentration is increased, a tendency is shown for reaction 3 (page 6) to become rate-controlling. This would involve a dependence on the BTCM concentration to the power 3/2 as opposed to 1/2. Before reaction 3 becomes completely rate-controlling however, polymerisation kinetics take control, with a square root dependence on initiator concentration. It thus follows that in conditions of excess BTCM, k_p and k_t are equivalent to k_2 and k_4 respectively. For very large excess of vinyl chloride over BTCM concentration, k_p will be the velocity coefficient for the propagation reaction in the photochemical polymerisation of vinyl chloride sensitised with BTCM and k_t will be the velocity coefficient for termination through the interaction of pairs of radical chains.

Over the range of concentrations used, Table 20 (page 123) shows that termination is fairly accurately second order, so that the kinetics derived earlier may be applied to the system.

The determination of the kinetic chain life-time, rate of reaction*, etc. has been discussed earlier and with the exception of the note below requires no further comment. As will be seen from Table 24 (page 127), the values obtained for the kinetic chain life-time by both methods were in excellent agreement once more.

The significance of the actual values obtained for the velocity coefficients has been discussed in Chapter 9.

* In the case of excess BTCM, the reaction rate in absolute units was calculated as in Chapter 6, since the 1:1 adduct was produced.

For excess vinyl chloride (polymerisation conditions), the rate of removal of monomer was calculated.

Chapter 9. General Discussion.

In the preceding chapters, the techniques and methods used in the work, their limitations, the specific results obtained and the scheme of work have been discussed. The present chapter deals with the broader principles involved and the conclusions which have been reached. This has been done to avoid submerging the latter in a mass of detail.

The discussion of results obtained in this type of research is somewhat difficult because of the inherent errors involved in most of the methods for measuring parameters involved in chain reactions. Consequently, it is not easy to distinguish between significant differences in results and differences which are due to the limitations of the techniques avaliable at present.

In evaluating velocity coefficients, for instance, a knowledge of the kinetic chain life-time and the rate of initiation is required as well as the rate of reaction. It is difficult to ensure the accuracy of the first-mentioned to within a factor of 2. The apparent rate of initiation may vary by a factor of 3 or more, depending on the medium used in the estimation. It is obvious therefore that great care must be exercised in ascribing any particular significance to several of the results. With this proviso in mind, the general picture obtained from the results of the work will be discussed.

From the results quoted in Chapter 3, it is obvious that over a very wide range of concentrations, no polymer is produced by the photochemical reaction between vinyl acetate and BTCM. This fact, of course, is not in agreement with the results of Melville et al,[7] whose values for the velocity coefficients indicated that polymerisation should occur.

The only apparent explanation for this anomaly is that either the $T(VA)^{\cdot}$ radical produced by step 2 (page 6) is so unreactive towards vinyl acetate that further addition to this monomer is extremely unlikely or that the value obtained by Melville et al[7] for k_3 (see Chapter 1) is incorrect and should be much greater.

With the former idea in mind, the photochemical polymerisation of vinyl acetate was attempted, using benzoyl peroxide as initiator and in the presence of the 1:1 adduct of vinyl acetate and BTCM. The reasoning behind this attempt has been described in Chapter 3. As the predicted complete inhibition did not occur, it would appear that the first of these alternatives is not the cause of the absence of polymerisation.

As the above line of research was somewhat unsatisfactory, the possibility was examined that the value obtained by Melville et al[7] for k_3 might be incorrect. The first method used was the attempted measurement of the ratio of the velocity coefficient for the chain transfer of a BTCM molecule with a $T(VA)_n^{\bullet}$ radical (k_{tr}) to the velocity coefficient for the addition of the same radical to monomeric vinyl acetate (k_p) . When $\underline{n} = 1$, k_{tr} and k_p will be synonomous with k_3 and k_7 (pp. 6, 12). It was hoped that this procedure would give a precise value for the ratio of the probability of transfer to the probability of polymerisation, ie, that the ratio of k_{tr}/k_p would be independent of the $\overline{DP}$ of the radical. This however, did not prove to be the case.

