VINYL POLYMERIZATION IN THE PRESENCE OF METAL SALTS

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

by

THOMAS O'NEILL

Department of Pure and Applied Chemistry,
University of Strathclyde.

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SUMMARY

A study has been made of the behaviour of cupric chloride in dimethyl formamide solution in systems containing a vinyl monomer polymerizable by a free radical mechanism.

Although ultra-violet irradiation of such systems has been found to cause photolysis of the cupric species to cuprous with, in some cases, the formation of insoluble polymer, no measurable rates of polymerization have been detected.

This observation has been explained as due to a rapid termination reaction between the cupric species and the polymerization chain-carrying radical.

That the reaction between cupric chloride in dimethyl formamide solution and polymer radicals does proceed at a rate comparable to that observed in radical-radical interactions has been verified in the case of the monomers, styrene and methacrylonitrile.

The polymerization of these monomers initiated with 1-1' azobisisobutyronitrile and inhibited by cupric chloride in dimethyl formamide has been studied at 50°, 60° and 70° C. The salt has been found to behave as an ideal inhibitor in these polymerizations, and from a study of the acceleration period following complete inhibition the rate constant for the reaction between the cupric species and the polymer radical has been found to be of

the order of 10^6 mole^{-1} l sec^{-1} in the case of both monomers. The rate constant for the interaction of two polymer radicals under these conditions is of the order of 10^7 mole^{-1} l sec^{-1}.

Activation energies for the termination reaction in these systems have also been measured.

The photochemically induced polymerization of acrylonitrile initiated and retarded by ferric choride in dimethyl formamide has been studied. Rates of reduction of the ferric salt in this system have been measured by u.v. spectrophotometry and by titration.

Chlorine-36 labelled ferric chloride has been prepared and used in the preparation of polymer. Scintillation counting techniques have been applied on such polymer with a view to elucidating the nature of the initiation and termination reactions.

The general purpose of the work has been to contribute to an understanding of the factors governing radical-salt oxidation-reduction reactions in non-aqueous media.

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CHAPTER I

INTRODUCTION

THE ROLE OF METAL SALTS IN VINYL POLYMERIZATION

1.1 Metal Salts as Initiators of Polymerization

The current interest in salts of polyvalent metals as photo-and thermal initiators of free radical polymerizations may be traced back to Fenton's work on the oxidizing properties of the ferrous ion - hydrogen peroxide system[1].

Haber and Weiss studied this system in acid media and elucidated the mechanism of the oxidation reaction on the then novel basis of a chain reaction involving inorganic free radials[2]. The main feature of the Haber-Weiss scheme is the production of hydroxyl radicals by an intermolecular one electron transfer reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + {}^{\cdot}OH$$

Interest in the Haber-Weiss reaction was greatly stimulated by the discovery that the radicals generated could initiate the polymerization of vinyl monomers[3]. The low activation energy of the initiation step relative to that for the thermal decomposition of a free radical initiator such as an organic diazo compound gave a considerable practical importance to this Haber-Weiss based 'Reduction-Activation' system.

Concurrently with these studies, investigations were being made on aqueous solutions of polyvalent metals salts.

These systems were shown to consist not only of free ions and undissociated molecules but also of various intermediate ion-pair complexes[4]. The absorption spectra of these solutions were explained by postulating electron transfer processes between the components of these complexes. Thus light absorption by aqueous solutions of a ferric salt would be attributed to the electron transfer reaction

$$Fe^{3+}X^- \xrightarrow{h\nu} Fe^{2+}X$$

$Fe^{3+}X^-$ is an ion pair complex (where X may be OH, Cl, N_3 etc.)[5]

The product $Fe^{2+}X$ is metastable. Dissociation into the hydrated ferrous ion and the radical $X^{\cdot}$ takes place readily.

Free radical generation by such a process was first confirmed by Evans and co-workers[6] who found that photolysis of aqueous solutions of ferric salts initiated the polymerization of vinyl monomers. In a subsequent paper[7] a kinetic scheme based on the above photo-induced initiation step was developed by these workers.

Work in this field has been further developed by a study of the photochemistry of reducing ions in aqueous solutions[8]. These systems can also initiate polymerization by virtue of electron transfer processes of the type

$$M^{Z+}.HOH \xrightarrow{h\nu} M^{(Z+1)+} + OH^- + H^{\cdot}$$

Atomic hydrogen is here the initiating radical.

Dainton has studied these systems in some detail[8] and has found that the energy required to promote the electron transfer reaction in linearly related to the ionization potential of the reducing ion. A complicating factor can arise in these systems if the reaction product $M^{(Z+1)+}HO^-$, is itself capable of photoreduction as is the case with ferrous ion for example.

More recent work by Edgecombe and Norrish[9] has established that cerous ions in aqueous solution, which are known to initiate polymerization by a purely thermal dissociative electron transfer reaction[10], do so photochemically also.

Comparatively little has been done on the photochemistry of transition metal salts in non-aqueous media. Bengough and co-workers have reported the polymerization of acrylonitrile photoinitiated and retarded by ferric chloride in dimethylformamide (DMF) solution[11]. This work was the precursor of that reported in the first part of this thesis. Work done by Kochi[12] on the photolysis of cupric chloride in organic media will be referred to in the next section.

1.2 Metal Salts as Inhibitors of Polymerization

Within the last decade or so it has become clear that salts of polyvalent metals can enter into redox reactions with organic free radicals[13].

Such reactions may be formally described by the equations.

$$R\cdot + M^{Z+} \longrightarrow M^{(Z-1)+} + R^+$$

$$R\cdot + M^{(Z-1)+} \longrightarrow M^{Z+} + R^-$$

The ionization potential of the ions involved and the redox potentials for the processes

$$R \longrightarrow R^{+} + e$$

$$R + e \longrightarrow R^{-}$$

are found to influence greatly the rates of these redox reactions[14].

Examples of these reactions which may be cited are the oxidation of polyacrylamide radicals by Fe^{3+}_{aq}, $Fe^{3+}OH^{-}$ and Cu^{2+} ions[15] and the reduction of polyacrylonitrile radicals by Cr^{2+}_{aq} ions in aqueous media[16].

Dainton and co-workers have recently suggested that there exists a fundamental difference in the mechanisms of these radical oxidation and radical reduction reactions[17]. The former is thought to occur by an electron transfer process possibly involving quantum-mechanical tunnelling whereas the latter is typical of a H-atom transfer process.

The interaction of organic free radicals with transition metals salts in non-aqueous media has been studied by several workers.

Bamford has investigated the effect of $FeCl_3$ on the 1-1' azo-bis-isobutyronitrile (AIBN) initiated polymerization of several vinyl monomers in dimethylformamide solution. The ferric chloride molecule, or some more complex species, oxidizes the polymer radicals in these systems. The influence of radical structure is apparent from the fact that ferric chloride behaves as an ideal inhibitor towards vinyl acetate and styrene, whereas acrylonitrile, methacrylonitrile, methyl acrylate and methyl methacrylate polymerizations are only retarded by the salt. The effect of the electron withdrawing substituents of these four monomers on a radical oxidation reaction is thought to be mainly responsible for such differences in reactivity. The existence of polar effects from the polymer chain which affect radical-salt interaction is inferred by Dainton and co-workers[21] from the low activity of polymethacrylonitrile radicals to ferric chloride in DMF relative to 2-cyanoisopropyl radicals (from the decomposition of AIBN).

The effect of cupric chloride in DMF on vinyl polymerization has been reported by Monteiro[22,23] and by Bengough[24]. It is found that this salt is a more powerful inhibitor than ferric chloride, induction periods being observed in the polymerizations of acrylonitrile and methylmethacrylate in this system. In the case of acrylonitrile retardation of polymerization is observed at the end of the induction periods. This, together with the development of a yellow coloration in the reaction mixture has been attributed to complex formation between the polymer radicals and the cuprous species produced in the termination step[23].

The use of these salts as polymerization inhibitors and retarders has rapidly gained currency because of their freedom from the complicating side reactions associated with conventional quinone inhibitors and radical inhibitors like diphenylpicryl hydrazyl. Thus information on the mechanism of polymerization such as rates of initiation and kinetic chain lengths can be obtained simply and unequivocally from these systems[13,18].

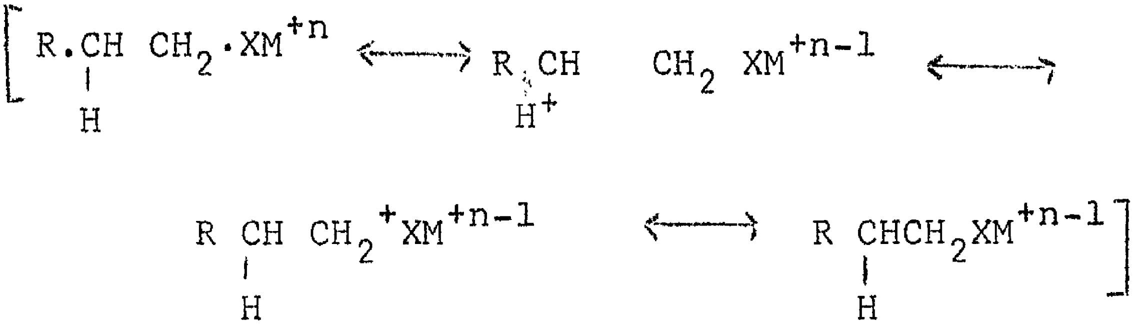
The influence of the anionic group on these salt-radical reactions has been studied and found to be considerable. Entwistle has shown that in DMF solution ferric bromide inhibits methylmethacrylate polymerization whereas ferric perchlorate has no effect[25]. In the case of simpler organic radicals Kochi and co-workers find that the reactions of cupric chloride and bromide may be described as halide additions whereas cupric sulphate favours olefin formation[26] and other salts promote radical coupling[27].

The dependence of the reaction on the nature of the anionic group has been explained by postulating a bridged transition state involving electron transmission through the anionic ligand such as envisaged by Taube[28]. This scheme may be represented thus

$$R + M^{n}X_{n} \longrightarrow \left[R\cdots\cdot X\cdots\cdots M^{n}X_{n-1}\right] \longrightarrow$$

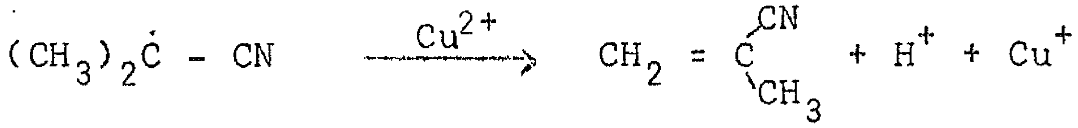
$$RX + M^{n-1}X_{n-1}$$

Kochi and co-workers have suggested[26] that ligand addition reactions and electron transfer processes leading to olefinic products may proceed via an identical transition state represented by canonical forms of the type



$$\left[R\cdot\underset{\substack{|\\ H}}{CH}\ CH_2\cdot XM^{+n} \longleftrightarrow R\,\underset{H^+}{CH}\quad CH_2\ XM^{+n-1} \longleftrightarrow R\ \underset{\substack{|\\ H}}{CH}\ CH_2{}^{+}XM^{+n-1} \longleftrightarrow R\ \underset{\substack{|\\ H}}{C}HCH_2XM^{+n-1} \right]$$

It is of interest that in radical scavenging reactions involving cupric halides, from the Sandmeyer reaction to recent work by Dainton and co-workers[29], the products are those of halogen addition, whereas in the work of Monteiro[23] referred to earlier conductivity measurements favour the following termination step with primary radicals



$$(CH_3)_2\dot{C} - CN \xrightarrow{Cu^{2+}} CH_2 = C\begin{matrix}\diagup CN\\ \diagdown CH_3\end{matrix} + H^+ + Cu^+$$

The object of the work reported in this thesis has been to study reactions of the type described in this section as they occur in DMF solution between cupric and ferric chlorides and polymer radicals. The photochemistry of these systems has been investigated as has the behaviour of cupric chloride as an ideal inhibitor in the AIBN initiated polymerization of styrene and methacrylonitrile.

CHAPTER II

Photolysis of Cupric Chloride in presence of a Monomer

Ferric chloride in DMF solution has been shown to behave as a photoinitiator and as a terminator of the polymerization of acrylonitrile in accordance with the general reactions[11]:-

Photoinitiation

$$\mathrm{FeCl_3} \xrightarrow{h\nu} \mathrm{FeCl_2} + \mathrm{Cl}^{\bullet}$$

Termination

$$\sim\sim \mathrm{CH_2\,\dot{C}HCN} + \mathrm{FeCl_3} \longrightarrow \sim\sim \mathrm{CH_2\overset{Cl}{\overset{|}{C}}HCN} + \mathrm{FeCl_2}$$

$$\text{OR} \sim\sim \mathrm{CH_2\dot{C}HCN} + \mathrm{FeCl_3} \longrightarrow \sim\sim \mathrm{CH = CHCN} + \mathrm{FeCl_2} + \mathrm{HCl}$$

An indication that cupric chloride might behave similarly was given by a preliminary investigation in this department[30] into the photolysis of acrylonitrile solutions of this salt in the course of which low rates of polymerization were observed.

The work described in this chapter was therefore undertaken as an extension of the above in order to compare the behaviour of of cupric chloride in such a system with that of ferric chloride.

2.1 Estimation of Cuprous Copper in presence of DMF

As a preliminary step in this work a satisfactory method was required for estimating copper in the concentration range $10^{-2} - 10^{-5}$ molar in presence of DMF.

A standard method for the determination of cupric copper was first examined. This involved the reaction of the cupric species with potassium iodide in neutral or mildly acidic medium, and titration with thiosulphate of the iodine liberated to the starch end-point. The sensitivity of the method however, proved too low for use in the system under consideration.

A more satisfactory method was found in the estimation of cuprous copper by redox titration of the ferrous ion produced on addition of a cuprous solution to an acidified excess of ferric solution. The procedure is described below.

2.1.1 Materials

Anhydrous Cupric Chloride (Hopkin and Williams Fine Chemical Grade) was used as supplied.

Dimethyl Formamide (B.D.H. grade) was freed of moisture by shaking with phosphorus pentoxide over five one-hour intervals followed by two distillations from this drying agent under reduced pressure.

Ceric Ammonium Sulphate (B.D.H. grade) was used as the oxidizing solution in titrations. An approximately $^{N}/_{100}$ solution was prepared by dissolving ca 6.5 g in 500 ml 2N sulphuric acid and making up to one litre with distilled water.

The ceric solution was standardized against weighed portions of arsenious oxide using osmium tetroxide catalyst and ferroin indicator.

Redox Indicator

(a) Ferroin (tris-o-phenanthroline ferrous sulphate) indicator solution was prepared by dissolution of

0.991 g o-phenanthroline in 66 ml aqueous solution containing 0.459 g ferrous sulphate.

(b) N-phenyl anthranilic acid indicator was prepared from 0.25 g of the acid dissolved in 5 ml of 5% sodium carbonate solution diluted to 250 ml with distilled water.

2.1.2 Procedure

The method was tested using DMF solutions of cuprous chloride prepared by U.V. irradiation of de-aerated solutions of the cupric salt. The test solution was added to an acidified excess of ferric alum solution and titration was carried out with standard ceric solution in presence of an indicator.

The DMF in the system was found to interfere with the indicator colour change in the case of both ferroin and N-phenylanthranilic acid to the extent that reproducible results could not be obtained.

When the titration was followed potentiometrically, however, the end-point could be detected quite satisfactorily and this, therefore, was the method used in the work that followed.

2.2 Monomer Systems

The photolysis of cupric chloride in DMF solution was studied in the presence of the following monomers: methyl methacrylate, vinylidene chloride, isobutene, methacrylonitrile and acrylonitrile.

2.2.1 Materials

With the exception of isobutene, the monomers were purified before use as follows. Stabilizer (hydroquinone or tert-butyl catechol) was removed by washing several times with dilute sodium hydroxide solution, followed by dilute sodium carbonate solution and finally with distilled water. After drying over calcium chloride the monomers were twice distilled with collection of the middle fractions. The final purification stage was carried out on a vacuum line where the monomers were de-aerated by repeated distillation into a cold trap (at - 78°C with acetone - Drikold slurry or at - 196°C with liquid nitrogen) under an ambient pressure of ca. 10^{-4} torr, and finally photochemically prepolymerized to approximately 5% conversion using 1-1' azobisisobutyronitrile as initiator. After prepolymerization the residual monomer was distilled off into a cooled reservoir on the vacuum line and stored for use.

Isobutene was prepared by dehydration of iso-butanol over heated kaolin and distilled on the vacuum line before use.

An attempt was made initially to prepare methacrylonitrile by phosphorus pentoxide dehydration of acetone cyanhydrin in liquid sulphur dioxide as reported by Bieber[31]. The product obtained could not be sufficiently purified, however, and use was subsequently made of the material supplied by Eastman Kodak.

2.2.2 Apparatus

All photolysis reactions were carried out under vacuum. A Pyrex glass vacuum line of standard design was constructed for this purpose, the pumping system being a 3-stage mercury diffusion pump backed by an Edwards rotary oil pump. The pressure maintained in this system, as measured by Pirani gauge, was found to be strongly influenced by the cold-trap coolant used, liquid nitrogen giving a residual pressure of ca. 10^{-4} torr whereas with acetone-Drikold coolant a vacuum of ca. 10^{-3} torr could not be exceeded. This would seem to be attributable to the vapour pressure of monomer adsorbed on the walls of the system and on stopcock grease, as it was not observed prior to introduction of monomer into the system.

The photolyses were carried out at 25°C in Pyrex glass dilatometers consisting of a cylindrical bulb of capacity approximately 5 ml surmounted by a 1 mm bore Veridia capillary stem incorporating a constriction for flame sealing under vacuum and a B.10 ground glass cone for connection to the vacuum line.

A lagged, thermostatically controlled Pyrex water bath fitted with irradiation and observation windows was used to ensure uniform reaction conditions from one run to the next.

The temperature was controlled to ± $0.01^{\circ}C$ by a 100-watt bulb heater operating on a mercury-toluene regulator controlled relay circuit.

The radiation source used for the reactions was an unfiltered 125-watt Osira mercury vapour lamp with stabilized input.

2.2.3 Procedure

Dilatometer volumes were calibrated by filling to a mark on the stem with Analar acetone from a micro-burette.

The reaction mixture was introduced into the dilatometers as follows. The required volume of a standard stock solution of cupric chloride in DMF was run into the vessel and pure DMF added to give the desired final monomer to solvent ratio. The dilatometer was then put on to the vacuum line and the system de-aerated by repeated cooling - pumping - heating cycles.

The required volume of monomer was then distilled into the dilatometer from the reservoir and the filled vessel was removed from the line by flame sealing and collapse of the constriction.

The dilatometer prepared in this way was immersed in the thermostat bath at $25^{\circ}C$ and let come to thermal equilibrium. A cathetometer reading to 0.01 mm was used to detect any change in meniscus level during photolysis. A run was begun and ended by removal and replacement of a shield on the lamp window, times of irradiation being measured with a stopwatch reading to 0.2 seconds.

2.2.4 Observations and Discussion

No measurable rates of polymerization were observed during photolysis of cupric chloride in DMF solution in the presence of any of the monomers studied, although in all cases reduction of cupric chloride to cuprous occurred, and, in the case of acrylonitrile at low DMF concentrations, some insoluble polymer was formed.

The apparent lack of photoinitiation by cupric chloride in these systems is in contrast to the behaviour expected from the ferric chloride work mentioned earlier.

The observations may be explained on the basis of a termination reaction between polymer radical and salt which is much more rapid with cupric chloride than with ferric. Cupric chloride is, in fact, a more efficient inhibitor than the ferric salt: the rate constant for the radical-salt termination reaction for methylmethacrylate polymerization at 60°C, for example is ca. 7.7×10^5 mole^{-1} l sec^{-1} for cupric chloride[24] and ca. 3.1×10^3 mole^{-1} l sec^{-1} for the ferric[32].

Thus, although photolysis of the cupric species may generate free radicals, these could not initiate long chains until the cupric chloride concentration, and therefore, the rate of initiation had fallen to a very low value.

That no rates of polymerization could be measured during irradiation of the cupric chloride, acrylonitrile, DMF system, whereas rates have been obtained in the absence of DMF would seem to indicate that DMF renders the terminating species more reactive towards the polyacrylonitile radicals.

Although this effect may be partially explained by the higher monomer concentration in the bulk polymerizations, DMF does appear to behave in a way quite different from that observed in the ferric chloride system where the termination raaction between radical and salt is approximately forty times more rapid in the absence than in the presence of DMF[19].

This behaviour could possibly be due to a configuration of ligands in the DMF - cupric chloride complex that is more favourable for electron transfer from radical to salt than is the case for the terminating species which exists in acrylonitrile solutions. It may be that for cupric chloride this effect is more important than any stabilization of the terminating species by complex formation with DMF, whereas the opposite is the case for ferric chloride.

CHAPTER III

POLYMERIZATION OF STYRENE IN PRESENCE OF CUPRIC CHLORIDE

The AIBN initiated polymerization ofstyrene in the presence of cupric chloride in DMF has been studied at 50°, 60° and 70°C. It has been confirmed that the salt behaves as an ideal inhibitor in this system as reported by Monteiro[23], i.e., the rate attained after inhibition equals the rate in the absence of inhibitor.

A study has been made of the acceleration period following inhibition in order to evaluate k_x/k_p for the system (where k_x is the rate constant for the reaction between polystyryl radicals and cupric chloride in DMF, and k_p is the the rate constant for the polymerization propagation step) and so to compare radical-salt reactivities with those observed in other systems. The effect of temperature variation on this ratio has been investigated and the Arrhenius activation energy for the inhibition reaction has been determined.

The rate constant and activation energy of the initiation reaction have been measured from rates of removal of inhibitor from the system at the three temperatures quoted.

3.1 Theory

3.1.1 Inhibition of Polymerization

An ideal scheme for the polymerization of a monomer in the presence of a retarder or inhibitor may be represented as follows:-

			Rate
Initiation	:	$C + M \longrightarrow R$	I
Propagation	:	$R + M \longrightarrow R$	$k_p [R][M]$
Termination	:	$R + Z \longrightarrow \text{Polymer etc.}$	$k_x [R][Z]$
		$R + R \longrightarrow \text{Polymer}$	$k_t [R]^2$

Where C is a primary radical produced by initiator decomposition, M is a monomer molecule, R is a polymer radical containing one or more monomer units and Z is a molecule of inhibitor, which in this case is $CuCl_2$ so that the termination step may be rewritten

	Rate
$R + CuCl_2 \longrightarrow CuCl + \text{Polymer}$	$k_x [R] [CuCl_2]$

In order to express k_x/k_p in terms of quantities which can be measured experimentally the above kinetic scheme can be developed as follows.

From the scheme we can write

$$dR/dt = I - k_x [R] [CuCl_2] - k_t [R]^2 \qquad (1)$$

and

$$\frac{d [CuCl_2]}{dt} = -k_x [R] [CuCl_2] \qquad (2)$$

for the rates of concentration change for radical and inhibitor respectively.

If we assume a stationary state in radical concentration i.e., that the rate of change of radical concentration is much smaller than either the rate of initiation or of termination, we can write as a good approximation

$dR/dt = 0$

∴ From eqn. (1)

$$I = k_x [R][CuCl_2] + k_t [R]^2 \qquad (3)$$

Differentiation of equation (3) with respect to time gives

$$\frac{d[CuCl_2]}{dt} = - \frac{I + k_t [R]^2}{k_x [R]^2} \cdot \frac{d[R]}{dt} \qquad (4)$$

By equation (2)

$$\frac{d[CuCl_2]}{dt} = -k_x [R][CuCl_2]$$

∴ Combination of equations (3) and (4) gives

$$- \frac{I + k_t [R]^2}{k_x [R]^2} \cdot \frac{d[R]}{dt} = - I + k_t [R]^2 \qquad (5)$$

which on rearrangement and integration yields

$$- \frac{[R]_s}{[R]} + \ln \frac{[R]_s + [R]}{[R]_s - [R]} = k_x [R]_s t + A \qquad (6)$$

where $[R]$ is radical concentration at time t, $[R]_s$ is the value of $[R]$ when $[CuCl_2]$ = zero, and A is an integration constant. If we define the reduced rate, ϕ_t, as the ratio of the reaction rate at time t to that attained when $[CuCl_2]$ falls to zero, then since the reaction rate is taken to be

$$- d[M]/dt = k_p [R][M] \qquad (7)$$

we can write $\phi_t = [R]/[R]_s$ provided that monomer concentration does not change during the run.

We may now rewrite equation (6) in terms of ϕ_t as follows

$$-{}^{1}/_{\phi_t} + \ln \frac{1 + \phi_t}{1 - \phi_t} = k_x [R]_s\, t + A \qquad (8)$$

By plotting ϕ_t against $k_x [R]_s t + A$ and fitting experimental values of ϕ_t to the curve, or by plotting the l.h.s. of equation (8) against time, we can arrive at a value for $k_x [R]_s$. This leads us to a value for ${}^{k_x}/_{k_p}$ by virtue of the relationship

$$ {}^{k_x}/_{k_p} = k_x [R]_s [M] \Big/ {}^{-dM}/_{dt} \qquad (9)$$

in which all the terms on the r.h.s. are known or measurable.

This treatment, first derived by Bamford and coworkers[19], will be referred to in what follows as Bamford's method.

An alternative means of measuring k_x/k_p experimentally has been developed by Bengough[24] from the simple kinetic scheme given above. This method, to be referred to as Bengough's method, is described below.

At any time t there is assumed to exist a stationary radical concentration, $[R]_t$, according to the relationship

$$ d[R]_t/_{dt} = I - k_x [R]_t [CuCl_2] - k_t [R]_t^2 = 0 \qquad (10)$$

Solution of this quadratic in $[R]_t$ gives

$$[R]_t = -k_x [CuCl_2] \Big/ 2k_t + \{ (k_x^2 [CuCl_2]^2 + 4Ik_t)^{\frac{1}{2}} \Big/ 2k_t \} \qquad (11)$$

When $[CuCl_2]$ has fallen to zero, the final radical concentration, $[R]_s$, will equal $({}^{I}/_{k_t})^{\frac{1}{2}}$. Since

$\phi_t = [R]_t / [R]_s$, we get from equation (11) that

$$\phi_t = \{ (k_x^2 [CuCl_2]^2 + 4Ik_t)^{\frac{1}{2}} - k_x [CuCl_2] \} / 2(Ik_t)^{\frac{1}{2}} \qquad (12)$$

Rearrangement and squaring give us

$$k_x = \{ (1 - \phi_t^2) / \phi_t \} (Ik_t)^{\frac{1}{2}} / [CuCl_2] \qquad (13)$$

Every term on the r.h.s. of equation (13) can be measured experimentally except $[CuCl_2]$, the value of the cupric chloride concentration at any point during the reaction

We must, therefore, express $[CuCl_2]$ in terms of measurable quantities.

Equation (2) tells us that

$$- d[CuCl_2]/dt = k_x [R]_t [CuCl_2]$$

i.e. $$-1/k_x \int_{[CuCl_2]_o}^{[CuCl_2]} \frac{d[CuCl_2]}{[CuCl_2]} = \int_o^t [R]_t \, dt \qquad (14)$$

and also we have from equation (7) that

$$\int_o^t [R]_t \, dt = -1/k_p \int_{[M]_o}^{[M]} \frac{d[M]}{[M]} \qquad (15)$$

Equating (14) and (15) and integrating give us

$$(k_p/k_x) \ln ([CuCl_2] / [CuCl_2]_o) = \ln ([M] / [M]_o) \qquad (16)$$

i.e. $$[CuCl_2] = [CuCl_2]_o \{[M]/[M]_o\}^{k_x/k_p} \tag{17}$$

Expressing monomer concentrations in terms of fractional conversion from monomer to polymer, equation (17) leads us to the desired expression for $[CuCl_2]$, viz.

$$[CuCl_2] = [CuCl_2]_o (1 - F)^{k_x/k_p} \tag{18}$$

where $[CuCl_2]_o$ is the initial cupric chloride concentration and F is the fractional conversion.

Substitution for $[CuCl_2]$ from equation (18) into equation (13) gives us the final expression:

$$k_x = \{(1 - \phi_t^2)/\phi_t\} (Ik_t)^{\frac{1}{2}} \Big/ [CuCl_2]_o (1 - F)^{k_x/k_p} \tag{19}$$

This expression can be solved for k_x/k_p by plotting the logarithm of any one of the variables, $(1-\phi_t^2)/\phi_t$, I or reciprocal $[CuCl_2]_o$ against the logarithm of (1-F) for fixed values of the other two variables. Such a plot should be linear of slope equal to k_x/k_p.

In the work described below the experimental data were treated according to both Bamford's and Bengough's methods and comparison made of the results obtained from each.

3.1.2 Rates of Initiation

Measurement of rates of initiation by the use of inhibitors has the advantage of simplicity over other possible methods involving, for example, kinetic chain length or molecular weight measurements.

The experimentally determined rate of removal of an inhibitor is related to the rate of initiation by a factor which depends on the number of chain carrying radicals which react with each inhibitor molecule. The unambiguous determination of this number, however, is rendered difficult in general by lack of knowledge of the exact mechanism of the inhibition reaction.

The use of cupric chloride resolves this difficulty since the inhibition reaction involves reduction of the salt to cuprous chloride. There is thus in this case a one to one correspondence between radicals reacted and inhibitor removed, and we may write that

$$-\frac{d\,[CuCl_2]}{dt} = I$$

$$\text{or} \qquad \frac{[CuCl_2]_o}{t} = I$$

where t is the inhibition period for an initial cupric chloride concentration, $[CuCl_2]_o$.

Bamford and coworkers[19] have shown that a more exact measure of the inhibition period than that obtained by extrapolation back to the time axis of the linear part of the conversion - time curve can be arrived at as follows.

Expressing equation (8) as a definite integral between the time limits of zero and t, we get

$$\frac{1}{\phi_o} - \frac{1}{\phi_t} + \ln\left(\frac{1-\phi_o}{1+\phi_o} \cdot \frac{1+\phi_t}{1-\phi_t}\right) = k_x \left[R\right]_s t \qquad (20)$$

where ϕ_o is the initial value of ϕ_t

$$\text{i.e.} \quad \phi_o = (Ik_t)^{\frac{1}{2}} / k_x \left[CuCl_2\right]_o \qquad (21)$$

If ϕ_o is very much less than unity (as it will be in an inhibited or strongly retarded reaction) then we may simplify equation (20) thus;-

$$\frac{1}{\phi_o} - \frac{1}{\phi_t} + \ln\left(\frac{1+\phi_t}{1-\phi_t}\right) = k_x \left[R\right]_s t \qquad (22)$$

By substituting in equation (22) a value for ϕ_t such that

$$\frac{-1}{\phi_t} + \ln\left(\frac{1+\phi_t}{1-\phi_t}\right) = 0 \qquad (23)$$

we get

$$\frac{1}{\phi_o} = k_x \left[R\right]_s t' \quad \text{which from equation (21) gives}$$

$$t' = \frac{\left[CuCl_2\right]_o}{I}$$

where t' is the value of t corresponding to the ϕ_t value which satisfies equation (23). Solution of the latter gives $\phi_t = 0.648$.

Thus the time by which the reaction rate reaches 0.648 of its final value is a more meaningful measure of the inhibition period than that normally used. It may be shown however, that the error involved in the extrapolation method is normally so small as to be negligible in the measurement of rates of initiation (see reference 24).

3.2 Experimental

3.2.1 Materials

Styrene (B.D.H. Grade) was freed of inhibitor by washing successively with dilute aqueous solutions of sodium hydroxide and sodium carbonate. The monomer was then washed with water, dried over calcium chloride and twice distilled under vacuum. The final distillations and prepolymerization were carried out on the vacuum line as described earlier.

1-1' Azobisisobutyronitrile (ex. Kodak Ltd.) was recrystallized from dilute ethanol solution before use (m.p. of product 101-102°C).

Analar Chloroform for the preparation of initiator solutions was freshly distilled before use.

The cupric chloride and dimethyl formamide used have been described in Chapter II.

3.2.?. Apparatus

A diagram of the vacuum line used is given in Fig.1. On account of the low volatility of the monomer (b.p. = 145.2°C at 760 mm) it was necessary to heat the line to ensure satisfactory distillation. The heating arrangement (shown schematically in Fig.1) consisted of nichrome wire windings (resistance = 3.4 ohms per yd) connected to mains via a variable transformer. The operating potential was 12 volts.

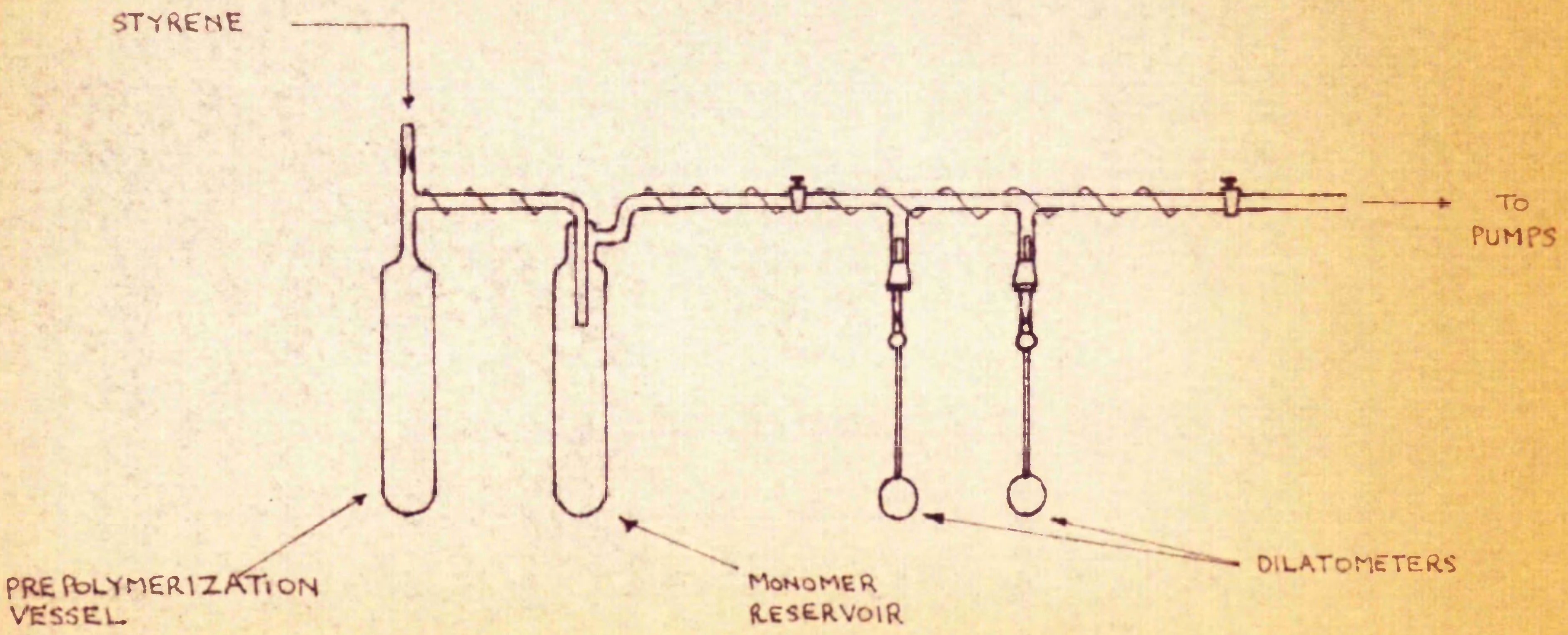


FIG. 1 VACUUM LINE FOR STYRENE WORK

To minimize air leakage into the heated line greased joints and stopcocks were avoided where possible, glass to glass seals being used instead. Where lubricated joints were unavoidable, Edwards high vacuum silicone grease was used.

The thermostat bath used for the reactions was as described in section 2.2.2. The higher temperatures required were maintained using a 'Variac' controlled 800 watt background heating coil.

The reactions were carried out in vacuo in dilatometers sealed on the line. For a preliminary study of the effect of cupric chloride in DMF on the polymerization of styrene, dilatometers of the type described earlier were used. A more precise study of the acceleration period of the reaction was carried out using dilatometers with an approximatley 12 ml capacity disc-shaped bulb and a stem of 0.8 mm bore 'Veridia' capillary.

Such bulbs were used for improved heat transfer so that the acceleration period could be followed in a thermally stable system. This is particularly important in this system because of the very rapid acceleration to final rate over a period of no more than two minutes in general.

The reactions were followed using a cathetometer with a vertical graduated scale in its field. Rates were measured by following the descent of the meniscus past the scale graduations using as a time base an Elliot D.C. recording voltmeter (chart drive speed = 12 in per min) incorporating a press button switch.

3.2.3 Procedure

Dilatometers were calibrated as follows: calibration was made to a mark on the stem and the volume noted. This represented the required volume of monomer and solvent at the reaction temperature. The corresponding volume at 0°C was calculated for a monomer : solvent ratio of 4:1 vol/vol and the dilatometer was again calibrated to this volume. This procedure was adopted to obviate the need for a measuring vessel on the vacuum line so that monomer could be transferred from the reservoir to the dilatometers (cooled in an ice-water mixture) in one distillation.

Initiator was introduced into the dilatometers in standard chloroform solution and the solvent was then pumped off on the vacuum line.

The required concentrations of cupric chloride and DMF were introduced and the system de-aerated as described in Chapter II.

The line heating system was then switched on and monomer distilled directly from the reservoir (heated on a water bath) into the dilatometers at 0°C. When the required volume of monomer had been distilled in the dilatometers were sealed with a flame at the constriction.

After being vigorously shaken to ensure good mixing of the reactants, the dilatometers prepared in this way were placed in the thermostat bath and observations on the inhibition and polymerization begun when the meniscus reached its highest level on the stem, which was approximately four minutes after immersion of the dilatometer.

The initial stages of the inhibition period were followed using a stopwatch. At the onset of the acceleration period time measurement was transferred to the recording voltmeter after correlation with the watch had been made. The acceleration period was then followed by breaking the recording circuit and so getting a recorded 'blip' each time the meniscus crossed a graduation in the cathetometer telescope field.

In this way a record was taken during the acceleration period and beyond into the final rate of volume contraction against time which could be converted to a % polymerization - time plot from a knowledge of monomer and polymer densities. Such a plot was then used for measurement of reduced rates by drawing tangents to the curve and the ϕ_t values so measured were used to determine the k_x/k_p ratio for the system by the methods of Bengough and Bamford described earlier.

The density data for styrene and polystyrene used for calculation of conversion factors are those quoted by Patnode and Scheiber[33]. These are as follows:

Temperature	Monomer Density (g/ml)	Polymer Density (g/ml)	% Conversion for 1% contraction
50°C	0.878	1.043	6.34
60°C	0.869	1.040	6.08
70°C	0.860	1.037	5.83

3.3 Results and Discussion

3.3.1 The System at 60°C

The system was studied first of all at 60°C at a monomer : solvent ratio of 4:1 volume to volume corresponding to a monomer concentration of 6.67 mole l^{-1}.

Runs carried out at initiator concentrations of 2×10^{-2} and 4×10^{-3} mole l^{-1} gave mean polymerization rates of 4.91 and 2.06% conversion per hour respectively. This corresponds to a rate dependence on the initiator concentration to the power 0.54, which has been taken to indicate the absence from the system of retarding or catalysing impurities.

The effect of cupric chloride in DMF on the polymerization was studied at an AIBN concentration of 4×10^{-3} mole l^{-1} at salt concentrations up to a maximum of 5.66×10^{-4} mole l^{-1}.

From the polymerization - time curves given in Fig.2 the final rate can be seen to be independent of the initial cupric chloride concentration. This indication that the cuprous chloride most probably formed in the inhibition reaction has no effect on the polymerization is in accord with Monteiro's observations[23].

Some results of this work are tabulated in Table 1 below:-

TABLE 1

RESULTS FOR STYRENE POLYMERIZATION AT 60°C IN PRESENCE OF CUPRIC CHLORIDE IN DMF.

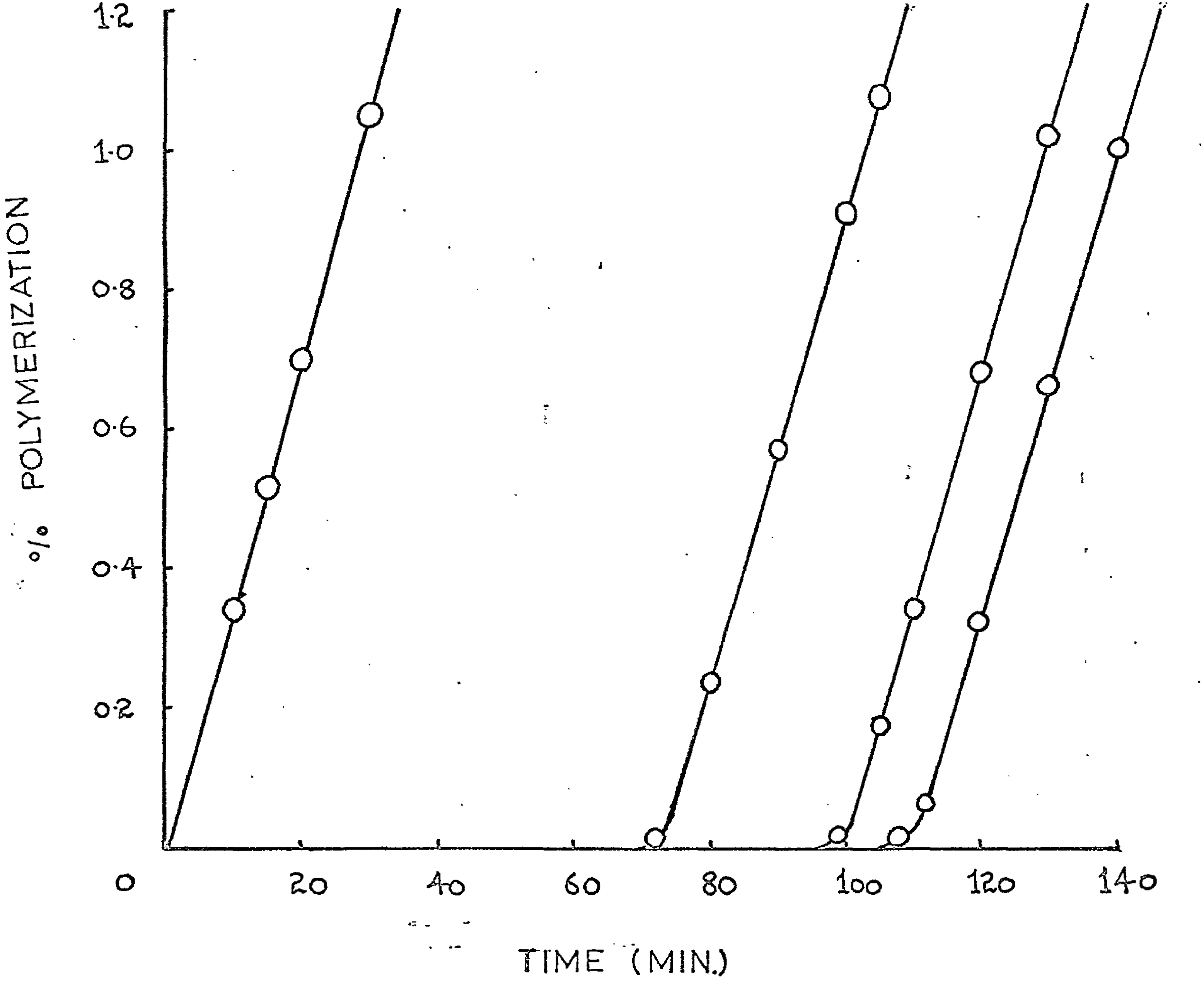
$[\text{AIBN}] = 4 \times 10^{-3}$ mole l^{-1} $[\text{M}] = 6.67$ mole l^{-1}

$[\text{CuCl}_2]$ mole l^{-1} $(\times 10^4)$	Inhibition Period (min)	Final Rate	
		% conv/hr	mole $l^{-1}\text{sec}^{-1}$ $(\times 10^5)$
zero	zero	2.06	3.82
2.50	50	2.10	3.90
3.50	73	2.00	3.71
4.00	83	2.02	3.73
5.00	100	2.17	4.02
5.66	110	2.07	3.84

From the above results it can be seen that for all runs the AIBN decomposed during the inhibition period was negligible as far as any effect on the final rate is concerned.

The plot of inhibition period (obtained by simple extrapolation of the conversion-time curve back to zero

FIG. 2 INHIBITION OF STYRENE POLYMERIZATION BY CUPRIC CHLORIDE IN DMF AT 60°C.



conversion) against cupric chloride concentration shown in Fig.3 is linear through the origin indicating no inhibition in the absence of cupric chloride. The slope of this line, i.e. the rate of removal of the salt from the system gives a value for I, the rate of initiation of 8.33×10^{-8} mole l^{-1} sec^{-1}, assuming 1:1 stoichiometry between radicals removed and salt reduced.

The rate constant of initiation, $2k_i$, as defined by the relationship,

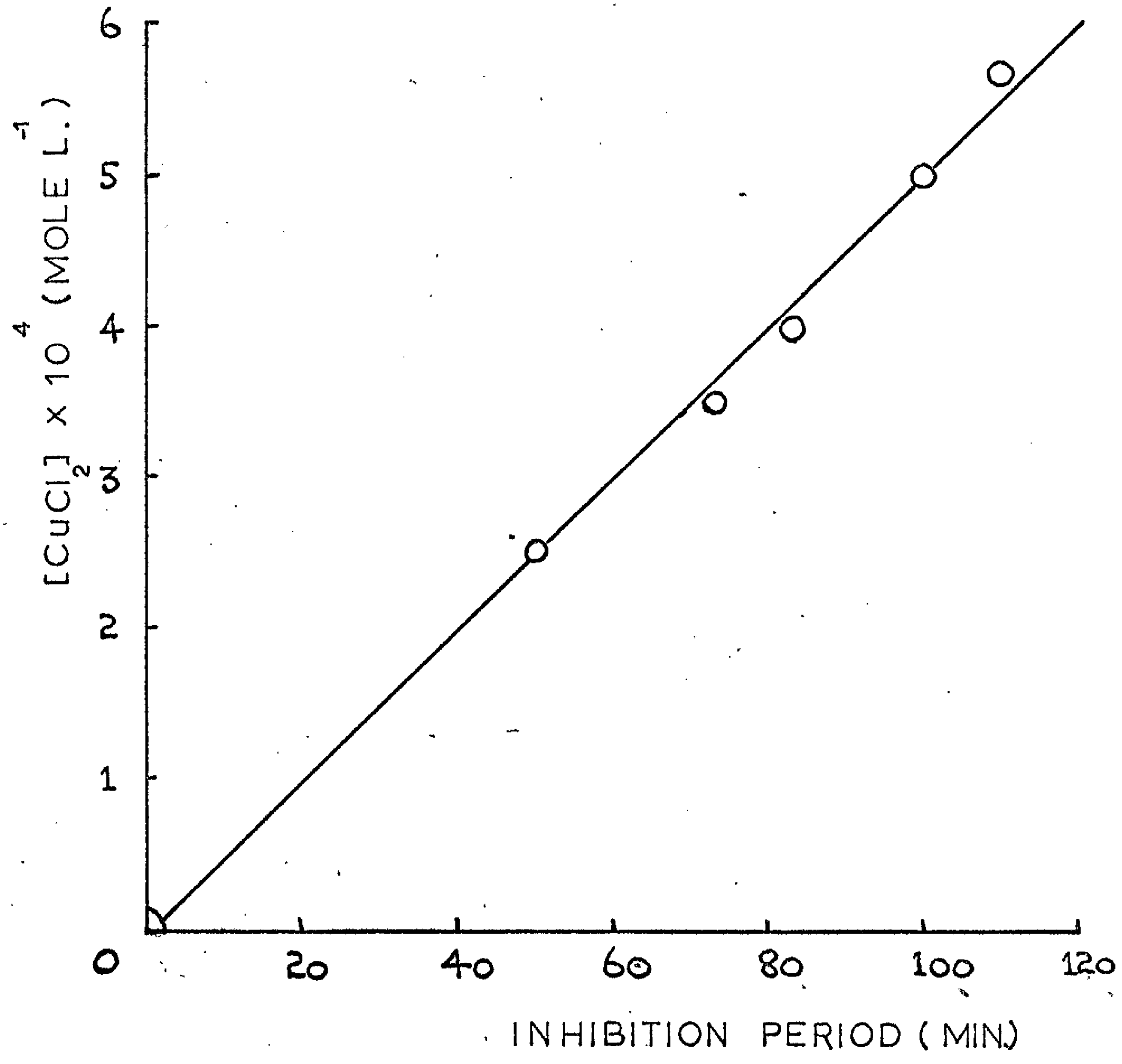
$$I = 2k_i [AIBN]$$

is thus found to be 2.08×10^{-5} sec^{-1}.

This value is rather lower than that found by Monteiro[23] for this system, ($k_i = 1.15 \times 10^{-5}$ sec^{-1}), but considerably higher than that of $2k_i = 1.40 \times 10^{-5}$ sec^{-1} found by Bamford and coworkers[34] in the ferric chloride inhibited polymerization of styrene initiated with AIBN at 60°C.

The difference in the $2k_i$ values may perhaps be explained on the basis of the higher monomer concentrations used in the present work, viz. 6.67 mole l^{-1} as compared with 2.18 mole l^{-1} in the work of Bamford et al. Although in the latter investigation no significant variation in $2k_i$ was found over the monomer concentration range from 0.435 to 2.18 mole l^{-1}, it is probable that as the DMF concentration is further decreased to that used in the present work (20% by volume) the rate of initiator decomposition will increase,

FIG. 3 DEPENDENCE OF INHIBITION PERIOD ON [$CuCl_2$] AT 60°C



it being known that AIBN decomposes thermally more slowly in DMF than in most other solvents. Thus, whereas Dainton and coworkers[21] find a value at 60°C for k_d, the first order rate constant for AIBN decomposition, of 1.01×10^{-5} $\sec^{-1}$ in DMF, Bevington[35] quotes the corresponding value in benzene solution to be 1.20×10^{-5} $\sec^{-1}$.

Using this latter value for kd leads to an efficiency of initiation for the present system of approximately 85%.

The inhibition period in this system is followed by a rapid acceleration up to the final rate. In Fig.4 a conversion-time plot over such an acceleration period is given for a run at a cupric chloride concentration of 3.5×10^{-4} mole l^{-1} and an AIBN concentration of 4×10^{-3} mole l^{-1}.