Figure 8 shows that for growing radicals of high $\overline{DP}$, the value of k_{tr}/k_p is 0.6 whereas for very short chains (low $\overline{DP}$), Figure 9 shows that k_{tr}/k_p is 40 or more. The result of the experiment in which one half of the reaction product was isolated by the distillation technique and the other by precipitation to give products of $\overline{DP}$ 25.5 and 1200 is consistent with the above values so long as the value of k_{tr}/k_p decreases rapidly as the $\overline{DP}$ of the attacking radical increases to 4 or greater. It follows that for systems in which the initial mole ratio of BTCM to vinyl acetate is of the order of 10^{-2}, the expected $\overline{DP}$ (using $k_{tr}/k_p = 40$) would be less than 4 and no high polymer would be formed. For mole ratios of around 2×10^{-3}, the calculated $\overline{DP}$ would be about 12 using a value of 40 for k_{tr}/k_p and about 830 using a value of 0,6 for k_{tr}/k_p.

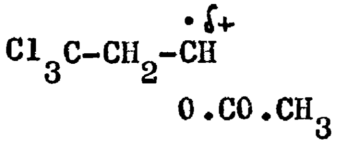
Obviously the fact that a mixture of low and high molecular weight material is produced in the region in which this experiment was carried out lends weight to the idea that the value of k_{tr}/k_p falls rapidly as the size of the radical increases beyond DP = 4. If, on the other hand, the change in value of k_{tr}/k_p were very gradual, the unusual distribution of high and low polymer would not be produced and the discontinuity in Figure 9 would not be evident.

The rate of reaction (measured by contraction) was also obtained for the different BTCM/vinyl acetate mole ratios in the feed and is shown in Figure 10. It will be seen from this that the rate is fairly constant for low BTCM/vinyl acetate mole ratios and falls very rapidly in the region where high polymer is not formed in the reaction. The rate again increases in the region where the 1:1 adduct is produced. This peculiar rate curve is difficult to explain. It may be that the value of k_p falls rapidly for radicals of $\overline{DP}$ 2, 3, and 4 and then gradually increases as the growing radical chain increases in length. This idea gains some support from the recent work of Robb and Vofsi[10] who found a 35-fold fall in the value of k_p as the $\overline{DP}$ changed from 2 to 3 in the telomerisation of styrene with BTCM. The matter will however, remain undecided until more accurate methods are available for separating the reaction products, and molecular weight distributions of the products are obtained.

The difference between the values of k_{tr}/k_p for small and large radicals is more readily understood, since the influence of the trichloromethyl group upon the polarity of the free radical $T(VA)_n^{\bullet}$ would be expected to decrease rapidly as n increases. Now, Price[56] has shown from co-polymerisation studies that the reactivity of a monomer is influenced by the polar characteristics of the radical and monomer.

Recently, several workers[57,58] have successfully applied these ideas to chain transfer reactions. Using their approach, the following conclusions were reached.[20]

The trichloromethyl group, having a negative inductive effect will induce a slight positive charge on the $T(VA)_1^{\bullet}$ radical as shown:-



$$\mathrm{Cl_3C{-}CH_2{-}}\underset{\mathrm{O.CO.CH_3}}{\overset{\bullet\,\delta+}{\mathrm{CH}}}$$

As the $\overline{DP}$ of this radical increases, the electrophilic effect of the trichloromethyl group on the active centre of the radical will decrease, so that as n increases, the negativity of the active centre also increases. (The contributory effect of the acetate grouping will be independent of n).