Values of the reduced rate, ϕ_t, measured by drawing tangents to the experimental curve, have been used to determine the k_x/k_p ratio for the system by the methods of Bengough and Bamford described earlier.

In Fig.4 the probable error involved in drawing tangents at given points on the curve is shown. The corresponding error in the functions log $(1-\phi^2/_\phi)$ and $-1/_\phi + \ln\left(\frac{1+\phi}{1-\phi}\right)$ has been estimated in each case.

A plot is given in Fig.5 of log $\left(\frac{1-\phi^2}{\phi}\right)$ against log(1-F) for two runs at 60°C with initiator concentration of 4×10^{-3} mole l^{-1}. Curve a corresponds to an initial

FIG 4 ACCELERATION PERIOD AT 60°C

$[CuCl_2] = 3{\cdot}5 \times 10^{-4}$ MOLE L^{-1}

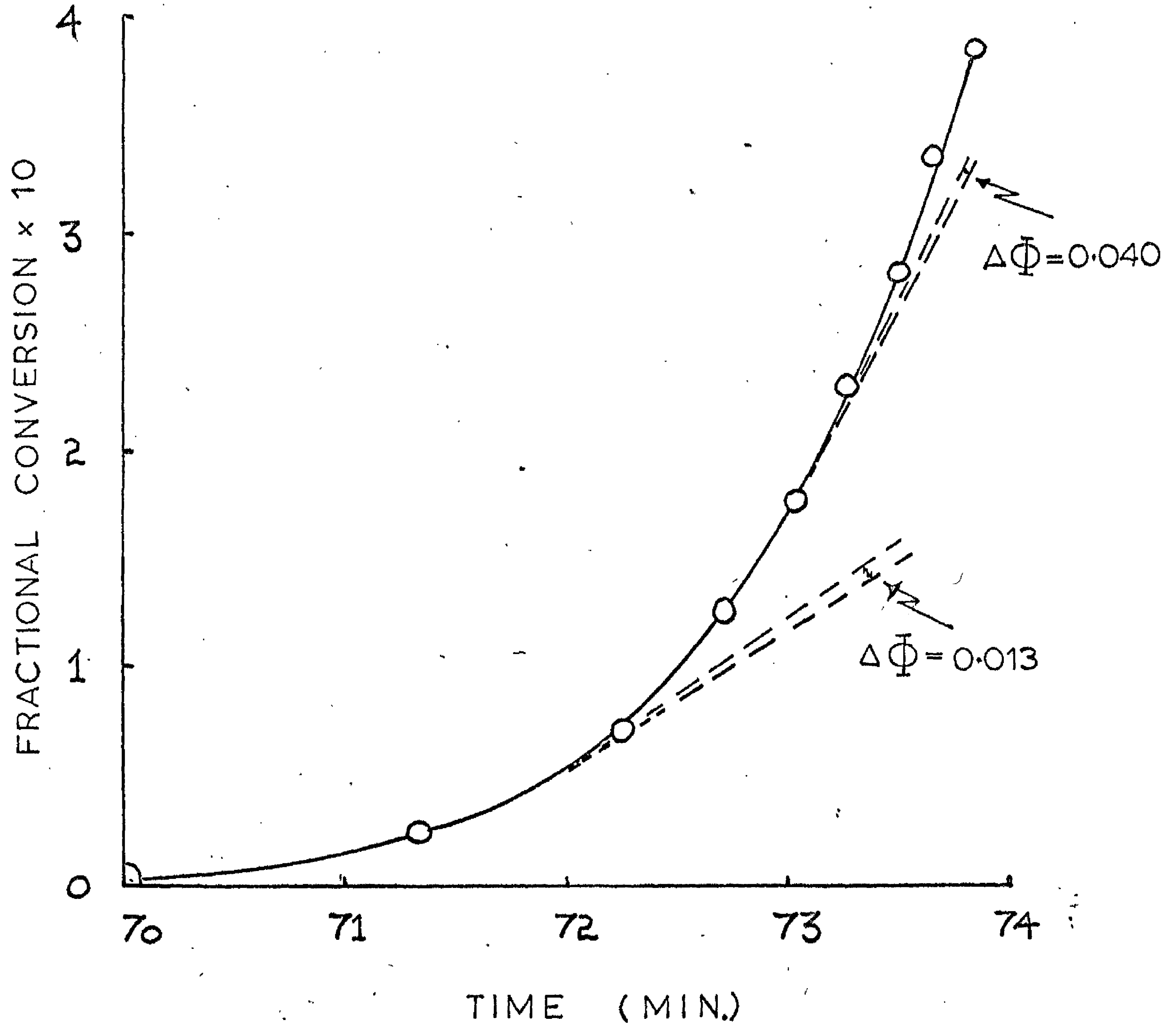
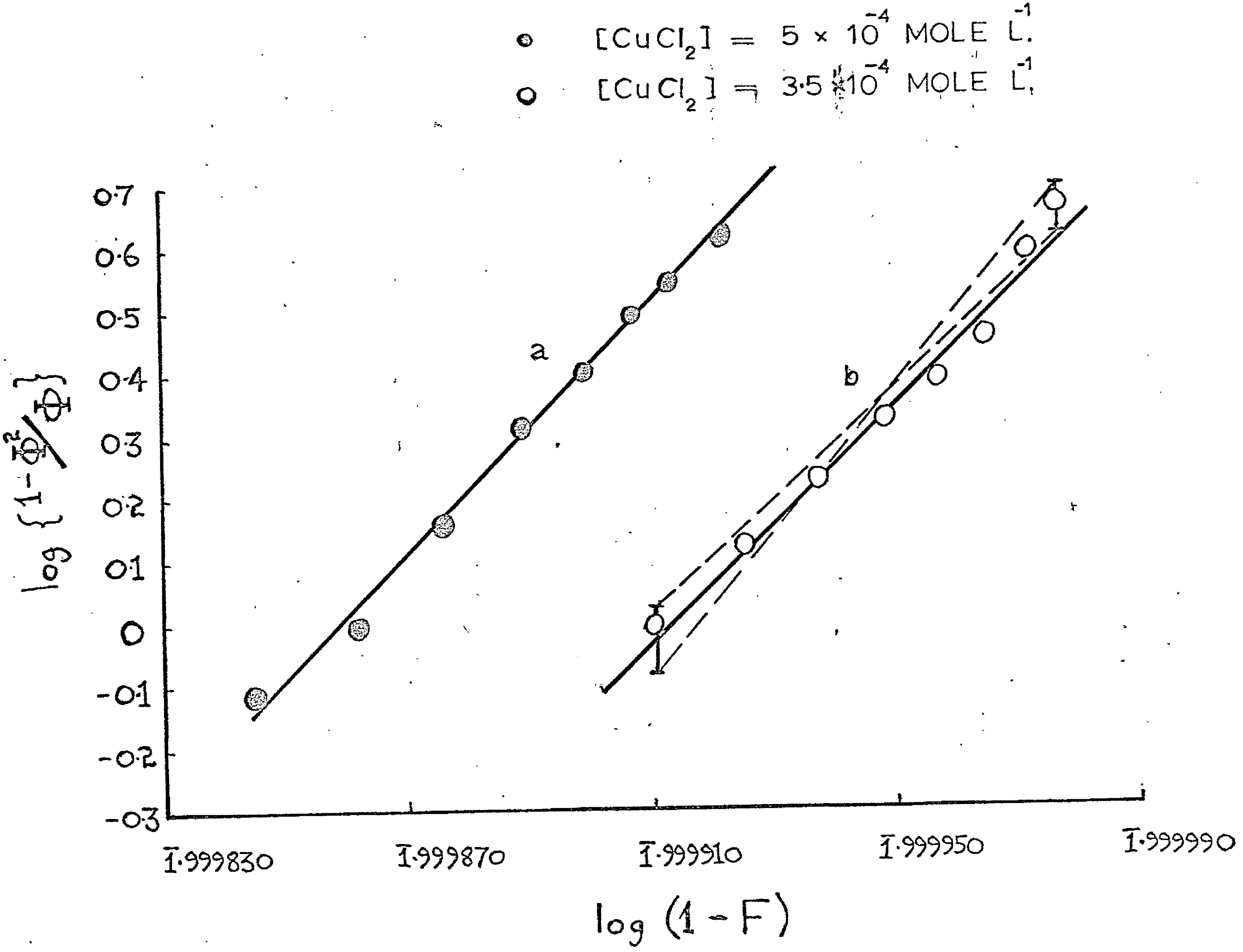


FIG. 5 RESULTS FOR STYRENE POLYMERIZATION AT 60°C



cupric chloride concentration of 5×10^{-4} mole l^{-1}, whereas curve b, derived from the plot in Fig.4 has an initial salt concentration of 3.5×10^{-4} mole l^{-1}. Both plots are of fair linearity which would indicate that the theoretical treatment is valid.

The best lines through the points have been derived by the method of least squares. In plot b possible extreme values of the gradients as estimated from the probable error in the upper and lower ϕ_t values measured have been shown as broken lines.

The gradients of the plots in Fig.5 give k_x/k_p values of 9,800 and 9,500 for curves a and b respectively. From curve b the slopes of the broken lines give extreme values for the ratio of 9,400 and 11,600. In this way we can obtain an indication of the accuracy of the determination for a given run.

The variation of the function log $(\frac{1-\phi^2}{\phi})$ with ϕ may be seen from Fig.6. In the range $0.2 < \phi < 0.7$ the function shows least dependence on ϕ. Because of this minimum dependence on ϕ and also on account of the greater error involved in assigning exact F values to ϕ_t measurement outwith this range, all calculations have been made using ϕ_t values between 0.2 and 0.7.

In Fig.7 there is given the plot of $-\frac{1}{\phi} + \ln(\frac{1+\phi}{1-\phi})$ against time for the same runs shown in Fig.5. Treatment of the

FIG. 6 VARIATION OF BENGOUGH'S FN. WITH REDUCED RATE

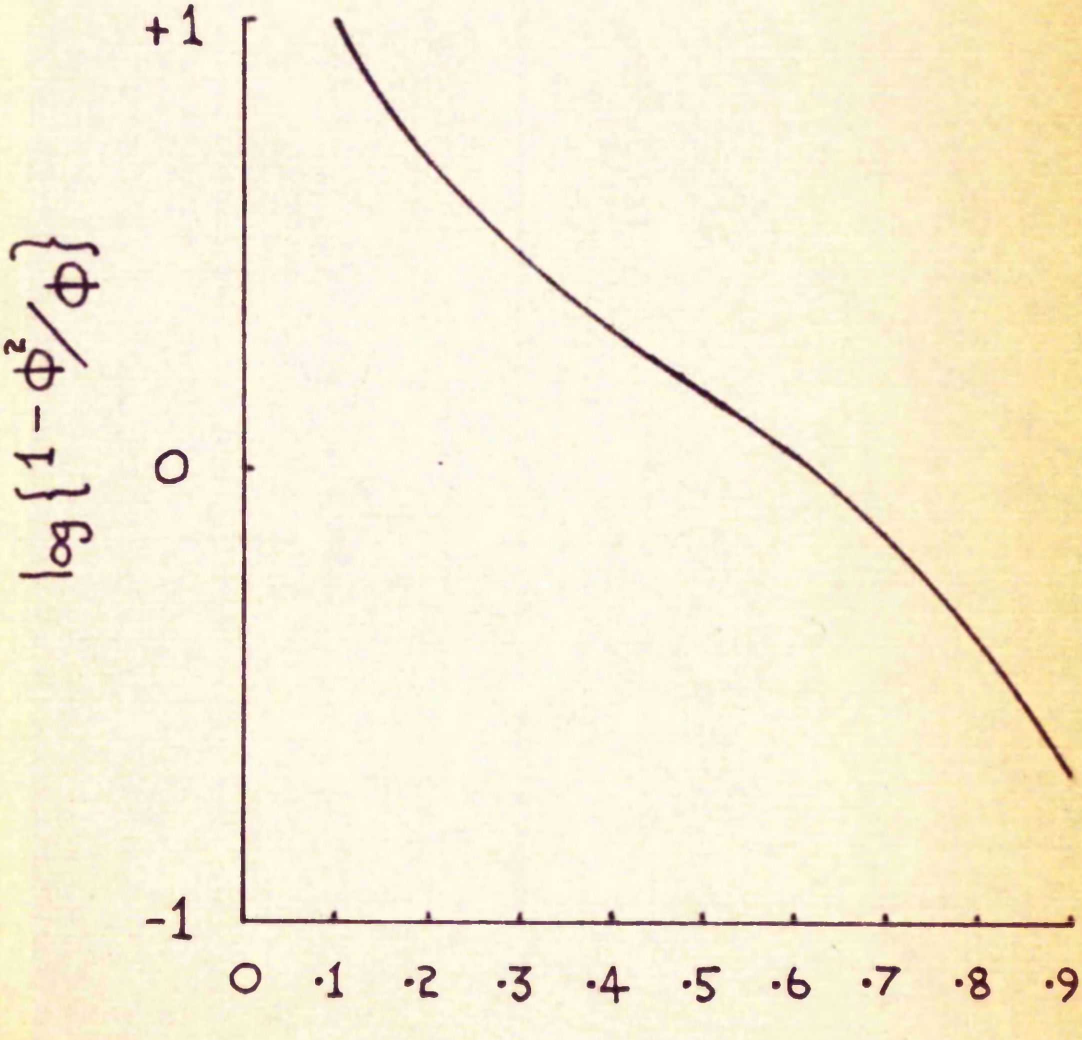
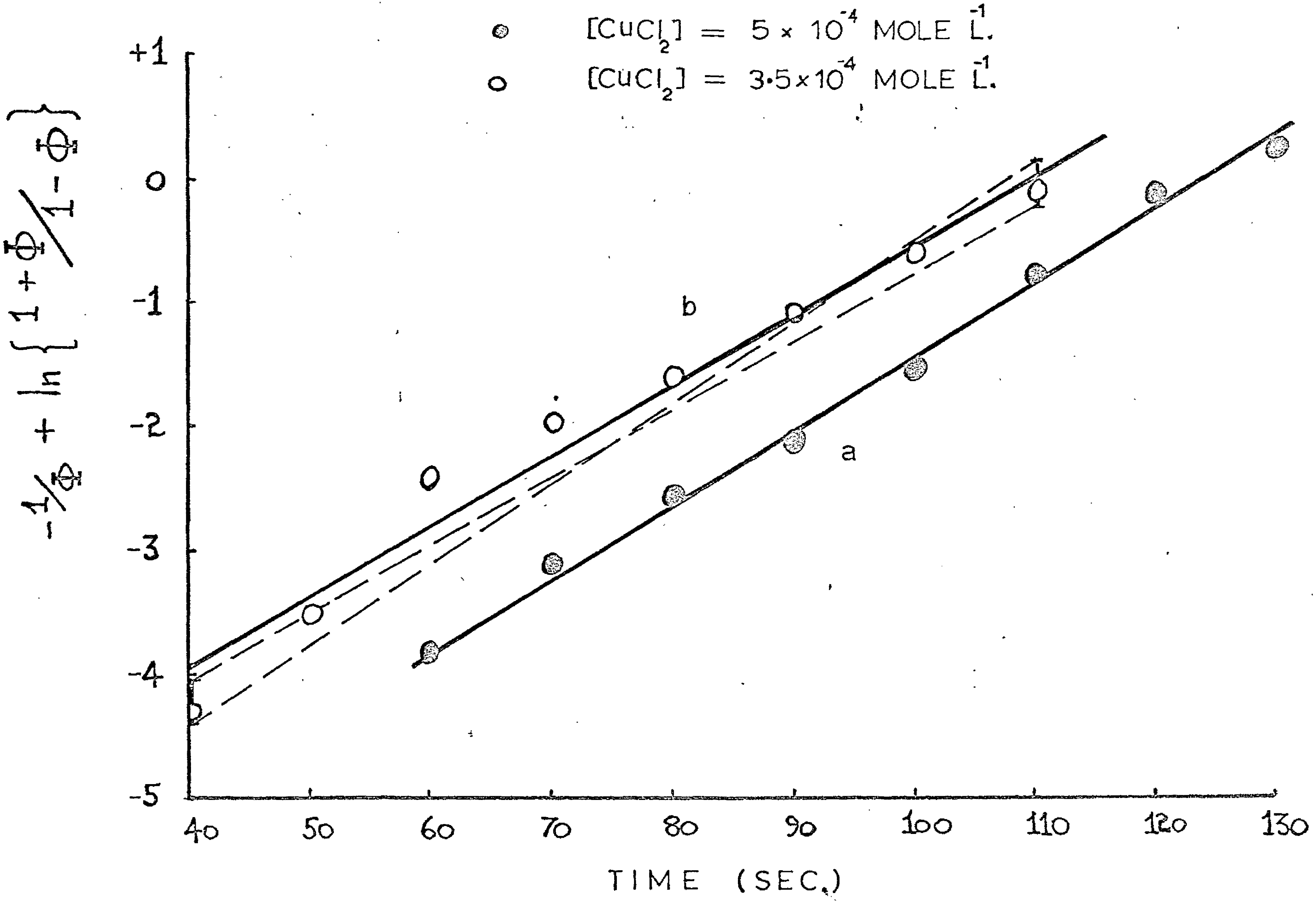


FIG 7 RESULTS FOR STYRENE POLYMERIZATION AT 60°C



experimental data by Bamford's method in this way leads to k_x/k_p values of 9,800 and 10,300 for runs a and b respectively. The values of the ratio for run b taken from the slopes of the broken lines as before define the range 10,100 to 11,600 as an indication of the accuracy obtained.

The plots in Fig.7 have once again been derived using ϕ_t values in the approximate range 0.2 to 0.7. Although as can be seen from Fig.8 the function $-\frac{1}{\phi} + \ln(\frac{1+\phi}{1-\phi})$ shows least sensitivity to error in ϕ in the range $0.4 < \phi < 0.8$, the range 0.2 to 0.7 has been used as a compromise because of the greater error involved in ϕ_t measurement at the high ϕ values. It may be noted in respect of errors involved that the function, $\log(\frac{1-\phi^2}{\phi})$ is less sensitive to ϕ than $-\frac{1}{\phi} + \ln\frac{1+\phi}{1-\phi}$ is, especially in the region $0.1 < \phi < 0.3$.

A list is given in table 2 of the experimental data for four runs at 60°C at a constant initial AIBN concentration of 4×10^{-3} mole l^{-1}. The k_x/k_p values obtained by treatment of these data according to the methods of Bengough and Bamford are listed in table 3.

FIG. 8 VARIATION OF BAMFORD'S FN. WITH REDUCED RATE

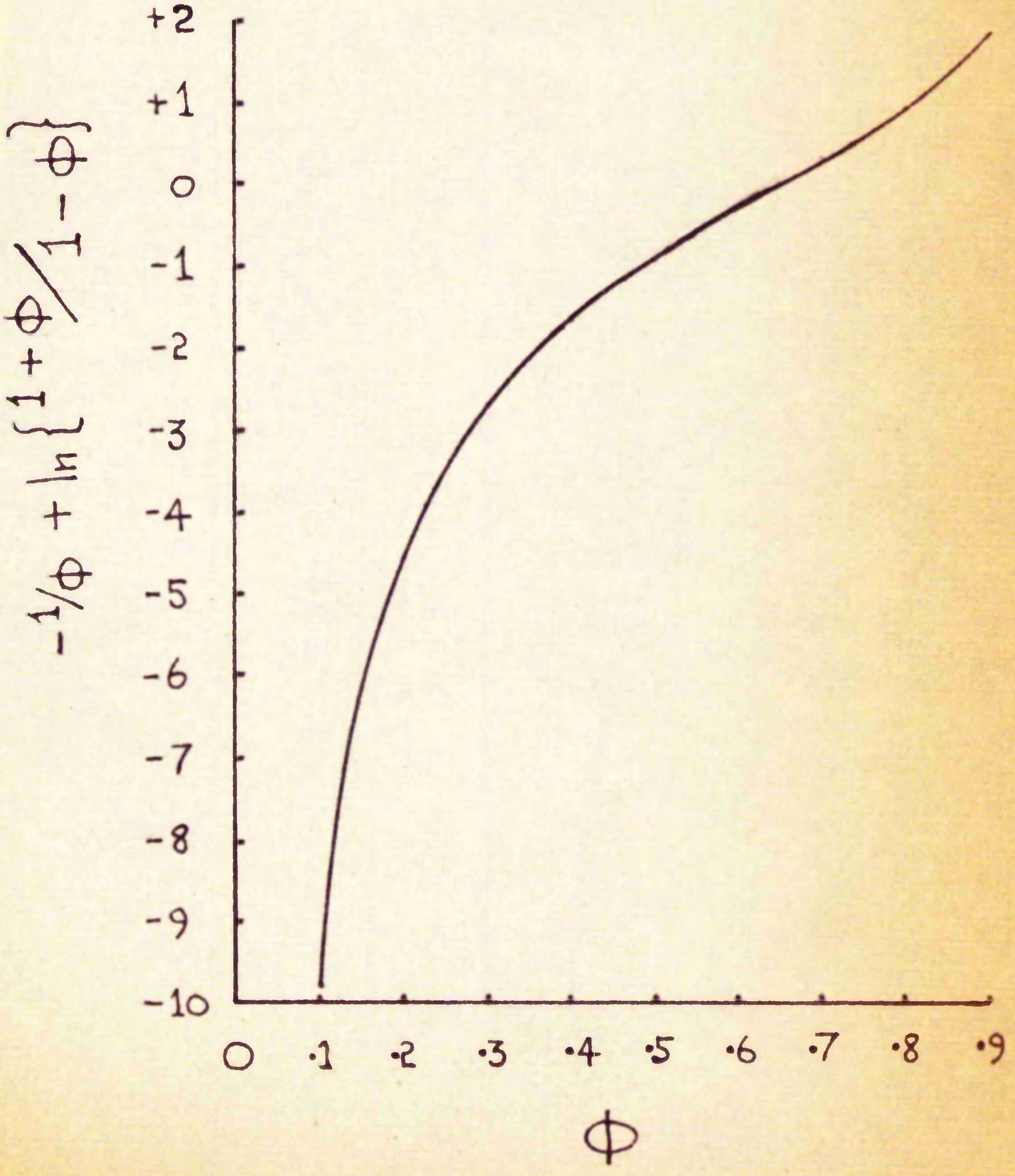


TABLE 2

EXPERIMENTAL DATA FOR EVALUATION OF k_x/k_p FOR STYRENE - CUPRIC CHLORIDE SYSTEM AT 60°C.

$[AIBN] = 4 \times 10^{-3}$ mole l^{-1}, $[CuCl_2]$ = 3.50 (i) 5.00 (iii)
(mole-l^{-1} x10^4) 4.00 (ii) 5.66 (iv)

Time (min. & sec.)	Fractional Conversion ($F \times 10^4$)	Reduced Rate (ϕ)	Time (min & sec)	Fractional Conversion ($F \times 10^4$)	Reduced Rate (ϕ)
(i)			(ii)		
72:00	0.523	0.212	82:30	0.945	0.213
72:10	0.654	0.248	82:40	1.08	0.262
72:20	0.811	0.325	82:50	1.23	0.336
72:30	0.994	0.365	83:00	1.47	0.444
72:40	1,20	0.4 5	83:20	2.05	0.632
72:50	1.46	0.470	83:30	2.43	0.715
73:00	1.73	0.545			
73:10	2.07	0.625			
(iii)			(iv)		
99:20	1.80	0.233	109:00	1.57	0.213
99:30	1.99	0.271	109:10	1.68	0.238
99:40	2.13	0.296	109:20	1.84	0.286
99:50	2.32	0.351	109:30	2.03	0.343
100:00	2.54	0.410	109:40	2.24	0.404
100:10	2.84	0.517	110:00	2.77	0.506
100:20	3.17	0.625	110;20	3.41	0.621
100:30	3.58	0.689	110:30	3.81	0.699

TABLE 3

LIST OF k_x/k_p VALUES AT 60°C FOR STYRENE - CUPRIC CHLORIDE SYSTEM

$[AIBN] = 4 \times 10^{-3}$ mole l^{-1}

Cupric Chloride Concentration (mole $l^{-1} \times 10^4$)	k_x/k_p	
	Bengough's Method	Bamford's Method
3.50	9500	10300
4.00	12500	14000
5.00	9800	9800
5.66	7900	8700

It can be seen from the above table that the k_x/k_p values obtained by Bengough's method are for the most part lower than the others although there is fair agreement between the methods. It is possible that the rather high values obtained for the run at 4.00 mole l^{-1} cupric chloride can be attributed to the fewer data used in the evaluation and the concommitant increased error involved.

The mean values of k_x/k_p from table 3 are 9,900 and 10,700 for Bengough's and Bamford's methods respectively.

Taking the value of Matheson et al[36] for k_p at 60°C of 176 mole^{-1} l sec^{-1} gives us a k_x value for the reaction of polystyrylradicals with cupric chloride in DMF of approximately 1.81×10^6 mole^{-1} l sec^{-1}. The constant for the corresponding reaction with ferric chloride in DMF at 60°C [19] is 9.41×10^{4} mole^{-1} l sec^{-1}. The higher reactivity of polystyryl radicals towards cupric chloride than towards the ferric salt is in keeping with the observed behaviour of the salts in the polymerizations of acrylonitrile[19] and methylmethacrylate[24,34].

The very high reactivity of the styryl radicals would again indicate that, as suggested by Bamford[19], polar effects play a more decisive role in determining the rate of these reactions than do general radical reactivities.

3.3.2 The System at 50°C

The behaviour of the cupric chloride, DMF, styrene system at 50°C has been found similar to that observed at 60°C. The salt behaves as an ideal inhibitor and can thus be used to determine rates of initiation and k_x/k_p values at this temperature.

For the study at this temperature an initiator concentration of 3×10^{-2} mole l^{-1} was used throughout while a cupric chloride concentration range up to 1.5×10^{-3} mole l^{-1} was studied.

Some results of this work are tabulated in table 4 and in Fig.9 a plot is given of the inhibition period - salt concentration dependence.

FIG.9 DEPENDENCE OF INHIBITION PERIOD ON [$CuCl_2$] AT 50 °C

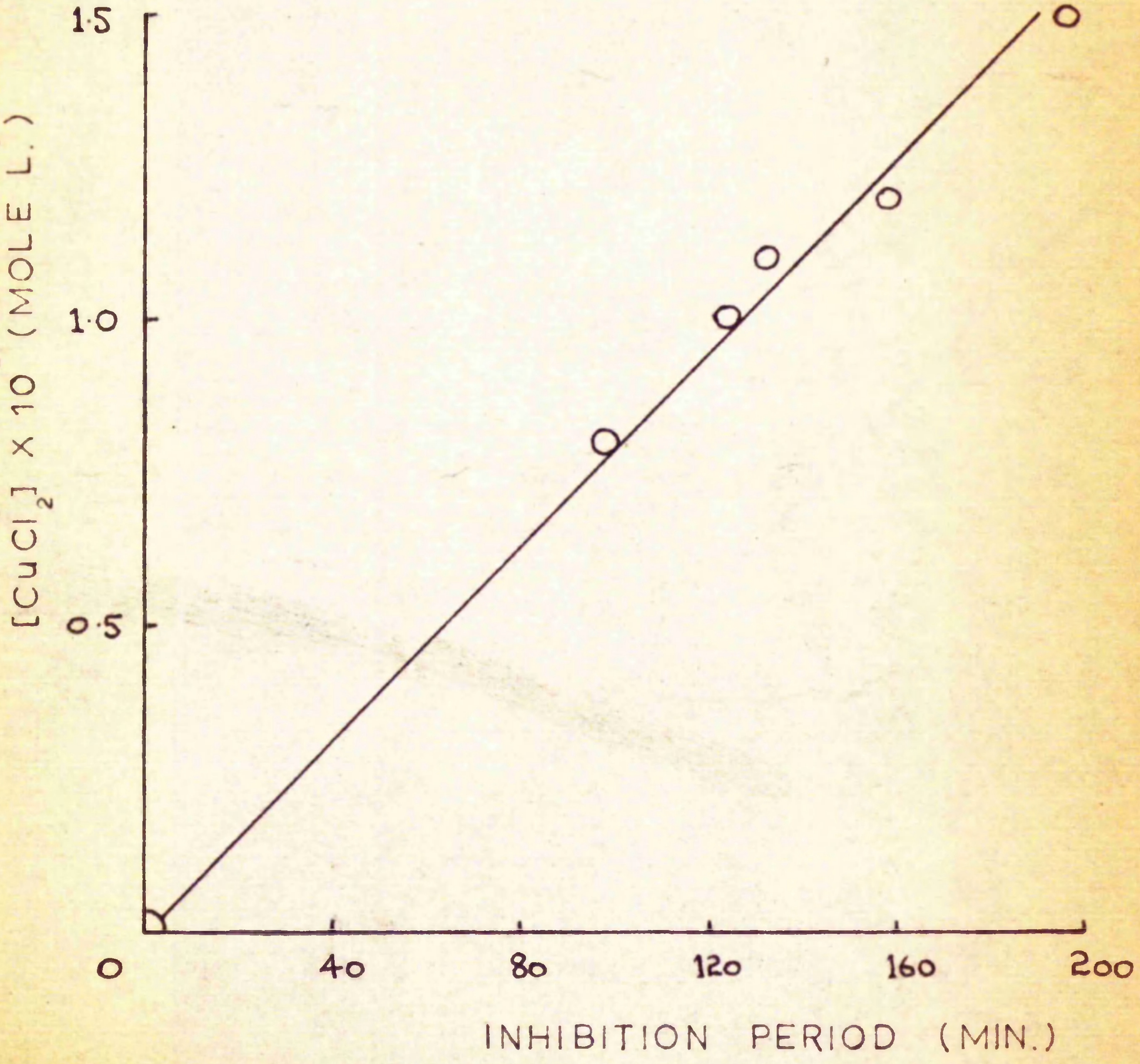


TABLE 4

RESULTS FOR STYRENE POLYMERIZATION AT 50°C IN PRESENCE OF CUPRIC CHLORIDE IN DMF

$[AIBN] = 3 \times 10^{-2}$ MOLE l^{-1}, $[M] = 6.74$ MOLE l^{-1}

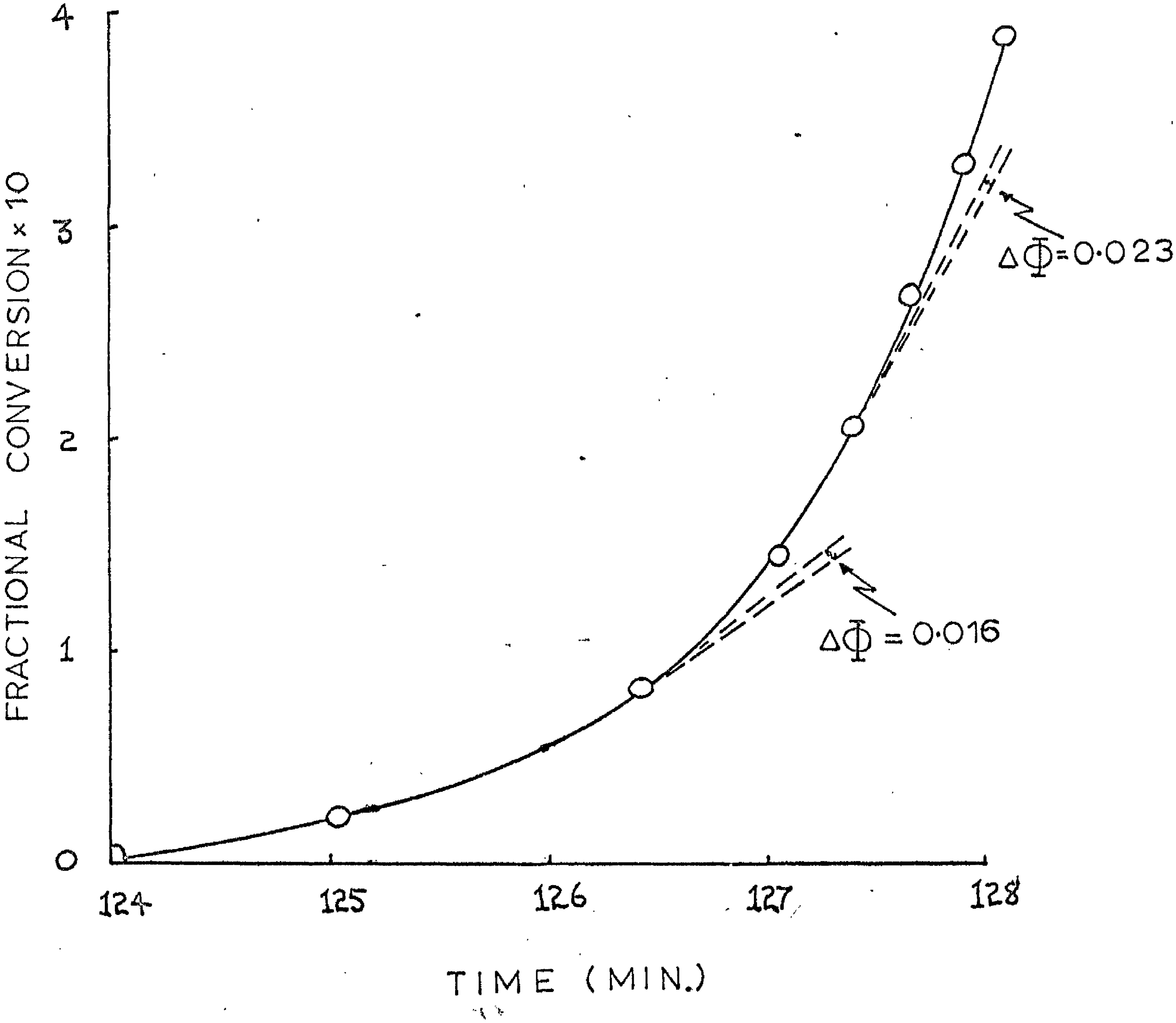
$[CuCl_2]$ mole l^{-1} $(x10^4)$	Inhibition Period(min)	Final Rate % conv./hr	mole $l^{-1}sec^{-1}$ $(x10^5)$
zero	zero	1.98	3.72
8	98	1.93	3.60
10	127	1.98	3.72
11	134	1.95	3.64
15	197	1.78	3.32

The rate of initiation has been measured from the slope of Fig.9 in the usual way and found to be 1.33×10^{-7}mole l^{-1} sec^{-1}. At the initiator concentration used this corresponds to a rate constant of initiation, 2ki, of 4.43×10^{-6} sec^{-1}.

The k_x/k_p ratio for the system at 50°C has been determined as described in the last section. A detailed plot of the acceleration period for a run at a cupric chloride concentration of 1.1×10^{-3} mole l^{-1} is given in Fig.10. The probable error in measuring ϕ_t at the upper and lower limits of the range are shown and the effect of

FIG. 10 ACCELERATION PERIOD AT 50°C

$[CuCl_2] = 1{\cdot}1 \times 10^{-3}$ MOLE L^{-1}.



this error on the final determination of k_x/k_p by the methods of Bengough and Bamford has been estimated as described earlier.

For the run plotted in Fig.10 a k_x/k_p value of 11,100 has been determined by Bengough's method. The error introduced into this determination by inaccuracy in ϕ_t measurement corresponds to a possible range of 10,800 - 12,000 for the ratio.

The corresponding results obtained by Bamford's treatment of the data are as follows. Determination of the slope of $-\frac{1}{\phi} + \ln\left(\frac{1+\phi}{1-\phi}\right)$ against time by the method of least squares leads to a k_x/k_p value of 12,200, while considerations of likely error in ϕ_t give the limits 11,100 and 12,400 for the ratio.

Table 5 shows experimental data for runs done at 50°C treatment of which by Bengough's and Bamford's methods has led to the k_x/k_p values collated in table 6.

TABLE 5

EXPERIMENTAL DATA FOR EVALUATION OF k_x/k_p FOR STYRENE - CUPRIC CHLORIDE SYSTEM AT 50°C.

[AIBN] = 3 x 10^{-2} mole l^{-1} [$CuCl_2$] (mole l^{-1} x 10^4) = 8(i), 11(iii), 10(ii), 15(iv).

Time (min & sec)	Fractional Conversion (Fx10^4)	Reduced Rate (ϕ)	Time min & sec)	Fractional Conversion (F x 10^4)	Reduced Rate (ϕ)
(i)			(ii)		
97:00	1.20	0.199	123:40	3.07	0.187
97:20	1.44	0.268	124:00	3.30	0.211
97:30	1.59	0.303	124:20	3.55	0.247
97:40	1.77	0.335	124:30	3.70	0.296
97:50	1.96	0.411	124:40	3.88	0.346
98:00	2.23	0.510	125:00	4.33	0.498
98:05	2.37	0.561	125:20	5.05	0.696
98:10	2.55	0.681			
(iii)			(iv)		
126:30	0.855	0.251	195:00	2.65	0.195
126:40	1.00	0.282	195:40	3.09	0.262
126:50	1.17	0.334	196:00	3.36	0.310
127:00	1.36	0.394	196:20	3.72	0.389
127:10	1.60	0.515	196:40	4.14	0.478
127:20	1.91	0.609	197:00	4.65	0.590
127:30	2.26	0.685			

TABLE 6

LIST OF k_x/k_p VALUES AT 50°C for STYRENE - CUPRIC CHLORIDE SYSTEM

[AIBN] = 3 x 10^{-2} mole 1^{-1}

Cupric Chloride Concentration (mole 1^{-1}x 10^4)	k_x/k_p	
	Bengou h's Method	Bamford's Method
8	12,600	12,100
10	10,100	10,700
11	11,100	12,200
15	7,500	7,500

There is quite good agreement and little scatter in the values obtained at the three lower inhibitor concentrations, whereas the result at 1.5 x 10^{-3} mole 1^{-1} salt is considerably lower than the others. The error associated with this value will be higher than with the others both because of the fewer ϕ_t values used in its determination and the absence from the latter of any ϕ value above 0.6.

3.3.3 The System at 70°C

Study of the inhibition of the reaction at this temperature in order to evaluate the k_x/k_p ratio is complicated by the fact that satisfactory recording of the acceleration period can be done only on a thermally stable system. Because of the relatively long time required for thermal equilibrium to be reached, even with the disc dilatometers used, it was necessary to have an inhibition period of at least about forty minutes duration for satisfactory study of the system.

In order to obtain an inhibition period in excess of 40 minutes the catalyst:inhibitor ratio has to be reduced to a level which makes no longer negligible the catalyst decomposed during the inhibition period so that rates of initiation may decrease significantly over the length of a run. This introduces further error into the determinations which has been tolerated in order to examine for any significant variation in the k_x/k_p ratio with increase in temperature.

The results summarized in table 7 for runs carried out at an initiator concentration of 1×10^{-3} mole l^{-1} show the effect described above.

Table 7

RESULTS FOR STYRENE POLYMERIZATION AT 70°C IN PRESENCE OF CUPRIC CHLORIDE IN DMF

$[AIBN] = 1 \times 10^{-3}$ mole l^{-1}, $[M] = 6.60$ mole l^{-1}

$[CuCl_2]$ mole l^{-1} ($\times 10^4$)	Inhibition Period (min)	Final Rate % conv./hr	Final Rate mole $l^{-1}sec^{-1}$ ($\times 10^5$)
zero	zero	2.82	5.17
3.0	43	2.79	5.11
4.0	57	2.54	4.65
5.0	85	2.48	4.55

These results have been plotted in Fig.11 and from the slope a mean rate of initiation of 1.07×10^{-7} mole $l^{-1}sec^{-1}$ has been taken. This would correspond to a $2k_i$ value of 1.07×10^{-4} sec^{-1} under the conditions studied.

The acceleration period following inhibition for a run at a cupric chloride concentration of 4×10^{-4} mole l^{-1} is shown in Fig.12 and the errors involved in measurement of gradient have been shown as before. The results obtained and the errors associated with the final k_x/k_p values are as follows.

The value of the ratio obtained from Fig.12 by Bengough's method is 8,300 with a possible range from 7,400

FIG. 11 DEPENDENCE OF INHIBITION PERIOD ON $[CuCl_2]$ AT 70°C

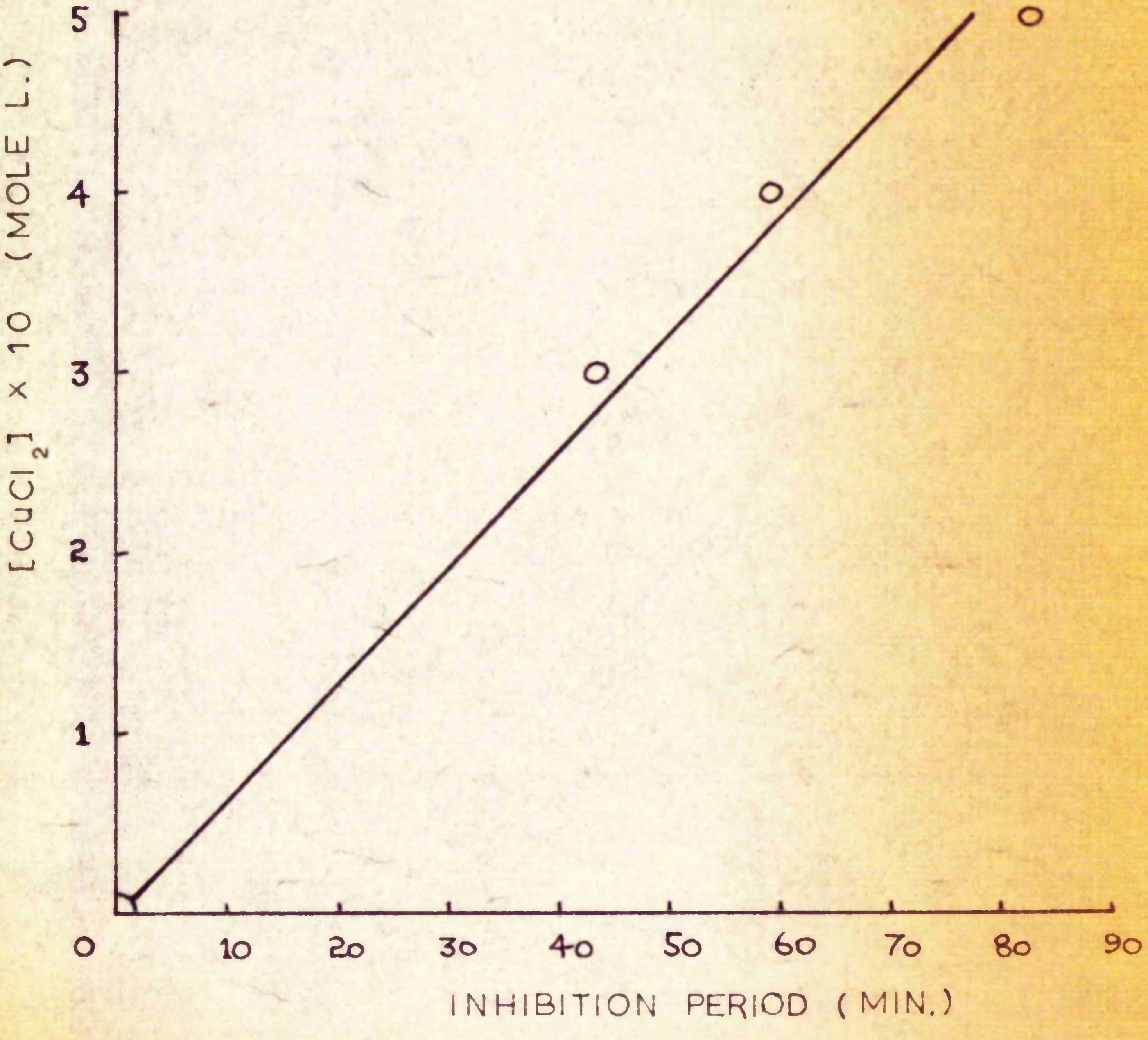
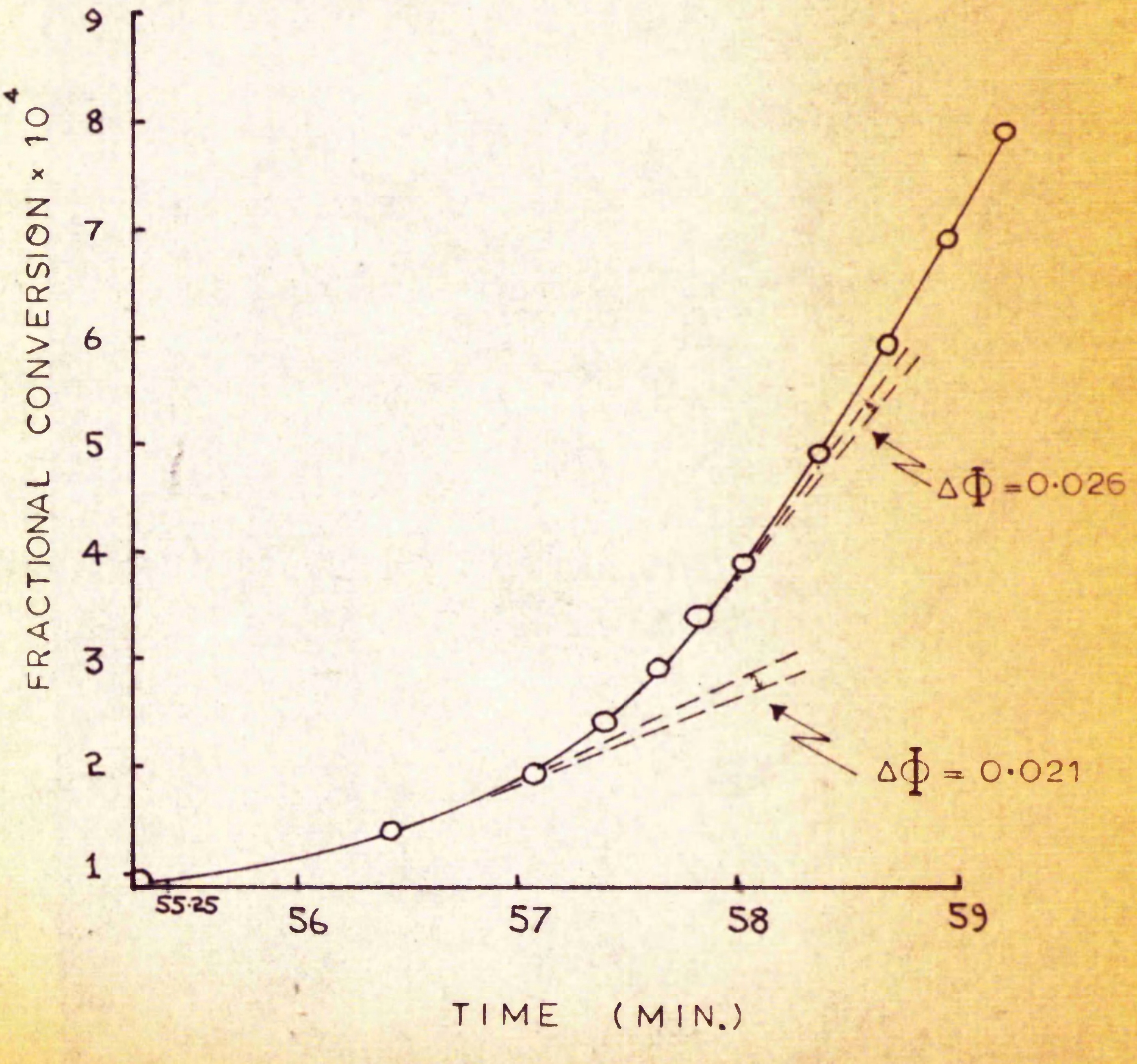


FIG. 12 ACCELERATION PERIOD AT 70°C

$[CuCl_2] = 4 \times 10^{-4}$ MOLE L^{-1}.



to 8,600 introduced from errors in ϕ_t measurement.

Bamford's method leads to the k_x/k_p ratio, 9,800 with a possible range from 8,400 to 9,900.

In tables 8 and 9 respectively are shown some experimental data at 70°C and the final determined values of k_x/k_p at this temperature.

TABLE 8

EXPERIMENTA DATA FOR EVALUATION OF k_x/k_p FOR STYRENE - CUPRIC CHLORIDE SYSTEM AT 70°C

$[\mathrm{AIBN}] = 1 \times 10^{-3}$ mole l^{-1} $[\mathrm{CuCl_2}]$ mole $l^{-1} \times 10^4$ = 3.0(i)
4.0(ii)
5.0(iii)

	Time (min & sec)	Fractional Conversion ($F \times 10^4$)	Reduced Rate (ϕ)
(i)	42:10	0.311	0.190
	42:20	0.479	0.256
	42:30	0.735	0.373
	42:40	1.07	0.479
	42:50	1.47	0.594
	43:00	1.97	0.660
(ii)	56:50	1.71	0.212
	57:00	1.87	0.248
	57:10	2.07	0.295
	57:20	2.29	0.352
	57:30	2.60	0.527
	58:00	3.98	0.711
(iii)	84:00	2.01	0.219
	84:10	2.15	0.248
	84:20	2.30	0.278
	84:30	2.49	0.310
	84:40	2.68	0.374
	84:50	2.93	0.440
	85:00	3.22	0.525
	85:20	3.91	0.630

TABLE 9

LIST OF k_x/k_p VALUES AT 70°C FOR STYRENE - CUPRIC CHLORIDE SYSTEM

$[AIBN] = 1 \times 10^{-3}$ mole l^{-1}

Cupric Chloride Concentration (mole $l^{-1} \times 10^4$)	k_x/k_p	
	Bengough's Method	Bamford's Method
3.0	10[illegible]00	12800
4.0	8300	9800
5.0	8300	7600

The error associated with the value of k_x/k_p determined at 3.0×10^{-4} mole l^{-1} cupric chloride will be mainly that involved through inaccuracy in ϕ measurement, whereas with the runs at the higher inhibitor concentrations the inconstancy of the rate of initiation over the run (an approximately 20% decrease in I for the highest salt concentration) introduces an unknown error. The highest values for the ratio are thus likely to be the most reliable.