The reactivity of this radical towards a vinyl acetate molecule (e-value negative from the Alfrey-Price scheme) and thus k_p, the velocity coefficient for the propagation reaction, would be expected to decrease with increasing value of n. The reactivity of the $T(VA)_n^{\bullet}$ radical towards BTCM (e-value positive from a comparison with data for tetrabromomethane[57]) and thus k_{tr} would be expected to increase with increasing value of n. This of course, would result in the ratio of k_{tr}/k_p increasing with increase in value of n, which is in complete disagreement with the results.

If on the other hand, BTCM had a negative e-value, the reactivity of the $T(VA)_n^{\bullet}$ radical towards both vinyl acetate and BTCM would be expected to decrease with increasing value of n, but possibly at different rates. In other words, k_{tr} and k_p would both decrease. If the former decreased more rapidly than the latter, the nett effect would be an overall decrease in the ratio of k_{tr}/k_p with increasing $\overline{DP}$ of the $T(VA)_n^{\bullet}$ radical.

It seems extremely unlikely however that BTCM should have a negative e-value in view of the comparison with tetrabromomethane[57], but there is no other apparent reason for the inversion in values of k_{tr}/k_p . It should be pointed out however, that other workers have found a decrease in the value of k_{tr}/k_p with increasing radical $\overline{DP}$ for reactions similar to the present one. The photochemical reaction between BTCM and vinyl chloride (e-value negative) displays the same effect.[59]

The same effect was also found by Robb and Vofsi,[10] as mentioned previously, for the telomerisation of styrene with BTCM. These workers obtained a value of 240 for k_{tr}/k_p in the above system for a styryl radical of $\overline{DP} = 3$, whereas the value of k_{tr}/k_p obtained by other workers[57,60,61] for the styrene-tetrabromomethane system is in the region of 2 when high polymer is formed. One would normally expect tetrabromomethane to be a more efficient chain transfer agent than BTCM, which would make the drop in value of k_{tr}/k_p with increase in radical $\overline{DP}$ more marked for the styrene-BTCM reaction.

Robb and Vofsi[10] noted a marked change in this ratio as n changes from 2 to 3. Such a variation was not observed in the present work for values of n of from 1 to 4. It is believed that this is probably fortuitous since errors are considerable in the region where 1:1 adduct is produced and a ±50% error is possible.

Even considering the large errors which are possible in the present work, however, the value of about 2.5 expected from the results due to Melville et al[7] for the ratio of k_3/k_p seems to be far too low. In other words, for the production of low molecular weight telomers, the ratio of k_{tr}/k_p is greater than 40:1. This indicates that the value obtained by Melville et al[7] for k_3 is in error if k_7 (page 12) is similar in value to the velocity coefficient for propagation in vinyl acetate polymerisation. On the other hand, it may well be that their value for k_3 is correct and k_7 is much lower than would be expected.

On obtaining this result it was considered advisable to re-evaluate where possible the velocity coefficients for the reaction. It was necessary firstly to investigate the dependence of rate of reaction on reactant concentration. From the results detailed in Chapter 5 (page 59) it will be seen that only under conditions of excess BTCM is there a single rate-controlling step. In the case of excess vinyl acetate dependences were obtained on the BTCM concentration to the power 0.75 and to the first power of the vinyl acetate concentration. Since in excess BTCM, the rate is proportional to the half-power of the BTCM concentration and to the first power of the vinyl acetate concentration, it would appear that here, step 2 (page 6) is rate-controlling. It would thus seem that as the vinyl acetate concentration increases, the reaction rate becomes increasingly dependent on reaction 3. The vinyl acetate concentration must be so high for reaction 3 to become completely rate-controlling, however, that it is impossible to follow rates, etc, because of the extremely small contractions involved. It is clear that at practicable concentrations of excess vinyl acetate, both reactions 2 and 3 contribute to the control of the overall reaction rate. Thus, under these conditions there is no single rate-controlling step and it is impossible to evaluate the velocity coefficients, which from the kinetic scheme would be k_3, k_5 and k_6. In excess BTCM, reaction 2 is rate-controlling and the main termination step is reaction 4. Under these conditions, therefore, k_2 and k_4 may be evaluated.