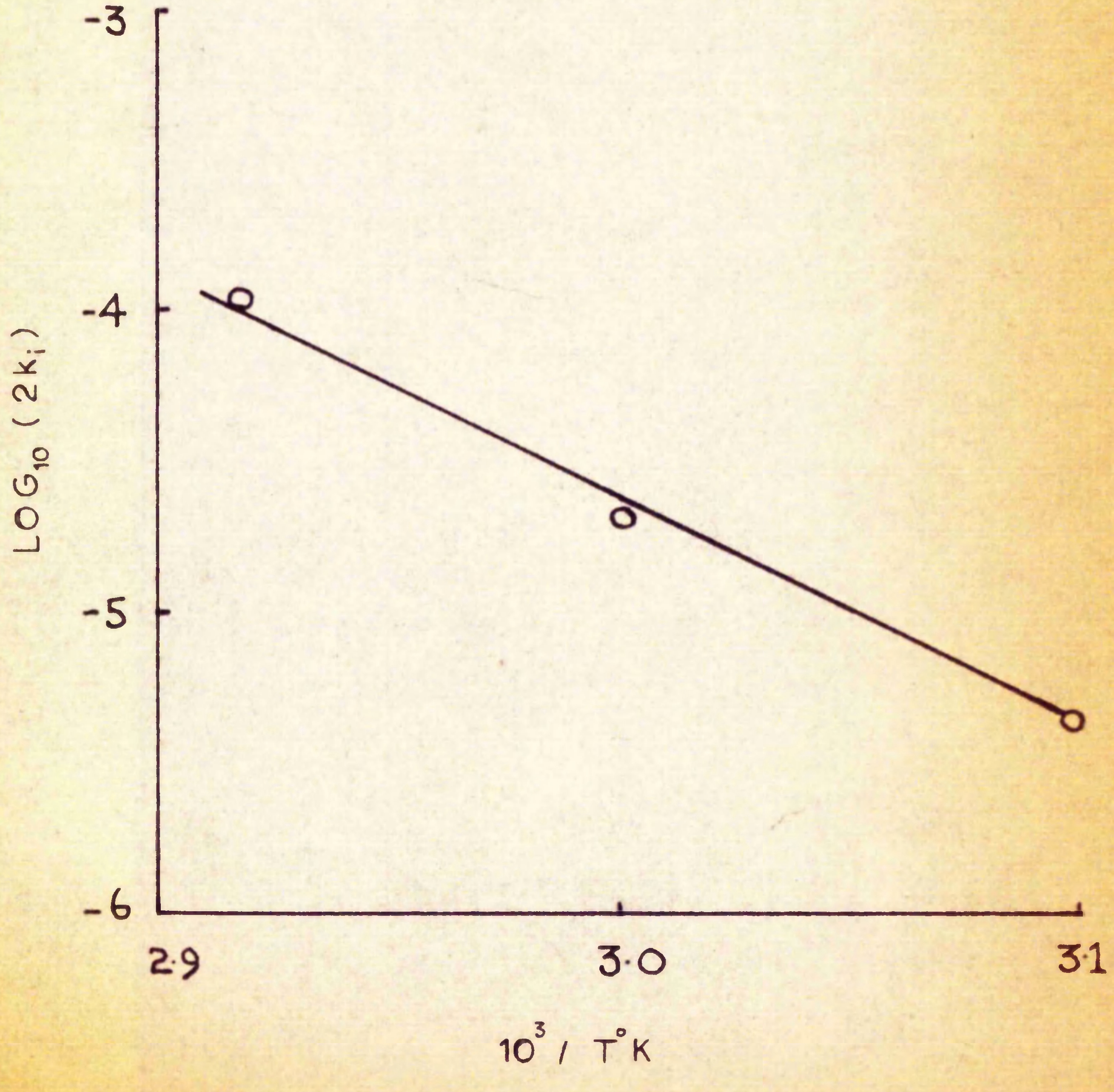
3.3.4 Activation Energies

Activation energies for the initiation and termination reactions have been measured using the data obtained at 50°, 60° and 70°C described in the previous sections.

The Arrhenius plot for the initiation reaction is shown in Fig.13. The activation energy measured from the slope of this plot is 34 k cal per mole. This value is lower

FIG 13 ARRHENIUS PLOT

FOR E_i DETERMINATION



than that quoted by Burnett of 36.4 k cal per mole[37]. It is likely that this discrepancy is in part due to the dubious nature of the $2k_i$ value at 70°C used in the present calculation.

An Arrhenius plot has been drawn in Fig.14 for the k_x/k_p values measured at the three temperatures. Mean values of the ratio have been used for this plot and the scatter in values obtained at each temperature is also shown.

The slope of the best line through the points gives a value of $E_p - E_x$, the difference between the activation energies for the propagation and termination reactions, of approximately +1 k cal per mole. The scatter about each point, however, is such that this value is meaningless except insofaras it is included in the more realistic result taken from the possible extremes of gradient in Fig.14 viz. $E_p - E_x = 0 \pm 5$ k cal per mole.

The overall activation energy for the polymerization, E_o has been determined by an Arrhenius plot of the logarithm of Rate/$[M]\,[AIBN]^{\frac{1}{2}}$ against reciprocal of absolute temperature. This plot is shown in Fig.15. The value of E_o obtained from the gradient is 22.6 k cal per mole.

For this system, E_o may be expressed as $E_o = \frac{1}{2}E_i + E_p - \frac{1}{2}E_t$ where E_t is the activation energy for the second order termination reaction. E_i has been found

FIG 14 ARRHENIUS PLOT

FOR $(E_p - E_x)$ DETERMINATION

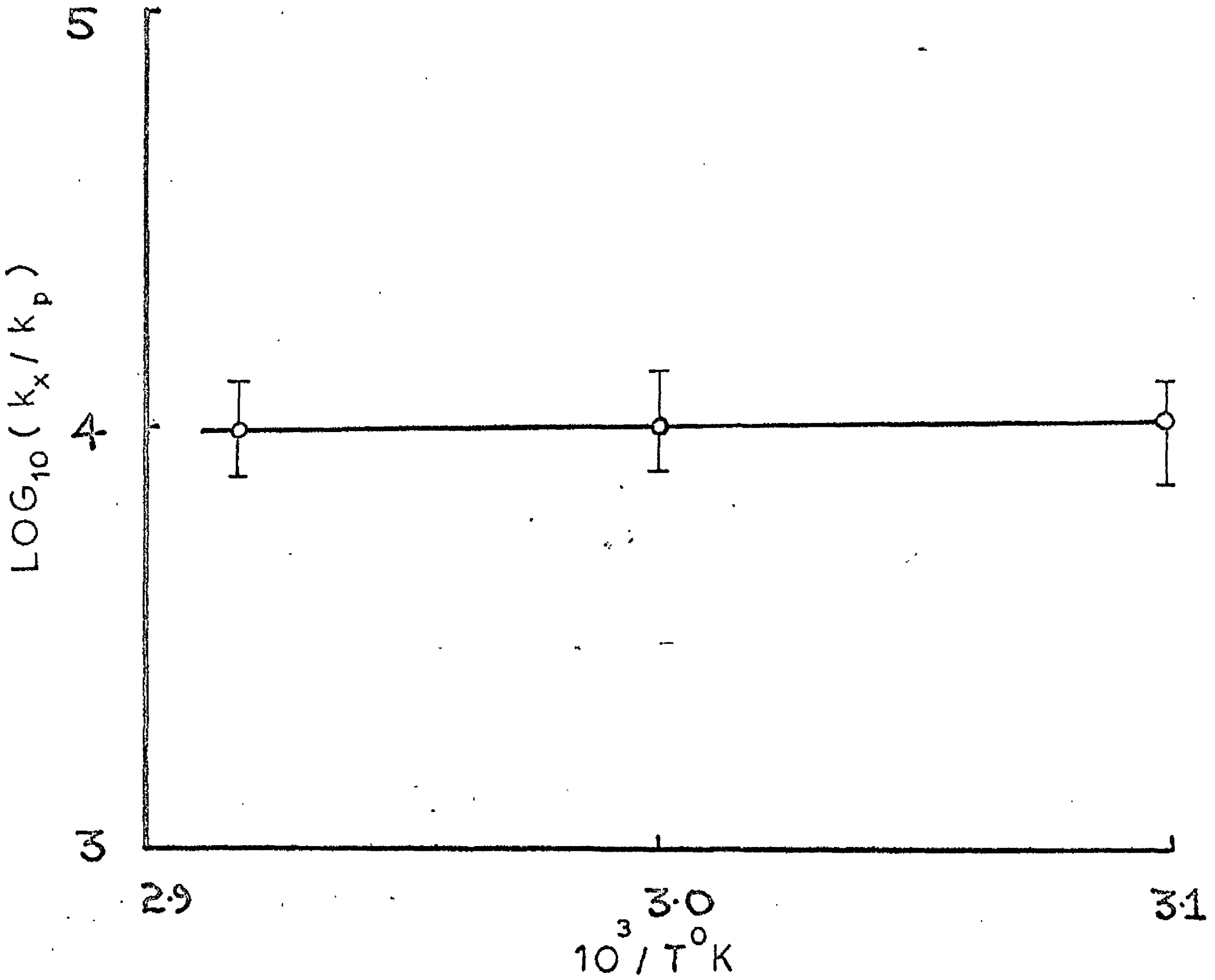
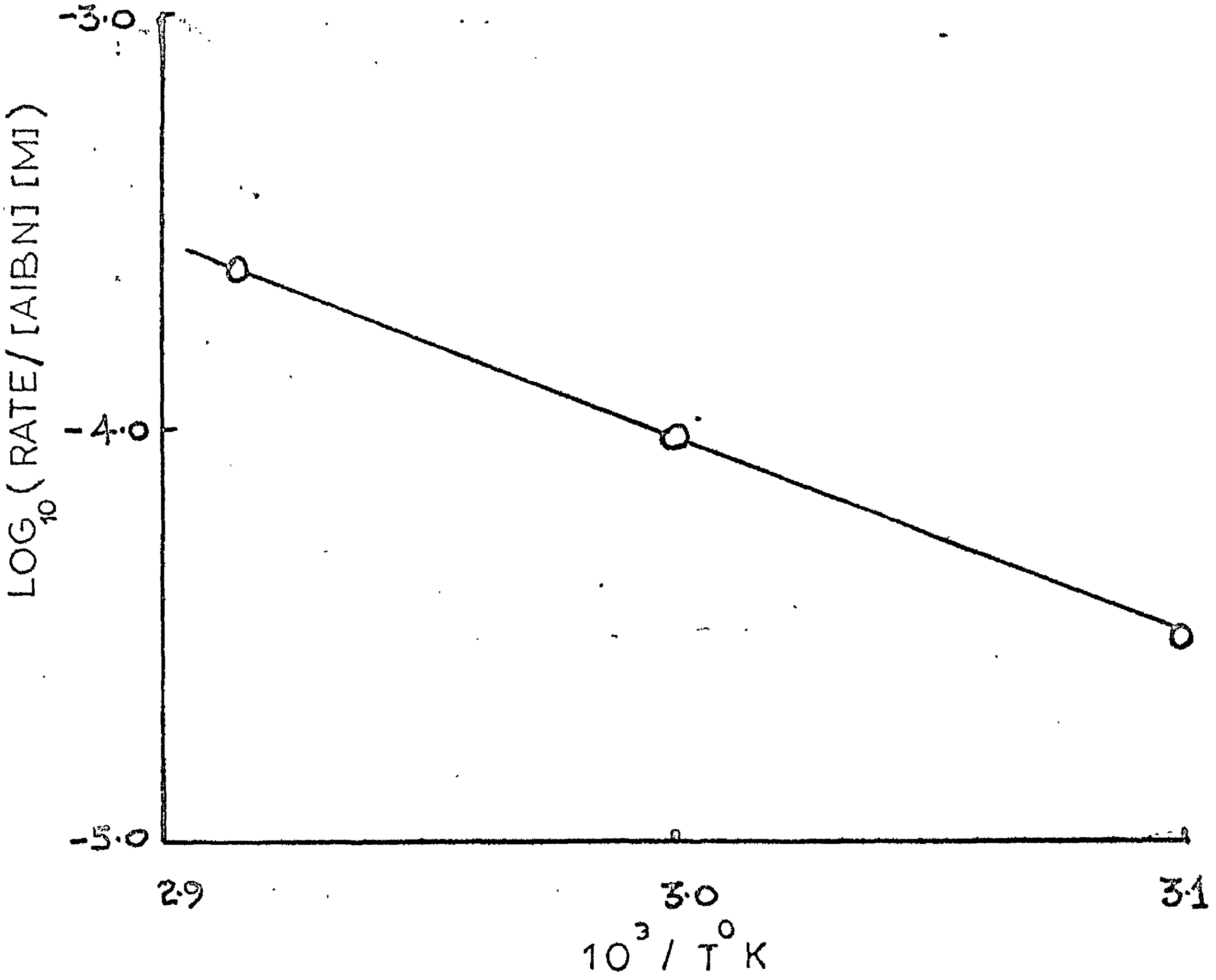


FIG 15 ARRHENIUS PLOT FOR E_0 DETERMINATION



to be 34 k cal per mole, Burnett has obtained a value of 1.9 k cal per mole for E_t[37], so that by substituting known values of the activation energies in our expression for E_o we arrive at a value of 6.6 k cal per mole for the activation energy of propagation. Burnett[37] has found an E_p value of 6.3 k cal per mole for the polymerization of styrene.

This derived value of E_p enables us to express the value of E_x as lying in the range 7 ± 5 k cal per mole.

3.3.5 Conclusion

It may be seen from the preceding sections that the treatments of Bengough and Bamford may be applied to this system for the evaluation of the k_x/k_p ratio.

It appears that error in reduced rate measurement contributes significantly to that involved in the final result, the extent of this contribution depending on the sensitivity of the given function to ϕ in the region measured.

The accuracy of the methods could be increased by such refinements of experimental technique as the use of a photographic or electrical method of following the acceleration period continuously, rather than by plotting points along its length as has been done here. In addition, the capacity of the dilatometers could be increased while keeping the capillary bore constant at 0.8 or 1.0 mm.

CHAPTER IV

Polymerization of Methacrylonitrile in presence of Cupric Chloride

The polymerization of methacrylonitrile initiated with AIBN and inhibited by cupric chloride in DMF has been studied at 50°, 60° and 70°C using techniques similar to those described in the preceding chapter.

Cupric chloride behaves as an ideal inhibitor in this polymerization. The product of inhibition which is likely to be simply cuprous chloride is inert and produces none of the retardation effects found in the cupric chloride inhibited polymerization of acrylonitrile in DMF solution[23].

Rates of initiation have been determined from simple inhibition period versus inhibitor concentration plots at the three temperatures and the activation energy for initiation in the system has been measured from an Arrhenius plot.

Measurement of reduced rates during the acceleration period following inhibition has led to values for k_x/k_p according to the methods of Bengough and Bamford discussed earlier. An activation energy for the termination step between radical and salt has been evaluated in a similar way to that for styrene given in the last chapter.

4.1 Procedure

The monomer used in the work was purified as described in Chapter II.

The polymerizations were carried out in dilatometers under vacuum as described for the earlier work. Methacrylonitrile is sufficiently volatile (b.p. = 90.3°C at 760 mm) for an ordinary vacuum line without heating system to be used.

Acceleration period studies were carried out using cylindrical-bulb dilatometers of capacity approximately 12 ml with a 1 mm bore 'Veridia' capillary stem.

A Ferrograph tape recorder was used to pre-record and play back a count-down at 30 second intervals over a period of 30 minutes so as to provide a time base for the acceleration period. This could then be followed simply in this way by taking cathetometer readings at ½-minute intervals without having to use a stopwatch.

Although a gain of about 1 second per minute was observed on playback the inaccuracy introduced was considered negligible.

4.2 Results and Discussion

4.2.1 Conversion Factors

The volume contraction-conversion relationship for the system at 50° and 70°C was determined by precipitation of the polymer from DMF solution in excess water and drying to constant weight at 50°C under reduced pressure. At both temperatures a linear relationship was found to hold between fractional contraction, V/V_o, and fractional conversion, F, up to about 10% conversion. The results can be expressed as follows.

At 50°C $V/V_o = 0.311\ F$
70°C $V/V_o = 0.314\ F$

A value for the conversion factor at 60°C was taken by linear interpolation from the above results thus

$$V/V_o = 0.312\ F$$

In their work on the bulk polymerization of methacrylonitrile[38] Grassie and Vance have reported the rather different relationships given below at the three temperatures.

At 50°C $V/V_o = 0.336\ F$
60°C $V/V_o = 0.347\ F$
70°C $V/V_o = 0.360\ F$

The relationships used for calculation of conversion values were those determined experimentally for the present system.

4.2.2 The System at 60°C

The inhibition of polymerization has been studied at a monomer:solvent ratio of 4:1 volume to volume, corresponding at 60°C to a monomer concentration of 9.06 mole l^{-1}.

The monomer was examined for active impurities under these conditions by carrying out runs at initiator concentrations of 1×10^{-2} and 3×10^{-2} mole l^{-1}. These

AIBN concentrations gave polymerization rates of 0.73 and 1.23% conversion per hour respectively. This corresponds to an initiator exponent of 0.48 which would indicate that no catalysing or retarding impurities are present.

The effect of cupric chloride on the polymerization in the concentration range up to 4 x 10^{-3} mole 1^{-1} has been studied at an initiator concentration of 3 x 10^{-2} mole 1^{-1}. It may be seen from the results plotted in Fig.16 that the final rate is independent of the initial cupric chloride concentration, i.e. that no retardation or catalysis by products occurs. Table 10 gives a summary of these results at 60°C.

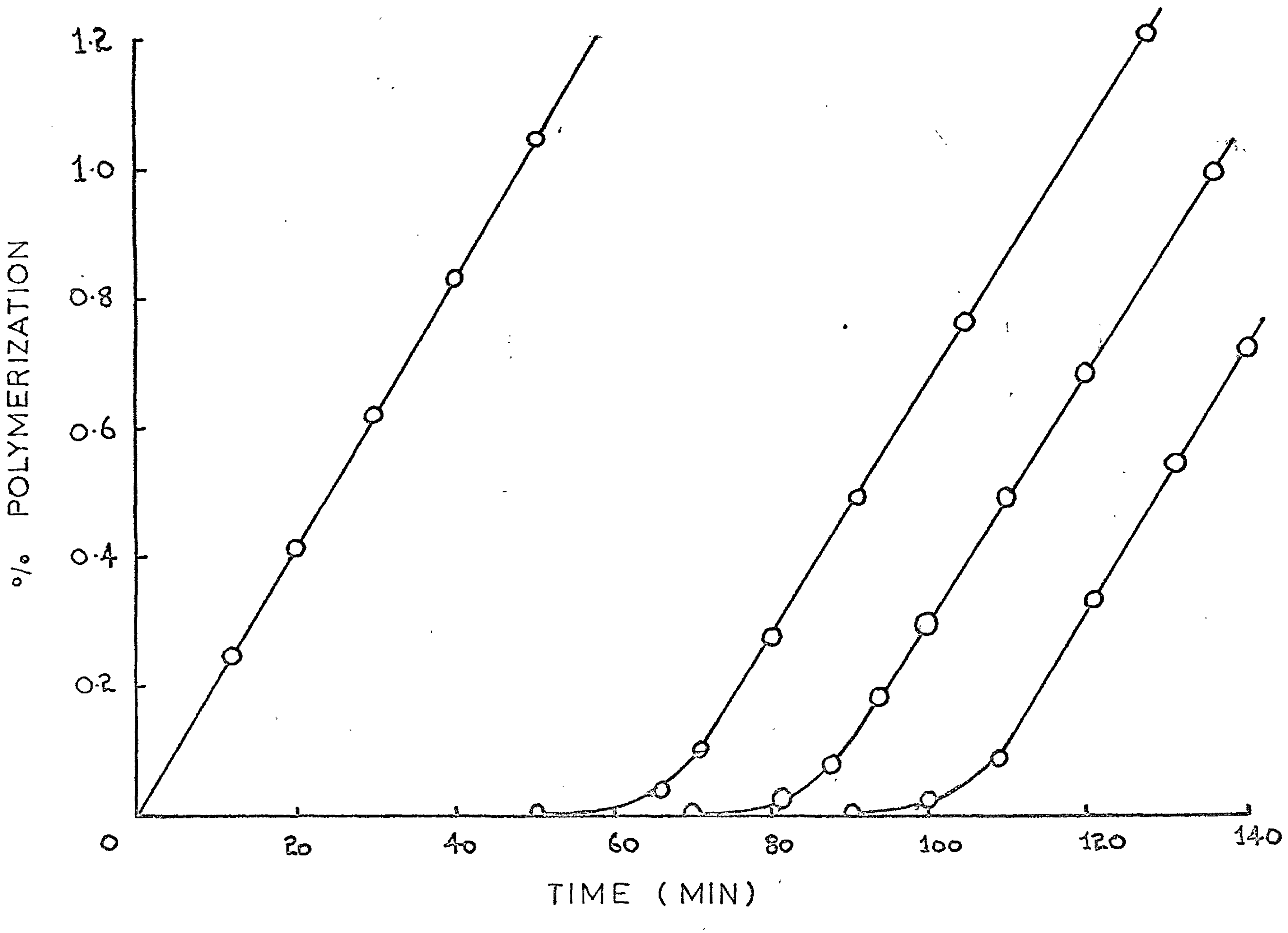
TABLE 10

RESULTS FOR METHACRYLONITRILE POLYMERIZATION AT 60°C IN PRESENCE OF CUPRIC CHLORIDE IN DMF.

$[AIBN] = 3 \times 10^{-2}$ mole 1^{-1}, $[M] = 9.06$ mole 1^{-1}

$[CuCl_2]$ mole 1^{-1} (x 10^3)	Inhibition Period (min)	Final Rate	
		% conv/hr	mole 1^{-1} sec^{-1} (x 10^5)
zero	zero	1.23	3.09
2.00	62	1.18	2.97
2.50	80	1.17	2.94
3.00	92	1.14	2.87
3.30	98	1.20	3.02
4.00	123	1.14	2.87

FIG 16 INHIBITION OF METHACRYLONITRILE POLYMERIZATION BY CUPRIC CHLORIDE IN DMF AT 60°C



A plot is given in Fig.17 of the dependence on inhibitor concentration of the inhibition period which has been derived from Fig. 16 by back-extrapolation to zero conversion in the usual way. The inhibition period increases linearly with cupric chloride concentration, and it can be seen from Fig.17 that there is no inhibition in the absence of cupric chloride.

The rate of removal of cupric chloride from the system is found from the slope of Fig.17 to be 5.45×10^{-7} mole l^{-1} sec^{-1}. At the initiator concentration used this rate of initiation corresponds to a value of 1.82×10^{-5} sec^{-1} for $2k_i$, the initiation rate constant.

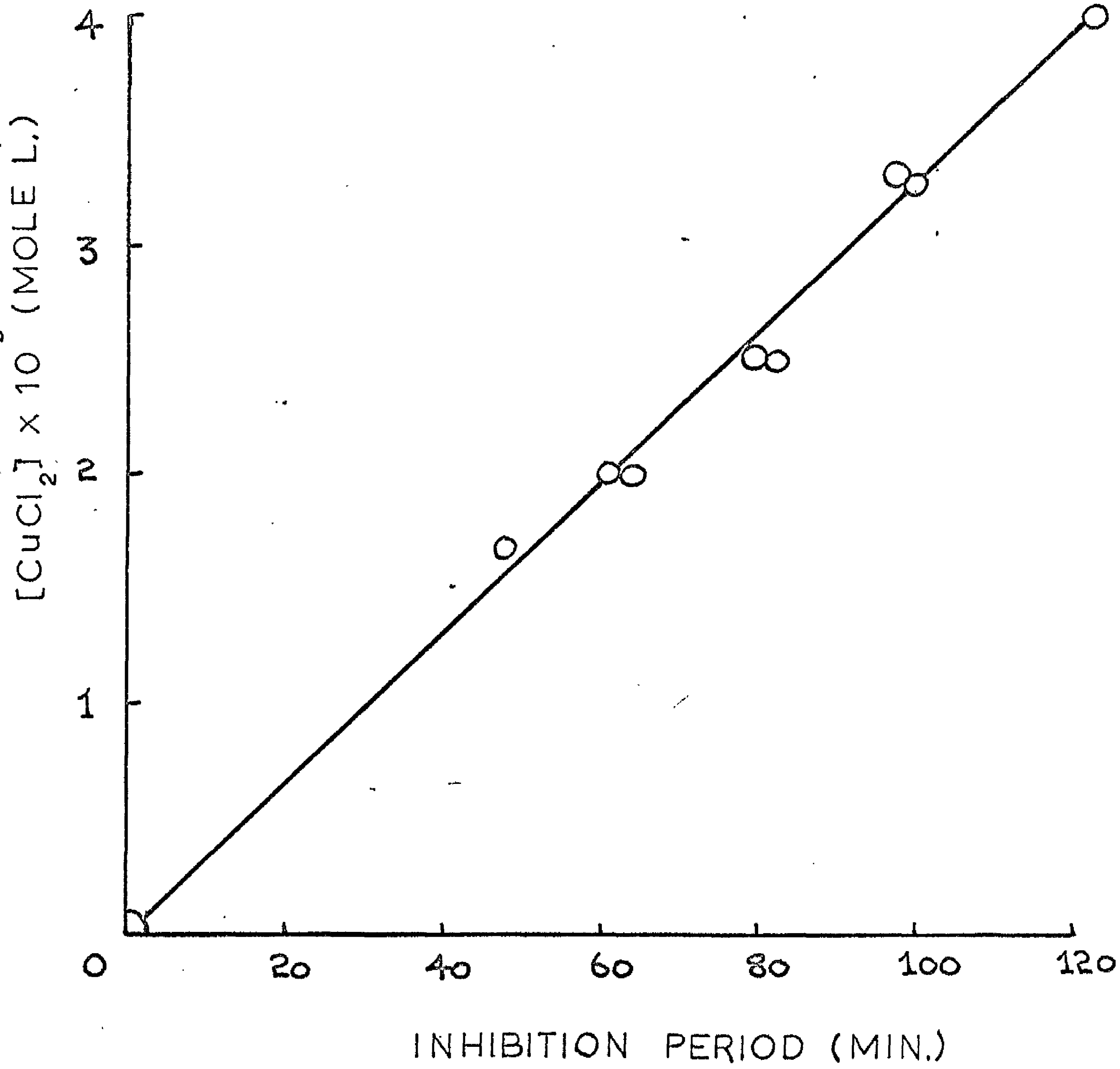
This $2k_i$ value is higher than that of 1.45×10^{-5} sec^{-1} found by Bamford and coworkers for this system using ferric chloride as a radical scavenger[32].