Now, Table 27 shows that the values obtained in the present work for k_2 and k_4 are in good agreement with those due to Melville et al.[7]

Table 27. Comparison of the author's results with those of Melville et al.[7]

	Author's results.		Melville's results.
	Monomer*	Chloroform*	Monomer*+
$k_2(25^{\circ}C)$ $(l.mole^{-1}$ $sec^{-1})$	950	1950	1120
$k_4(25^{\circ}C)$ $(l,mole^{-1}$ $sec^{-1})$	0.63×10^8	1.3×10^8	1.0×10^8

* Refers to the medium in which the rate of initiation determination was carried out.

\+ The rate of initiation was determined by measuring the rate of removal of tetrachloro-o-benzoquinone.

The agreement between the results shown in Table 27 indicate that the methods employed by each worker yield reasonably accurate values for the velocity coefficients. Thus, as Melville et al[7] attempted to evaluate k_3 in a region where reaction 3 is not rate-controlling, this would explain an incorrect value.

It should be pointed out that these workers obtained a 3/2 rate-dependence on BTCM concentration under these conditions, which indicates that reaction 3 is rate-controlling. This dependence may be inaccurate, however, since it was obtained from the results of only three experiments.

The suggestion that the value obtained for k_3 by Melville et al is too low is consistent with the idea that the ratio of k_3/k_p is incorrect and is much greater than is suggested by their results.

Figure 29 shows that the rate of removal of DPPH and thus the apparent rate of initiation varies considerably depending on the medium used in the estimation. This effect has been found with other systems.[62] No explanation can be confidently ascribed to this peculiarity without a great deal of research into the chemistry of inhibition. It may be that the $T(VA)^{\bullet}$ radicals, which are probably more reactive than trichloromethyl radicals attack the DPPH more rapidly.

Thus, in the presence of chloroform, the termination reaction between two trichloromethyl radicals may compete with the DPPH-trichloromethyl radical reaction and so reduce the rate of removal of DPPH. If, on the other hand, in the presence of a large excess of monomer, reaction 2 occurs to the exclusion of reaction 4 (page 6), then the more reactive $T(VA)^{\bullet}$ radical thus produced will probably react preferentially with DPPH, so that its rate of removal will be more rapid in the presence of monomer. This suggestion is of course purely conjecture and may be entirely incorrect.

Despite these difficulties in assigning a value to the rate of initiation, if caution is exercised in the interpretation of the results for various systems, reasonable comparisons may be made between them.

Although the fate of the bromine radical produced in the photolysis of BTCM is unknown, it does not affect the values obtained for the velocity coefficients since it is almost certainly included in the rate of initiation measurements. To all intents and purposes, it will behave as a trichloromethyl radical. The number of radicals produced by the photolysis of BTCM will be very small compared with the number of radicals produced by subsequent chain propagation. Thus, even if the bromine radical does produce high $\overline{DP}$ polymer chains, the number of such molecules will be extremely small and they will eventually transfer with BTCM to produce a trichloromethyl radical, so that in effect, a bromine radical will be equivalent to a trichloromethyl radical.

The photochemical reaction between vinyl chloride and BTCM will now be considered. The first comparison to be made between this and the previous reaction is of the values obtained for k_2. Since the same radical is present in both cases, the relative reactivities of the two monomers will clearly be obtained. If, for example, a monomer is highly reactive towards the trichloromethyl radical, the two species will have a great affinity for each other and k_2 will be large. If, on the other hand, the monomer reactivity is low, so also will be k_2.