It is again possible, as suggested for the styrene work in the preceding chapter, that monomer concentrations play a part in explaining this discrepancy. Bamford et al. used a monomer concentration of 6.00 mole l^{-1} in their work as compared to 9.06 mole l^{-1} in the present study.

Taking the value for k_d, the first order rate constant for decomposition of AIBN of 1.20×10^{-5} sec^{-1} used earlier, we get an efficiency of initiation of approximately 75%.

During the course of the inhibition period the yellow-green colour of the cupric chloride in solution fades

FIG. 17 DEPENDENCE OF INHIBITION PERIOD ON [CuCl$_2$] AT 60°C



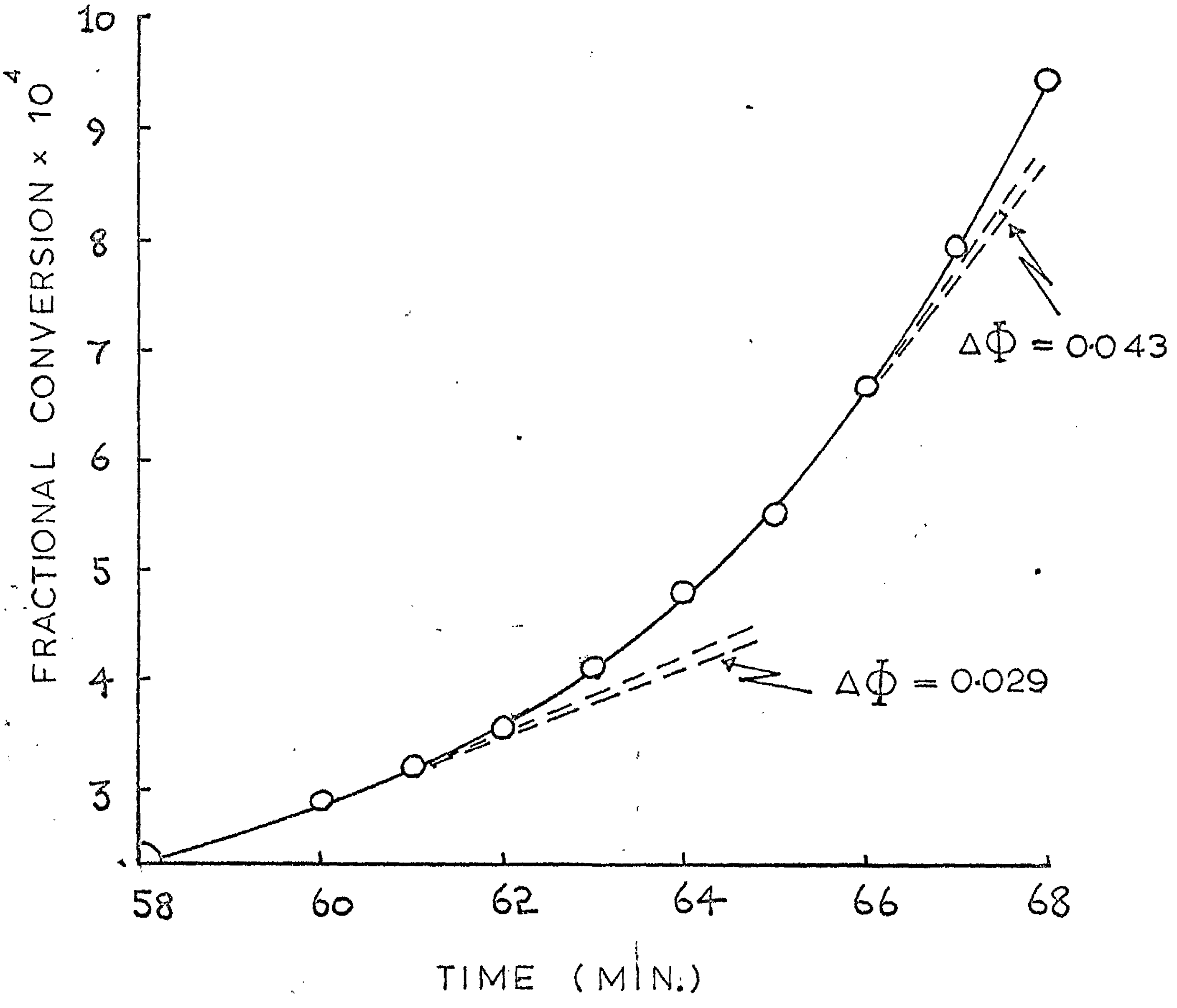
to give a colourless solution. No coloration of the type found in the acrylonitrile-cupric chloride-DMF system[23] develops. This would indicate that no interaction or complex formation takes place between the polymethacrylonitrile radicals and cuprous chloride. In the case of polyacrylonitrile radicals the interaction with cuprous chloride is thought to involve the substituent nitrile groups in co-ordinative bonding with the copper (1) species. A qualitative idea of this bonding is given by Blaker in a paper on the use of cuprous salts in dyeing of polyacrylonitrile fibres[39].

The absence of this effect with polymethacrylonitrile radicals may be due to some steric interference in bond formation by the substituent methyl groups. Polar effects in the polymer chain may also play some role by decreasing the effective electron density in the region of the nitrile groups although this effect is not likely to be important.

The acceleration period following inhibition was found to be of rather longer duration in this system than with styrene. This allowed the period to be followed using the pre-recorded time base rather than the constant speed recording voltmeter used for the styrene work. A detailed plot of the acceleration period for a run at a cupric chloride concentration of 2×10^{-3} mole l^{-1} is given in Fig.18. An initiator concentration of

FIG.18 ACCELERATION PERIOD AT 60°C

$[CuCl_2] = 2 \times 10^{-3}$ MOLE·L^{-1}.



3×10^{-2} mole l^{-1} has been used for all acceleration period work at 60°C.

The probable errors in drawing tangents to the curve are shown in Fig.18, and the effect of such errors on the determination of the k_x/k_p ratio by the methods of Bengough and Bamford have been estimated in the manner described in the preceding chapter.

A plot of log $(\frac{1-\phi^2}{\phi})$ against log (1-F) is given in Fig.19 for two runs at 60°C. Curve a corresponds to an initial cupric chloride concentration of 4×10^{-3} mole l^{-1} and curve b is that derived from the plot given in Fig.18 corresponding to an inhibitor concentration of 2×10^{-3} mole l^{-1}. The slope of the best lines to fit the experimental points has been determined by the method of least squares. An indication of the error introduced through inaccuracy in reduced rate measurement is given for curve b in Fig.19 by the broken lines drawn through extreme values of the function at high and low ϕ values.

The least squares gradient for curve b gives a k_x/k_p ratio of 4700, whereas the maximum and minimum values corresponding to the slopes of the broken lines are respectively 5400 and 4400. The least squares value for k_x/k_p from curve a in Fig.19 is 4000.

The plot of Bamford's function against time for these two runs is given in Fig.20 where curves a and b again

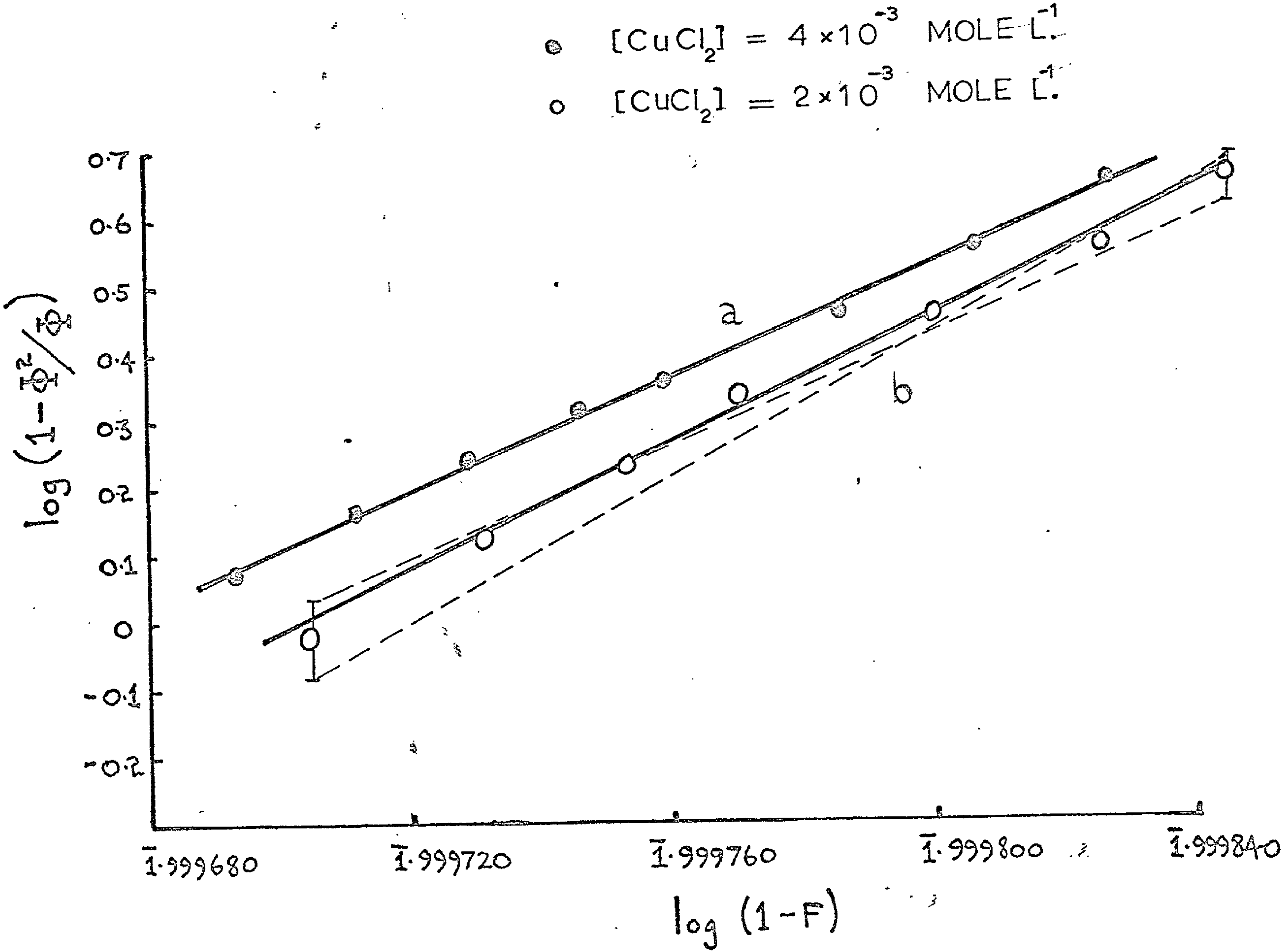
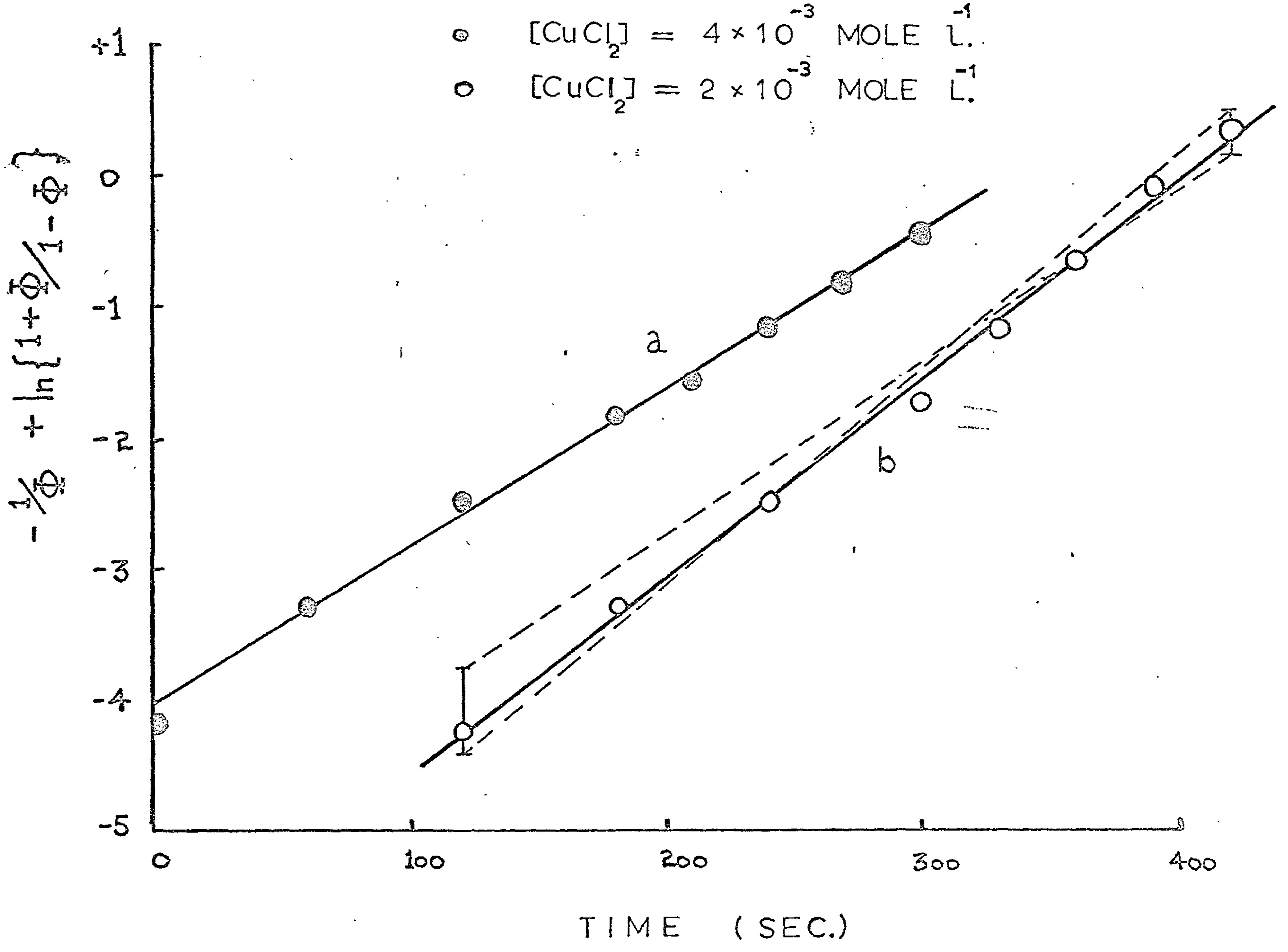


FIG 19 RESULTS FOR MAN POLYMERIZATION AT 60 C

FIG. 20 RESULTS FOR MAN POLYMERIZATION AT 60°C



correspond to cupric chloride concentrations of 4×10^{-3} and 2×10^{-3} mole l^{-1} respectively. The best lines through the points give k_x/k_p values of 4000 and 4600 respectively for the high and low inhibitor concentrations.

The extreme values of the ratio obtained as previously from the estimated error in the function at high and low ϕ values have been measured from the gradients of the broken lines shown for curve b in Fig.20. These values define the range 4400 to 5900 as an indication of the accuracy involved.

Experimental data used in the determination of the k_x/k_p ratio at 60°C are listed in Table 11 and in Table 12 the corresponding values of the ratio determined by the methods of Bengough and Bamford are given.

TABLE 11

EXPERIMENTAL DATA FOR EVALUATION OF k_x/k_p FOR METHACRYLONITRILE - CUPRIC CHLORIDE SYSTEM AT 60°C

[AIBN] = 3 x 10^{-2} mole l^{-1} $[CuCl_2]$ = (mole l^{-1}x10^3) = 2.0(i), 3.0(iii), 2.5(ii), 3.3(iv), 4.0(v).

	Time (min)	Fractional Conversion (F x 10^4)	Reduced Rate (ϕ)		Time (min)	Fractional Conversion (F x 10^4)	Reduced Rate (ϕ)
(i)	61	3.58	0.214	(ii)	80	3.60	0.230
	62	4.00	0.261		81	4.05	0.274
	63	4.60	0.316		82	4.69	0.324
	64	5.30	0.387		83	5.35	0.382
	64.5	5.69	0.460		83.5	5.71	0.420
	65	6.19	0.537		84	6.21	0.476
	65.5	6.81	0.630		84.5	6.69	0.536
					85	7.22	0.605
	66	7.45	0.700		85.5	7.84	0.703
(iii)	90	5.85	0.197	(iv)	96	4.52	0.242
	91	6.30	0.258		97	5.05	0.287
	91.5	6.58	0.288		98	5.65	0.347
	92	6.89	0.344		99	6.45	0.419
	92.5	7.26	0.375		99.5	6.95	0.515
	93	7.64	0.425		100	7.60	0.585
	93.5	8.03	0.516		100.5	8.12	0.666
	94	8.54	0.613		101	8.90	0.727
(v)	121	4.42	0.216				
	122	4.95	0.261				
	123	5.47	0.317				
	124	6.16	0.379				
	124.5	6.50	0.407				
	125	6.92	0.457				
	125.5	7.35	0.509				
	126	7.86	0.570				
	126.5	8.40	0.672				

TABLE 12

LIST OF k_x/k_p VALUES AT 60°C FOR METHACRYLONITRILE - CUPRIC CHLORIDE SYSTEM.

$[AIBN] = 3 \times 10^{-2}$ mole l^{-1}

Cupric Chloride Concentration (mole l^{-1} x 10^3)	k_x/k_p	
	Bengough's Method	Bamford's Method
2.00	4700	4600
2.50	3900	3800
3.00	5800	5700
3.30	4200	4200
4.00	4000	4000

There is good agreement between the methods, and, as can be seen from Table 12, there is relatively little scatter in the range of values obtained. The mean value of the ratio overall is 4500.

The activation energy data of Grassie and Vance[38] give a k_p value at 60°C of 200 mole^{-1}l sec^{-1}. This leads to a k_x value from the above results of approximately 9×10^5 mole^{-1}l sec^{-1} for the radical-salt termination reaction for this system.

The corresponding value for the methacrylonitrile-ferric chloride reaction at this temperature as determined by Bamford and coworkers[32] is 315 mole^{-1}l sec^{-1}.

There is thus a much greater difference between the reactivities of this monomer towards cupric and ferric chloride in DMF than is observed for the monomers, styrene and methyl-methacrylate, for example. Thus, on the basis of the published k_x values[24], methyl methacrylate radicals are terminated by cupric chloride in DMF more rapidly than by ferric chloride by a factor of approximately 200.

The corresponding factor for the methacrylonitrile system at 60°C is of the order of 3000.

4.2.3 The System at 50°C

Cupric chloride has been found to behave as an ideal inhibitor in this system at 50°C in a manner analogous to that observed at 60°C.

Runs for rate of initiation and k_x/k_p determination were carried out at an initiator concentration of 1×10^{-1} mole l^{-1}. Although the final rate obtained under these conditions was rather low (approximately 0.7% per hour), higher AIBN concentrations could not be used because of the escape from solution of the nitrogen produced in initiator decomposition. To offset the loss of accuracy caused by this low rate, dilatometers with a 0.8 mm bore capillary stem were used. In this way the acceleration period could be followed quite well using the same timing arrangement as at 60°C.

The effect of cupric chloride was studied at salt concentrations up to 2.68 x 10^{-3} mole l^{-1}. A summary of results obtained at 50°C is given in Table 13 from which it can be seen that the final rate obtained in each case is effectively the same.

TABLE 13

RESULTS FOR METHACRYLONITRILE POLYMERIZATION AT 50°C IN PRESENCE OF CUPRIC CHLORIDE IN DMF

$[AIBN] = 1 \times 10^{-1}$ mole l^{-1}, $[M] = 9.18$ mole l^{-1}

$[CuCl_2]$ (mole l^{-1}x10^3)	Inhibition Period(min)	Final Rate % conv/hr	Final Rate mole $l^{-1}sec^{-1}(x10^5)$
zero	zero	0.75	1.92
1.50	61	0.76	1.94
2.20	89	0.72	1.83
2.68	107	0.69	1.76

A plot of inhibition time against cupric chloride concentration is given in Fig.21 from which a rate of initiation of 4.12 x 10^{-7} mole l^{-1} sec^{-1} has been obtained. At the initiator concentration used this corresponds to a $2k_i$ value of 4.12 x 10^{-6} sec^{-1}. This value has been used in the determination of the activation energy of initiation in section 4.2.5 below.

Details of the acceleration period at 50°C for a run at a cupric chloride concentration of 2.2 x 10^{-3} mole l^{-1} are given in Fig.22. Once again the probable error in

FIG 21 DEPENDENCE OF INHIBITION PERIOD ON [CuCl$_2$] AT 50°C

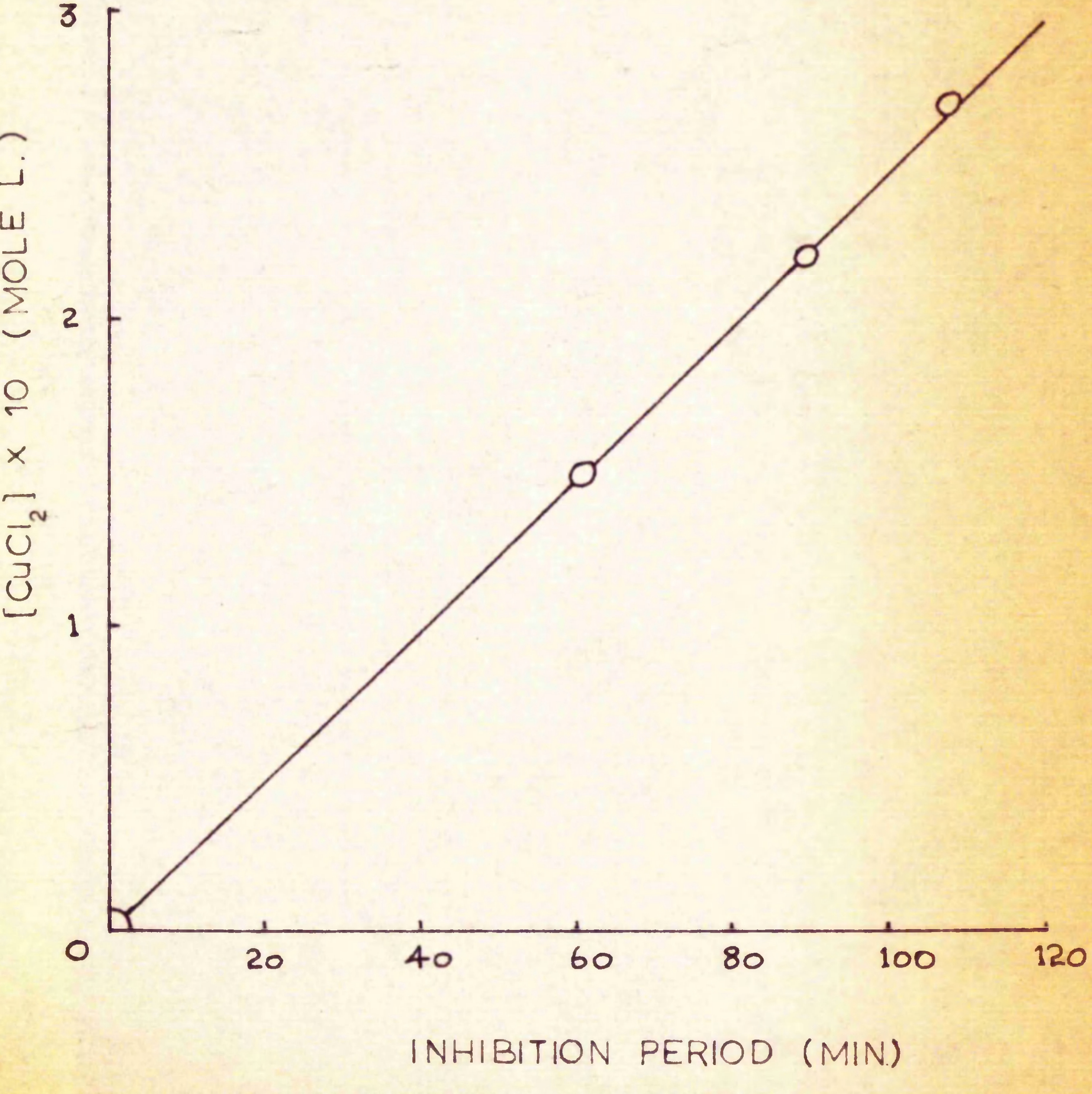
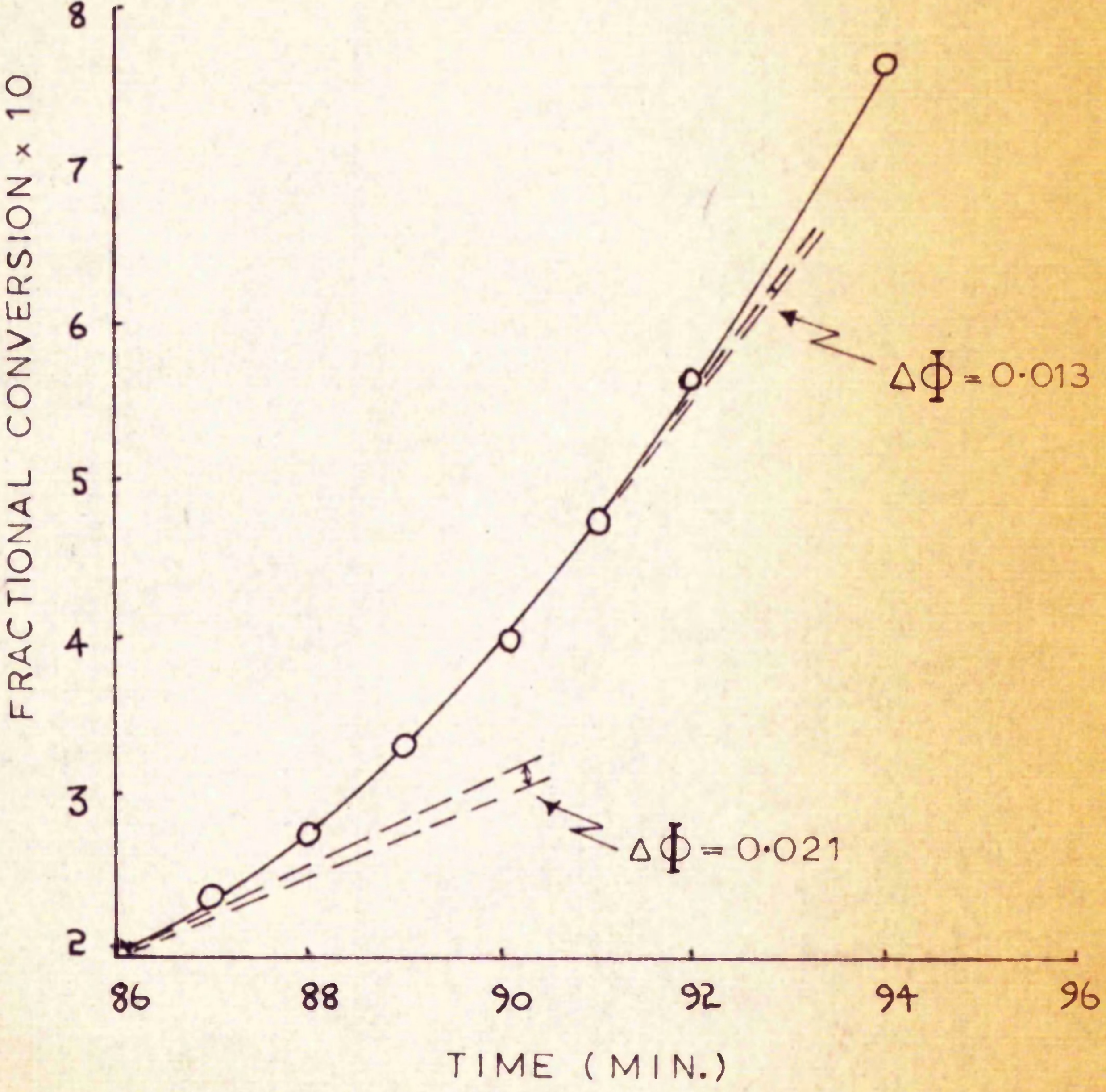


FIG. 22 ACCELERATION PERIOD AT 50°C

$[CuCl_2] = 2{\cdot}2 \times 10^{-3}$ MOLE L^{-1}.



measuring ϕ has been depicted, and the corresponding error in k_x/k_p as determined by the methods of Bengough and Bamford has been estimated.