Table 28 shows the relative reactivities of vinyl acetate and vinyl chloride on this basis and these values have been compared with results derived from copolymerisation studies.[38]

Table 28. Relative reactivities of monomers.[38]

Monomer	k_2(25°C) ($l;mole^{-1}sec^{-1}$)		Relative reactivity.		
			Present work (25°)		Co-polymerisation studies (60°)
	(A)	(B)	(A)	(B)	
Vinyl acetate	950	1950	1.0	1.0	1.0
Vinyl chloride	990	1950	1.05	1.0	1.2-1.8

(A) Monomer as medium in the rate of initiation measurement.

(B) Chloroform as medium in the rate of initiation measurements.

It will be seen from the results of the present work that the reactivity of vinyl chloride towards the trichloromethyl radical is very similar to that of vinyl acetate towards the same radical. Co-polymerisation studies show that the same sort of effect is displayed by these two monomers towards other radicals (Table 28). It would thus appear that the present technique offers a fairly reliable method of obtaining monomer reactivities towards various radicals, a conclusion supported by the work of Tutton.[63]

The two monomers in question would be expected to be of like reactivity because of the somewhat similar nature of their substituent groups. These do not differ greatly in size (a factor of approximately 2 is involved, the acetate group being the larger), they are both to some extent electrophilic and in neither case is resonance stabilisation evident to any extent.

It is noticeable that a difference of a factor of approximately 2 is found in the value of each of the velocity coefficients measured, depending on the medium used in the rate of initiation determination. On comparison with the results due to Melville et al[7], it would appear that if their assumption as to the number of radicals which react with one molecule of inhibitor is correct, then when DPPH is used as the inhibitor, the medium used should be the monomer if possible.

Despite the statement made in the first paragraph of the present chapter, it does appear that towards vinyl chloride, the reactivity of the $T(VCl)^\bullet$ radical is greater than that of the trichloromethyl radical itself. This statement is based on the fact that the value of k_2 is lower than that of k_p in the vinyl chloride -BTCM reaction. This, of course is consistent with the other results obtained.

Again, k_4 for the BTCM-vinyl chloride reaction is lower by a factor of 10 than k_t for this reaction in large excess vinyl chloride. This may be due to the steric hindrance effect of the large trichloromethyl groups. It is very difficult however, to correlate the values of the velocity coefficients for termination with the steric factors present in a series of monomers.

Tables 25 and 26 (pp. 128-9) show that the velocity coefficients for the photochemical polymerisation of vinyl chloride sensitised with AIBN are very similar to those for the BTCM-initiated polymerisation at very high vinyl chloride-BTCM mole ratios. Normal polymerisation seems to occur under these conditions therefore, and the influence of the trichloromethyl group decreases with increasing chain length, as would be expected and as has been assumed when discussing the change in value of the ratio k_{tr}/k_p with increasing $\overline{DP}$.

As stated previously, Burnett and Wright[14] evaluated the velocity coefficients for the homogeneous polymerisation of vinyl chloride in tetrahydrofuran, and Table 29 compares their results with those for the heterogeneous photochemical polymerisation sensitised with AIBN obtained in the present work.

Table 29. Comparison of the homogeneous and heterogeneous photo-sensitised polymerisation of vinyl chloride at $25^{\circ}C$.

Velocity coefficient ($l.mole^{-1}sec^{-1}$)	Heterogeneous* polymerisation	Homogeneous[14] polymerisation
k_p	ca 3000	6200
k_t	ca 2.3×10^{9}	1.1×10^{9}

* Quoted from results in chloroform for the rate of initiation measurements.

These results indicate that the reactivity of the growing radical is not affected to any great extent by its insolubility. Lower values might have been expected for the velocity coefficients in the heterogeneous phase than in the homogeneous phase because of the probability of the active centres of the radicals being encaged in the mass of solid, dead polymer.[64-65]

In conclusion, the results obtained in this research show that no polymer is produced by the photochemical reaction between vinyl acetate and BTCM when the mole ratio of the former to the latter is less than 100:1. Some very low molecular weight polymer is produced at much higher mole ratios. The reason for the absence of polymer formation over experimentally practicable concentrations is that the ratio of the velocity coefficient for transfer to the velocity coefficient for propagation, being of the order of 40:1 in the production of low molecular weight chains, successfully prohibits polymerisation. The unexpectedly high value of the ratio of k_{tr}/k_p under these conditions may be explained in two ways. If the velocity coefficient for chain transfer between a BTCM molecule and a $T(VA)_1^{\bullet}$ radical is sufficiently high, it will preclude the formation of polymer. Alternatively, the velocity coefficient for the addition of this radical to a vinyl acetate molecule (k_7 page 12) may be much lower than k_p for vinyl acetate polymerisation.

It is impossible to determine experimentally which of these factors is responsible for the high value of the ratio. However, k_3 (ie, k_{tr} for the $T(VA)^{\bullet}$-BTCM reaction) may be greater in value than was found by Melville et al[7] since they evaluated k_3 in a region where reaction 3 is not rate-controlling. This is of course consistent with the above idea.

By comparing the reactions between the two monomers and BTCM, it is clear that vinyl acetate and vinyl chloride show similar reactivity towards the trichloromethyl radical. This agrees with the results of co-polymerisation studies which show a close similarity in the relative reactivity of these monomers towards a number of radicals.

Finally, it has been found that the ratio of k_{tr}/k_p decreases from 40 to 0.6 in magnitude as the radical $\overline{DP}$ increases. The only apparent explanation of this is that, although according to the Alfrey-Price Q-e scheme, BTCM should have a positive *e*-value, it has in fact a negative *e*-value,

Although the present research has been fairly successful, a considerable number of improvements are possible. The most unreliable measurement in the evaluation of the velocity coefficients is without doubt the technique for measuring the rate of initiation. A great deal of work remains to be carried out on this topic. The kinetic chain life-time measurement is not flawless and the method of isolating and examining reaction products calls for refinement.

Once however, these experimental difficulties have been overcome, the principle behind this research will offer a very powerful tool in the evaluation of radical reactivities.

References.

1. Taylor and Jones, J. Amer. Chem. Soc., 1930, 52, 1111.

2. Kharasch, Jensen and Urry, J. Amer. Chem. Soc., 1947, 69, 1100.

Kharasch, Reinmuth and Urry, J. Amer. Chem. Soc., 1947, 69, 1105.

3. Kharasch, Jensen and Urry, J. Amer. Chem. Soc., 1945, 67, 1864.

4. Kharasch, Jensen and Urry, J. Amer. Chem. Soc., 1945, 67, 1626.

5. Kharasch and Sage J. Org. Chem., 1949, 14, 537.

6. Melville, Robb and Tutton, Disc. Faraday Soc., 1951, 10, 154.

7. Melville, Robb and Tutton, Disc. Faraday Soc., 1953, 14, 150.

8. Mayo, Disc. Faraday Soc., 1953, 14, 251.

9. Bartlett and Swain, J. Amer. Chem. Soc., 1946, 68, 2381.

10. Robb and Vofsi, Trans. Faraday Soc., 1959, 55, 558.

11. Halter and Matheson, Unpublished work.

12. Bengough and McIntosh, Unpublished work,

13. Bengough and Thomson, Chem. & Ind., 1957, 426.

14, Burnett and Wright, Proc. Roy. Soc. A, 1954, 221, 28.