The k_x/k_p value obtained from this run by Bengough's method is 5500, while the probable range given by error in ϕ measurement is from 5400 to 6400.

Bamford's treatment yields a least squares value of k_x/k_p of 6100 with a range of possible values from 6000 to 7200.

A list is given in Table 14 of the experimental data used in the calculation of the k_x/k_p ratio for the system at 50°C. Table 15 gives these values as determined by the two methods at the different inhibitor concentrations.

TABLE 14

EXPERIMENTAL DATA FOR EVALUATION OF k_x/k_p FOR METHACRYLONITRILE - CUPRIC CHLORIDE SYSTEM AT 50°C

$[AIBN] = 1 \times 10^{-1}$ mole l^{-1}, $[CuCl_2]$ (mole $l^{-1} \times 10^3$) = 1.50 (i), 2.20 (ii), 2.68 (iii).

	Time (min)	Fractional Conversion ($F \times 10^4$)	Reduce Rate (ϕ)
(i)	57	1.80	0.286
	58	2.20	0.356
	59	2.71	0.425
	60	3.28	0.472
	60.5	3.61	0.505
	61	3.90	0.526
	61.5	4.25	0.550
	62	4.60	0.586
	63	5.35	0.631
	64	6.21	0.663
(ii)	86	1.94	0.244
	87	2.34	0.326
	88	2.76	0.420
	88.5	3.03	0.460
	89	3.33	0.515
	89.5	3.66	0.563
	90	3.98	0.599
	90.5	4.35	0.635
	91	4.75	0.677
(iii)	103	3.94	0.228
	104	4.15	0.272
	105	4.45	0.322
	106	4.89	0.384
	107	5.36	0.430
	107.5	5.65	0.456
	108	5.91	0.495
	108.5	6.18	0.545
	109	6.53	0.609
	109.5	6.94	0.678

TABLE 15

LIST OF k_x/k_p VALUES AT 50°C FOR METHACRYLONITRILE - CUPRIC CHLORIDE SYSTEM

$[AIBN] = 1 \times 10^{-1}$ mole l^{-1}

Cupric Chloride Concentration (mole l^{-1} x 10^3)	k_x/k_p	
	Bengough's Method	Bamford's Method
1.50	3000	3200
2.20	5500	6100
2.68	5000	5100

The agreement between the methods for each run is fair although there is a considerable range between the maximum and minimum values obtained. This scatter is greater than that likely to be introduced by error in reduced rate measurement only. A possible contribution in this respect may be made by inaccuracy in drawing the true acceleration period curve through the experimentally determined points.

4.2.4 The System at 70°C

An initiator concentration of 1×10^{-2} mole l^{-1} was used for all runs at 70°C for determination both of the rate of initiation and of the k_x/k_p ratio for the system. The final rate obtained under these conditions was such as to allow the use of 1mm bore dilatometers of capacity about 12 ml for acceleration period measurements.

The lower rate of initiation observed in this system relative to styrene has allowed acceptable inhibition periods to be obtained without reducing by too much the initiator:inhibitor ratio. Thus it can be seen from Table 16 where some results of the work have been collated that the final rate obtained is not affected by initiator decomposition during inhibition.

TABLE 16

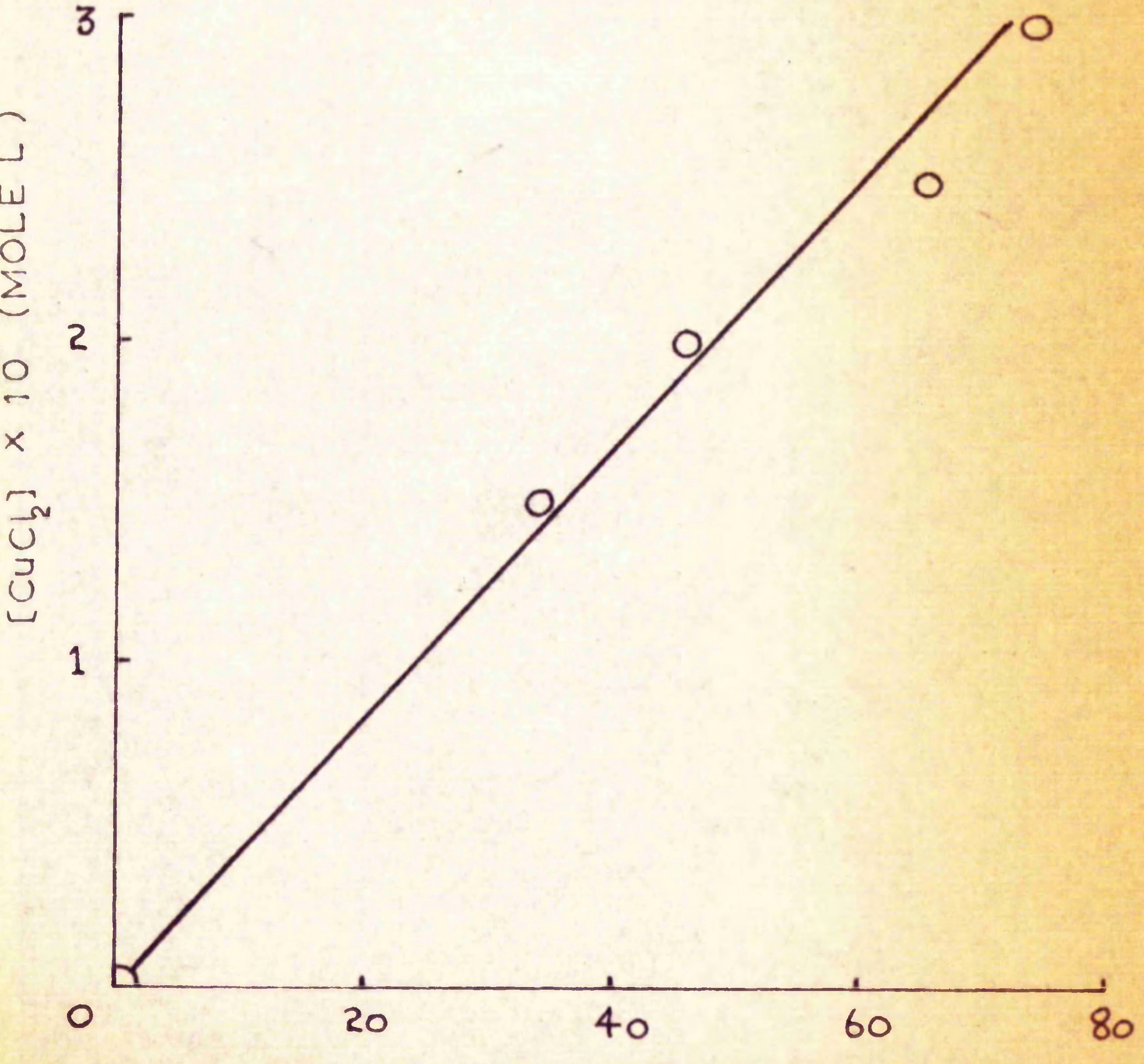
RESULTS FOR METHACRYLONITRILE POLYMERIZATION AT 70°C IN PRESENCE OF CUPRIC CHLORIDE IN DMF

$[\mathrm{AIBN}] = 1 \times 10^{-2}$ mole 1^{-1}, $[\mathrm{M}] = 8.96$ mole 1^{-1}

$[\mathrm{CuCl_2}]$ (mole $1^{-1} \times 10^{3}$)	Inhibition Period (min)	Final Rate	
		% conv/hr	mole 1^{-1} sec^{-1} ($\times 10^{5}$)
zero	zero	1.84	4.57
1.50	34	1.76	4.38
2.00	46	1.76	4.38
2.50	65	1.68	4.18
3.00	74	1.81	4.50

The plot of inhibition period against inhibitor concentration shown in Fig.23 has been derived from the above data. The dependence can be seen to be of fair linearity through the origin. The rate of initiation obtained from the slope of the curve is

FIG. 23 DEPENDENCE OF INHIBITION PERIOD ON [$CuCl_2$] AT 70°C



6.93×10^{-7} mole l^{-1} sec^{-1}, giving a rate constant of initiation at 70°C of $2k_i = 6.93 \times 10^{-5}$ sec^{-1}.

The conversion-time curve for a run at 70°C at a cupric chloride concentration of 2.5×10^{-3} mole l^{-1} is shown over the length of the acceleration period in Fig.24.

The k_x/k_p values obtained by treatment of the data from this run by Bengough's and Bamford's methods are as follows.

A least squares value of k_x/k_p of 4400 has been found by Bengough's method, with a probable error introduced from inaccurate ϕ measurement defining a range, 4300 - 5100.

Bamford's method yields a result $k_x/k_p \simeq 2700$ with a range from 2600 to 3100.

Lists of experimental data and derived results are given in Tables 17 and 18 respectively.

FIG. 24 ACCELERATION PERIOD AT 70°C

$[CuCl_2] = 2{\cdot}5 \times 10^{-3}$ MOLE L^{-1}

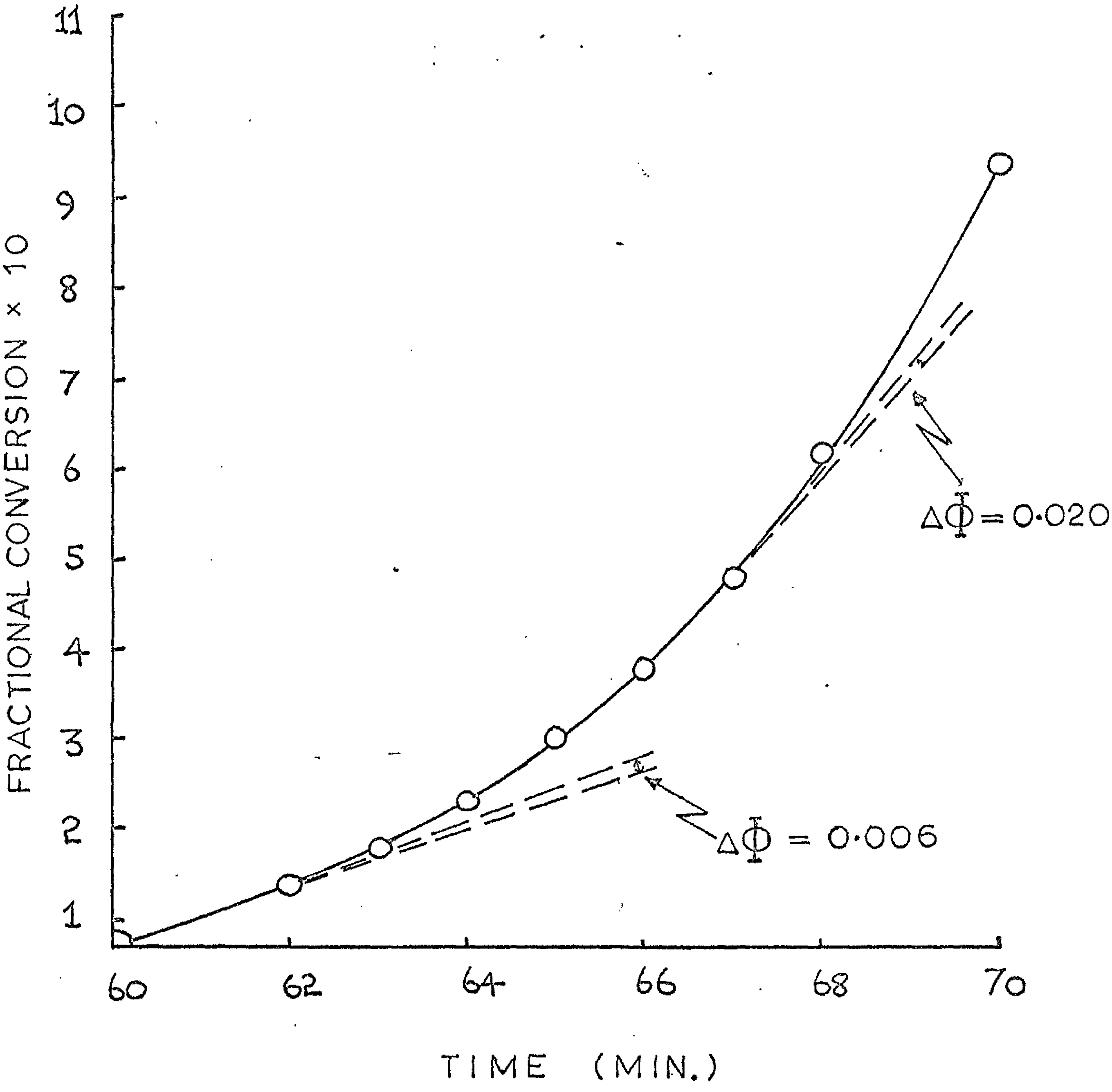


TABLE 17

EXPERIMENTAL DATA FOR EVALUATION OF k_x/k_p FOR METHACRYLONITRILE - CUPRIC CHLORIDE SYSTEM AT 70°C

$[AIBN] = 1 \times 10^{-2}$ mole l^{-1} $[CuCl_2]$ (mole $l^{-1} \times 10^3$) = 1.5(i), 2.5(iii), 2.0(ii), 3.0(iv)

Time (min)	Fractional Conversion ($F \times 10^4$)	Reduced Rate (ϕ)	Time (min)	Fractional Conversion ($F \times 10^4$)	Reduced Rate (ϕ)
(i)			(ii)		
32.5	0.91	0.192	44	0.91	0.189
33	1.05	0.234	44.5	1.11	0.235
33.5	1.33	0.298	45	1.34	0.292
34	1.66	0.405	45.5	1.65	0.346
34.5	2.08	0.529	46	2.01	0.425
35	2.64	0.623	46.5	2.47	0.540
35.5	3.26	0.719	47	3.03	0.673
(iii)			(iv)		
62	1.38	0.226	71	2.10	0.186
63	1.81	0.278	72	2.51	0.248
63.5	2.04	0.311	72.5	2.76	0.274
64	2.34	0.347	73	3.04	0.308
65	3.04	0.403	73.5	3.35	0.380
65.5	3.39	0.428	74	3.76	0.467
66	3.79	0.496	74.5	4.21	0.519
66.5	4.28	0.589	75	4.76	0.593
67	4.82	0.664	75.5	5.37	0.650
			76	6.04	0.715

TABLE 18

LIST OF k_x/k_p VALUES AT 70°C FOR METHACRYLONITRILE - CUPRIC CHLORIDE SYSTEM. [AIBN] = 1×10^{-2} mole l^{-1}

Cupric Chloride Concentration (mole $l^{-1} \times 10^3$)	k_x/k_p	
	Bengough's Method	Bamford's Method
1.50	8600	6100
2.00	8400	5500
2.50	4400	2700
3.00	5200	3500

The agreement between the methods and the scatter in the values obtained as shown in Table 18 are less satisfactory than those found at the lower temperatures. It is rather difficult to account for these discrepancies since there appears from the results in Table 16 to be no significant variation in the rate of initiation over the inhibition period. It is possible that errors in drawing the true curve over the rather shorter acceleration periods at this temperature make a larger contribution than at the lower tempetatures.

4.2.5 Activation Energies

Arrhenius activation energies have been determined from the experimental data at each temperature on rate of initiation, final rate of reaction and the derived k_x/k_p ratios.

The Arrhenius plot for the activation energy of initiation given in Fig.25 leads to an E_i value of 31 k cal per mole. The plot can be seen to be of good linearity and the value obtained from it is as expected for an AIBN initiated reaction.

The overall activation energy for the polymerization has been determined, as was done in the styrene work, by plotting log (Rate/$[AIBN]^{\frac{1}{2}}[M]$) against reciprocal temperature (^{o}K). This plot is given in Fig.26.

From the gradient of this plot an E_o value of 22.4 k cal per mole has been obtained. Expressing E_o in terms of the activation energies of the steps comprising the overall reaction, we have that $E_o = \frac{1}{2}E_i + E_p - \frac{1}{2}E_t$.

Grassie and Vance[38] give an E_t value of 5.0 k cal per mole, so that by substituting known activation energy values in the relationship we get an E_p value of 9.4 k cal per mole. The above authors have found an E_p value of 11.5 k cal per mole in their system.

The plot in Fig.27 gives the Arrhenius data for the k_x/k_p values at each temperature. The scatter in the values of the ratio has been shown and, as with the styrene results, this is so great that it is possible to express $E_p - E_x$ as a range of values only. The result obtained