15. Overberger et al, J. Amer. Chem. Soc., 1949, 71, 2661.

16. Goldschmidt and Renn, Ber., 1922, 55, 628.

17. Jenkins, Trans. Faraday Soc., 1958, 54, 1885, 1895.

18. Mayo, J. Amer. Chem. Soc., 1943, 65, 2324.

19. Mayo, J. Amer. Chem. Soc., 1948, 70, 3689.

20. Bengough and Thomson, Trans. Faraday Soc., 1960 (in press)

21. Findlay, Practical Physical Chemistry, p.106, (Longmans, Green, 1955).

22. Staudinger, Die Hoch Molekularen Organischen Verbindungen, (Berlin, 1932).

23. Nakajima, Chem. High Polymers (Japan), 1949, 6, 451.

24. Bengough, Trans. Faraday Soc.,1958, 54, 1560.

25. Tong and Kenyon, J. Amer. Chem. Soc.,1945, 67, 1278.

26. Bainton, Diaper, Ivin and Sheard, Trans. Faraday Soc.,1957, 53, 1269.

27. Evans and Tyrrall, J. Polymer Sci.,1947, 2, 387.

28. Bengough, Trans. Faraday Soc.,1958, 54, 54.

29. Bengough, Nature, 1957, 180, 1120.

30. Bengough and Thomson, Trans. Faraday Soc.,1959, 55, 268.

31. Duncan and Starling, Text-book of Physics, p. 332, (McMillan, 1918)

32. Int. Crit. Tables, 5, 107.

33. Matheson, Auer, Bevilacqua and Hart, J. Amer. Chem. Soc.,1949, 71, 2610.

34. Bawn and Mellish, Trans. Faraday Soc.,1951, 47, 1216.

35. Hammond, Sen and Boozer, J. Amer. Chem. Soc.,1955, 77, 3244.

36. Burnett, Trans. Faraday Soc.,1950, 46, 772.

37. Briers, Chapman and Walters, J. Chem. Soc., 1926, 562.

38. Bamford, Barb, Jenkins and Onyon, The kinetics of vinyl polymerisation by radical mechanisms . (Butterworth, 1958).

39. Burrell, Majury and Melville, Proc. Roy. Soc. A.,1951, 205, 309.

40. Majury and Melville, Proc. Roy. Soc. A.,1951, 205, 323 & 496.

41. Grassie and Melville, Proc. Roy. Soc. A.,1951, 207, 285.

42. Bengough and Melville, Proc. Roy. Soc. A.,1954, 225, 330.

43. Bengough and Melville, Proc. Roy. Soc. A.,1955, 230, 429.

44. Miyama, Bull. Chem. Soc. (Japan), 1956, 29, 711.

45. Bengough, Trans. Faraday Soc.,1958, 54, 868.

46. Burnett and Melville, Nature, 1945, 156, 661.

47. Burnett and Melville, Proc. Roy. Soc. A.,1947, 189, 456, 481 & 494.

48. Bartlett and Swain, J. Amer. Chem. Soc.,1945, 67, 2273.

49. Bartlett and Swain J. Amer. Chem. Soc.,1946, 68, 2381.

50. Bengough, McIntosh and Thomson, Nature, 1959, 184, 266.

51. Hougen and Watson, Chemical Process Principles, p.219. (Wiley, 1947)

52. Roff, Fibres, Plastics and Rubbers, p. 175, (Butterworth, 1957)

53. Bengough and McIntosh, Unpublished work.

54. Dana, Burdick and Jenkins, J. Amer. Chem. Soc.,1927, 49, 2801.

55. Dainton and Ivin, Trans. Faraday Soc.,1950, 46, 331.

56. Alfrey and Price, J. Polymer Sci., 1947, 2, 101.
Price, J. Polymer Sci., 1948, 3, 772.

57. Fuhrman and Mesrobian, J. Amer. Chem. Soc.,1954, 76, 3281.

58. Bamford, Jenkins and Johnston, Trans. Faraday Soc.,1959, 55, 418.

59. Bengough and Sharpe, Unpublished work.
60. Gregg and Mayo, J. Amer. Chem. Soc.,1953, 75, 3530.
61. Bamford and Dewar, Disc. Faraday Soc.,1947, 2, 314.
62. Bengough and McIntosh, Unpublished work.
63. Tutton, Ph.D. Thesis, (University of Birmingham, 1953)
64. Bengough, J. Polymer Sci., 1958, 28, 475.
65. Bengough and McIntosh, Unpublished work.