FIG. 25 ARRHENIUS PLOT

FOR E_i DETERMINATION

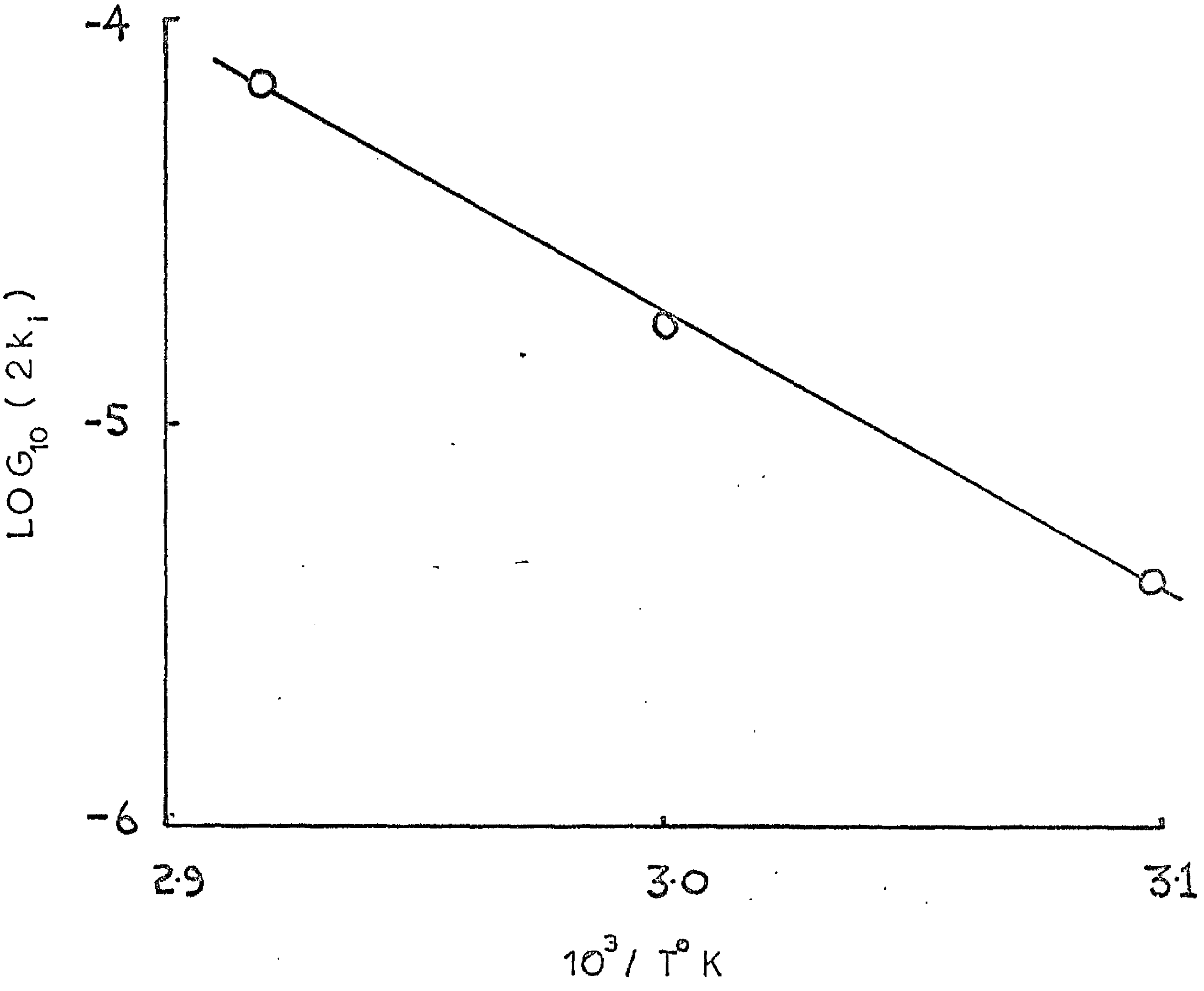


FIG.26 ARRHENIUS PLOT

FOR E_0 DETERMINATION

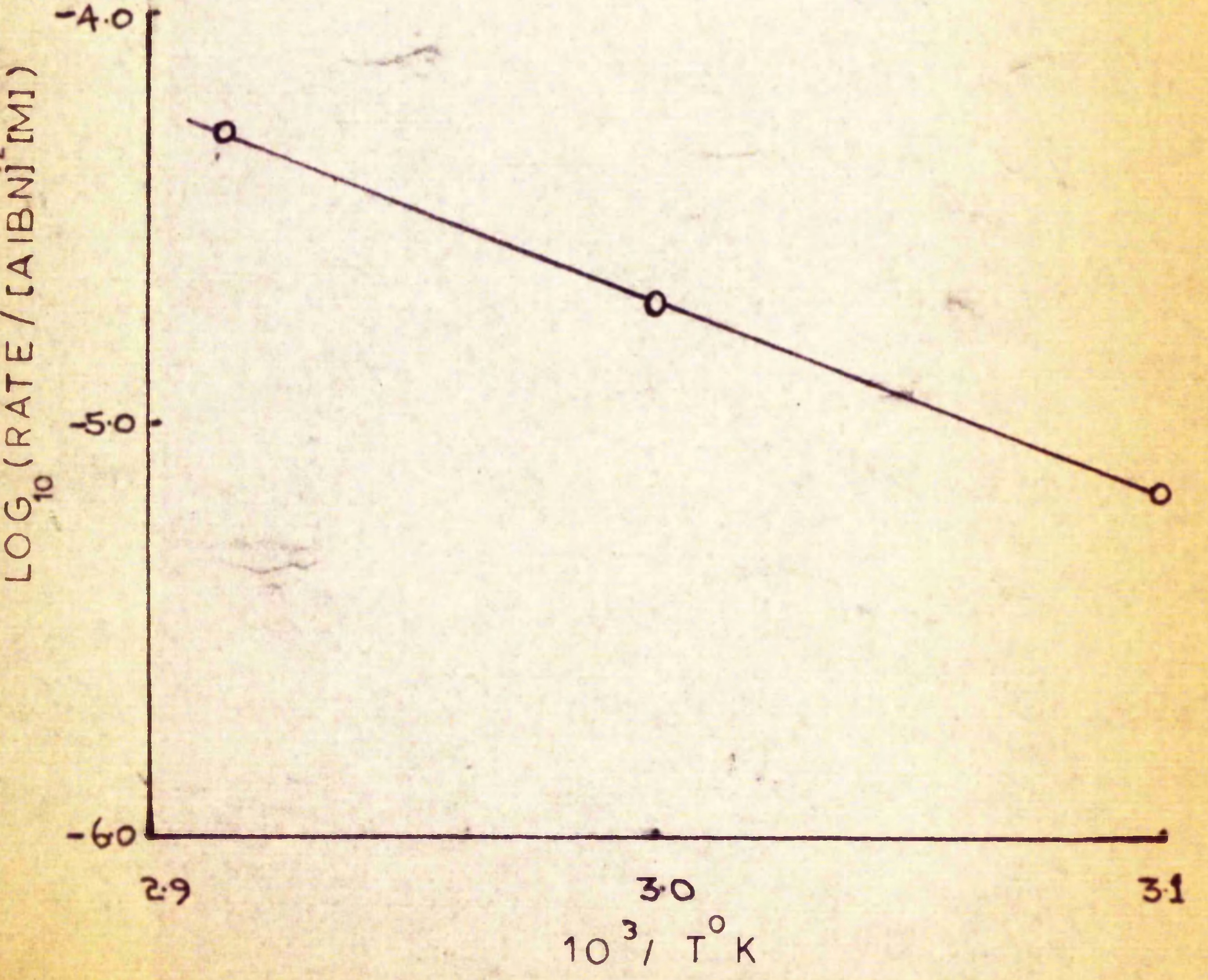
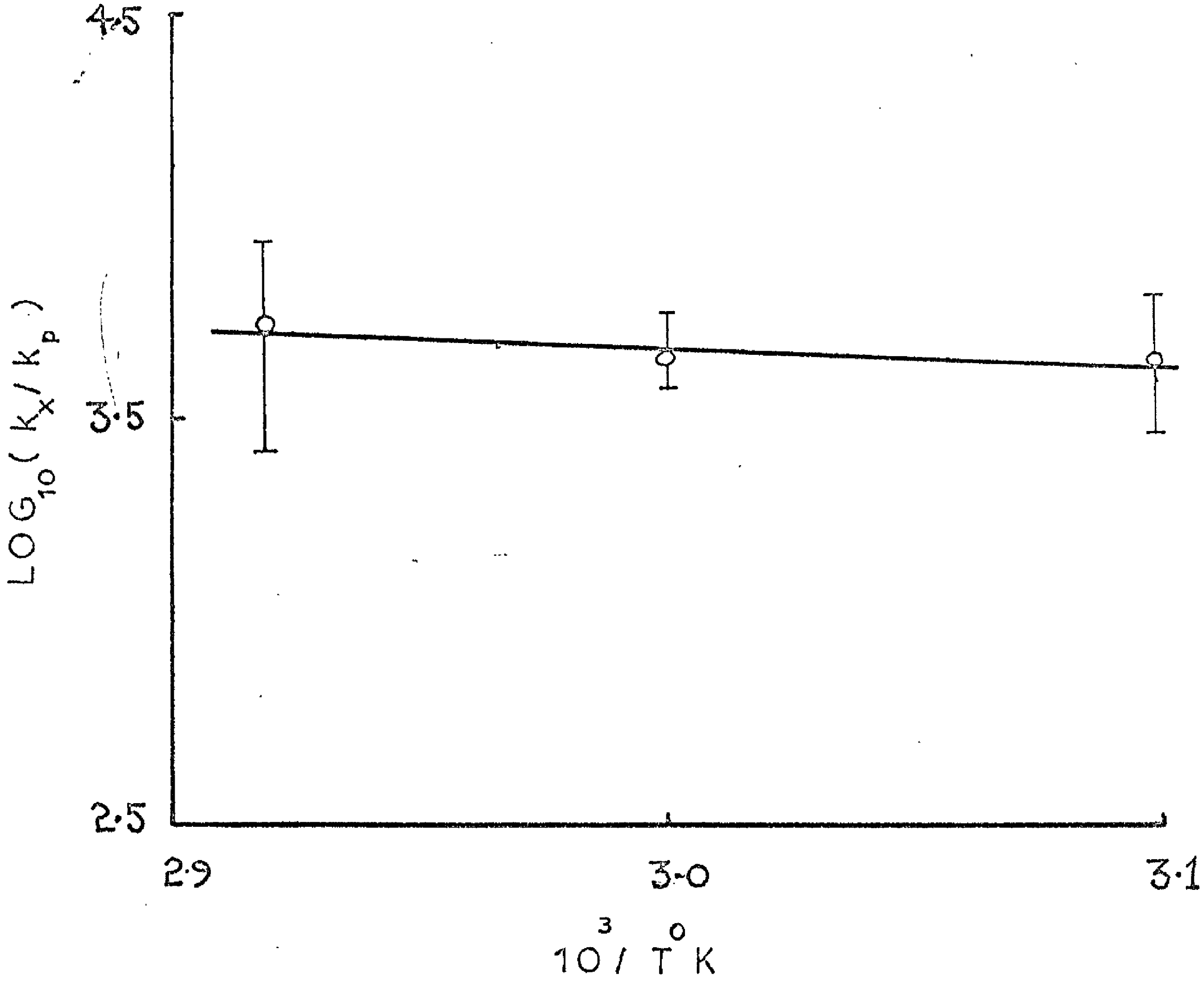


FIG 27 ARRHENIUS PLOT

FOR ($E_p - E_x$) DETERMINATION



from Fig.27 is that $E_p - E_x$ is approximately 0 ± 11 k·cal per mole. The slope of the best line through the mean values of the ratio (shown as points in Fig.27) gives an $E_p - E_x$ value of ca. - 4 k cal per mole.

Taking the value of E_p found of 11.5 k cal per mole gives us an E_x value for the first order termination reaction in the range $E_x = 12 \pm 11$ k cal per mole.

4.3 Conclusion

The point seems to be fairly well brought out in this work that although these methods do furnish useful means of measuring the radical-salt reaction rate constant from the k_x/k_p ratio, severe limitations in their usefulness are introduced in this system as can be seen from the results at 50°C and 70°C.

The difficulty in ensuring a constant rate of initiation over the inhibition period at 70°C when the initiator:inhibitor ratio is low does render the results at this temperature rather dubious.

Also the low rate of reaction renders it impossible to study the system below 50°C without using extremely high high initiator concentrations.

It is also not possible to extend the temperature range studied by using photochemical initiation because of the photochemical instability of the cupric chloride.

CHAPTER V

PHOTOINITIATED POLYMERIZATION OF ACRYLONITRILE IN PRESENCE OF FERRIC CHLORIDE IN DMF.

The homogeneous polymerization of acrylonitrile in DMF solution in the presence of ferric chloride has been studied in this department by Ross[40], who found that the salt behaves as a photoinitiator and as a retarder in this system.

At salt concentrations below 10^{-3} mole 1^{-1} the rate is directly proportional to the square root of the ferric chloride concentration, a result in accordance with ferric chloride initiating and termination being second order with respect to polymer radicals.

For ferric chloride concentrations above about 3×10^{-3} mole 1^{-1} it is found that the rate is proportional to the reciprocal of the ferric chloride concentration. This is as would be expected on the basis of termination exclusively by radical - salt interaction, since under these conditions effectively - 100% of the initiating radiation was absorbed by the ferric chloride and the rate of initiation was independent of the initiator i.e., ferric chloride, concentration.

It was found, however, that the behaviour of the system at the higher salt concentrations was less simple than expected. The intensity exponent in the rate equation was found not to be unity as expected on the basis of simple first order termination by the salt, but in fact the rate was seen to be defined by the equation

$$-\frac{d[M]}{dt} = \frac{k_p\ I^{0.65}[M]}{k_x\ [FeCl_3]}$$

Two possible mechanisms which would lead to a rate relationship in $I^{0.65}$ and $[FeCl_3]^{-1}$ have been suggested. These are as follows:-

(i) The observed relationship can be explained on the basis of a photoinitiation reaction with an efficiency which is inversely related to illumination intensity, i.e. that at high intensities a greater proportion of the primary radicals mutually interact than at lower intensities.

(ii) The second mechanism proposed seeks to explain the results by postulating a relationship between the rate of the termination reaction and the intensity of illumination. This has been done by supposing that there exist two distinct ferric chloride species in DMF solution one of which can terminate a growing chain only after excitation by absorption of light, so that the rate of termination would increase at higher light intensities and the observed rate relationship could hold.

There is described in the section that follows an attempt to eliminate one of the postulated mechanisms by measuring the $\overline{DP}$ of polymer prepared under conditions of differing light intensity. According to mechanism (i) no variation in $\overline{DP}$ with intensity of illumination would be expected whereas if mechanism (ii) presents a true picture an inverse relationship of some kind should exist between $\overline{DP}$ and I.

5.1 Molecular Weight Measurement by Viscometry

5.1.1 Materials

Ferric Chloride : the Analar anhydrous material as supplied by B.D.H. Ltd., was used without further purification.

Acrylonitrile, DMF were purified as described earlier.

4-Butyrolactone (B.D.H. Grade) was used as supplied without further treatment.

5.1.2 Apparatus

Flat bottomed cylindrical dilatometers were used in the preparation of polymer. These vessels were of approximately 15 ml capacity with 1mm Veridia stems. Glass-enveloped magnetic followers within the dilatometer bulb were used in conjunction with a magnetic stirrer to ensure good mixing in the system.

The reactions were carried out at 25°C in a thermostat bath similar to that described in section 2.2.2 The magnetic stirrer was mounted below the bath immediately beneath the dilatometer stand. This latter incorporated a collar which allowed uniform reaction conditions (with respect to the area irradiated) from one run to the next.

An Ubbelohde viscometer, modified to exclude as far as possible traces of moisture, was used for measurements of viscosity of polymer solutions.

5.1.3 Procedure

Dilatometers containing the required concentrations of ferric chloride and monomer were prepared in the manner described in Chapter II for the cupric chloride work. Reaction mixtures at constant salt and monomer concentrations of 5.00×10^{-3} and 3.02 mole l^{-1} respectively were used for the preparation of polymer.

In all runs the reaction was stopped at 2% conversion so as to ensure constancy of salt concentration over the run.

The intensity of illumination was varied using fine wire mesh screens of transmissions in the range 55-25%. In the work reported here polymers were prepared at full intensity and at 30% full intensity and these were examined viscomtrically for differences in molecular weight.

After a given run the polymer prepared was isolated by precipitation in excess non-solvent. In practice it was found very difficult to obtain polymer suitable for viscosity measurement because of the tendency of the polymer to go into suspension during precipitation

Occlusion of solvent in the precipitated polymer was also a source of difficulty.

A series of solvent, non-solvent systems was examined in the attempt to prepare satisfactory polymer. Mention of this is given below.

Solvent	Non-Solvent	Comment
DMF	Water; Methanol; AN	Tendency to solvent occlusion.
	Formamide; Benzene	Very poor non-solvents
	Acetone; Ethanol	Inefficient non-solvents
4-Butryolactone	Diethyl ether	System satisfactory,
	Water; Methanol	Solvent occlusion
Acrylonitrile solution of tetraethyl ammonium bromide	Methanol	Inefficient solvent for polymer.

It was found in practice, however, that polymer prepared by slow addition of a dilute DMF solution to an agitated excess of water was fairly satisfactory provided that thorough drying and grinding in a Gooch funnel was carried out before drying at 50°C under reduced pressure. This method was finally used in preference to the 4-Butyrolactone - diethyl ether system.

The intrinsic viscosity of polymer samples prepared at 100% and 30% full intensity was measured in DMF solutions at 25°C in a Ubbelohde viscometer. The relationship derived by Bamford and co-workers[41] was used for the calculation of molecular weights. This relationship is as follows.

$$[\eta] = 5.74 \times 10^{-4} M_n^{0.733}$$

where $[\eta]$, the intrinsic viscosity of the polymer, is given by $\lim\limits_{c \to o} (\eta_{sp}/C)$: η_{sp}, the specific viscosity, has been measured as $\frac{t - t_o}{t_o}$, where t is the time of flow through the viscometer capillary of a volume of polymer solution of concentration, C g per 100 ml, t_o is the time of flow of the same volume of pure solvent under the same conditions.

5.1.4 Results and Discussion

It was found that during the course of viscosity determinations the DMF used absorbed moisture to an extent which increased its viscosity significantly during the run; e.g. the flow rate of solvent in the system was found to decrease by about 3% over a run, despite the use of calcium chloride tubes to exclude atmospheric moisture.

This effect together with the not very satisfactory condition of the polymer available (badly discoloured, in general) produced results that are virtually impossible to interpret.

The results of two runs on polymers prepared at intensities of 100% and 30% are shown in Figs. 28 and 29 respectively. These results which were the most satisfactory obtained are tabulated along with other data

FIG 28 INTRINSIC VISCOSITY DETERMINATION

$I = 100\ \%\ I_0$

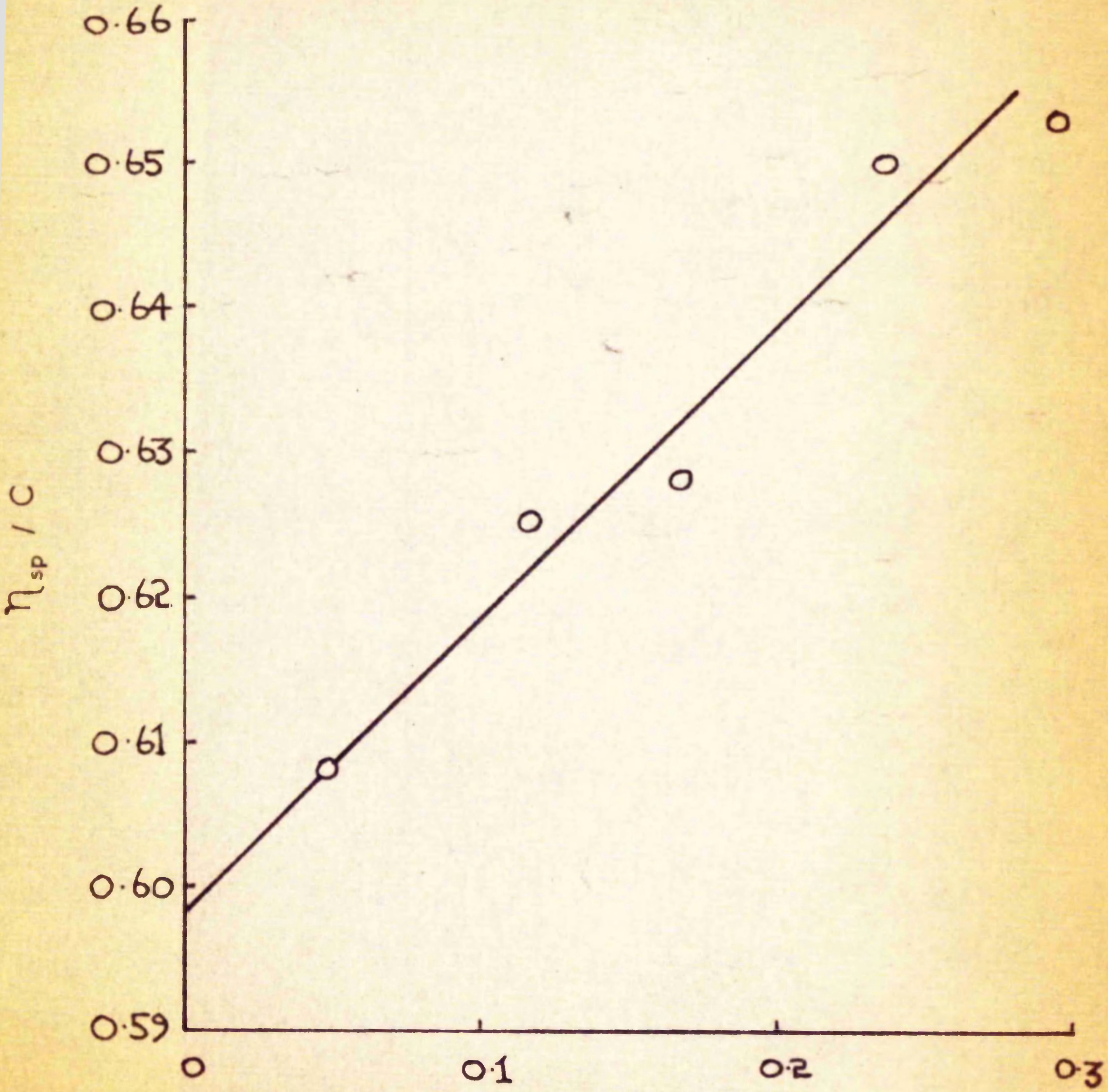
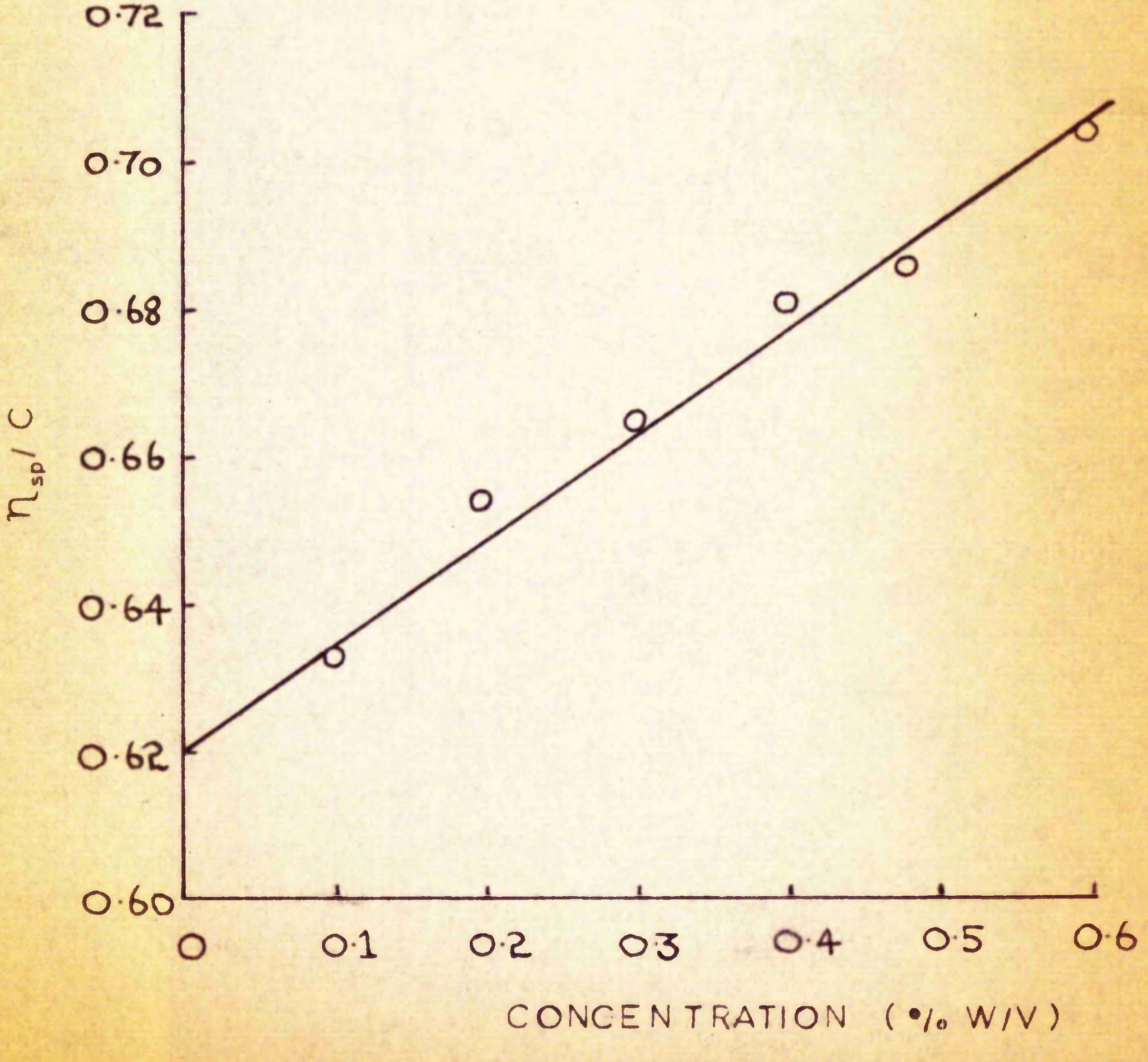


FIG 29 INTRINSIC VISCOSITY DETERMINATION

$I = 30\% I_o$



as an indication of the inaccuracy involved in the determinations.

The values of the intrinsic viscosities obtained from Figs. 28 and 29 are 0.598 and 0.620 respectively. Use of the Houwink equation given above leads to values of molecular weight of 13,000 and 13,700 at the high and low intensities respectively. These correspond to degrees of polymerization of 246 and 258 respectively.

It is impossible to lend any weight to these results, however, and this section may best be concluded by saying that the attempt to see which of the two mechanisms given above is in accordance with experience has not succeeded.

TABLE 19

DATA FROM VISCOSITY DETERMINATIONS IN DMF AT 25°C

(1) I = 100% I_o, (2) I = 30% I_o

(1)

C (% w/v)	η_{sp}/C	C (% w/v)	η_{sp}/C	C (% w/v)	η_{sp}/C	C (% w/v)	η_{sp}/C
0.209	0.709	0.378	0.680	0.334	0.589	0.295	0.653
0.105	0.700	0.302	0.707	0.275	0.595	0.236	0.650
0.070	0.664	0.252	0.685	0.229	0.603	0.169	0.628
0.053	0.678	0.189	0.695	0.172	0.584	0.118	0.625
0.035	0.686	0.126	0.710	0.115	0.594	0.047	0.608
		0.095	0.695				

(2)

C (% w/v)	η_{sp}/C	C (% w/v)	η_{sp}/C
0.598	0.704	0.380	0.821
0.478	0.686	0.304	0.822
0.398	0.681	0.254	0.803
0.298	0.665	0.190	0.796
0.199	0.654	0.095	0.745
0.099	0.633	0.048	0.693

5.2 Rates of Photolysis of Ferric Chloride measured by Spectrophotometry and by Titration.

Comparison by Ross[40] of the rates of photolysis of ferric chloride in DMF obtained spectrophotometrically and by titration led to results in which the estimation of ferrous ion by spectrophotometry gave values approximately double those obtained by titration.

This was explained by postulating the occurrence in solution of two ferric chloride species; one of which is more strongly absorbent and more readily reduced than the other.

Spectrophotometric measurements in the above work were carried out using a Unicam S.P. 1400 instrument, rates of removal of ferric iron being measured by following the decrease in optical density of the system at 480 mμ.

Since this wavelength corresponds to a shoulder on the absorption curve and not to any peak, it was thought worthwhile to repeat this work by estimating rates of removal of ferric chloride from optical density changes at absorption maxima in the near ultra-violet.

The high extinction coefficient of ferric chloride in DMF at these absorption maxima (approximately 5×10^3 l mole^{-1} cm^{-1} at both 325 and 365 mμ) makes it rather difficult to keep the optical density of the system in the required range (about from 0.2 to 1.0) at the ferric chloride concentrations used (ca. 5×10^{-3} mole l^{-1}) without reducing the path length to a very low value (approximately 0.02 cm). It was decided to offset this difficulty by introducing a uniformly absorbing wire gauze screen into the reference beam of the spectrophotometer (Perkin Elmer, 137 UV model) during a run. This had the effect of diminishing the optical density of the sample and allowed work to be done using concentrations of approximately 5×10^{-3} mole l^{-1} ferric chloride with 1mm path length cells.

The procedure and results of this study are given in what follows.

5.2.1. Experimental

The ferric chloride and DMF used have been described earlier.

Ceric ammonium sulphate solution, standardized against arsenious oxide as described in Chapter II, was used in the volumetric estimation of ferrous iron. Titrations were followed potentiometrically, the redox system in the presence of a platinum electrode being connected via a KCl bridge to a calomel half cell. The external circuit was completed via a Pye potentiometer.

A sketch of the cell used in the photolyses is given in Fig. 30. It can be seen to consist of a cylindrical flat bottomed bulb of capacity approximately 16 ml (diameter ca. 2cm) connected via a glass to quartz seal to a 1 mm path length quartz spectrophotometer cell. The stem of the vessel is fitted with a B.10 cone for connection to the vacuum line. The magnetic stirring arrangement described earlier was used, the vessel being held during photolyses in the same collared stand as before.

Photolyses were carried out at 25°C under vacuum. The u.v. source used was the mercury vapour lamp referred to in the second chapter. The cells were prepared for the runs by filling with the required volume of ferric chloride stock solution to give 15 ml at a concentration of 5×10^{-3} mole l^{-1} on dilution with DMF. This was the initial concentration in all the runs carried out.

The vessel was then put on to the vacuum line for degassing and finally sealed under vacuum.

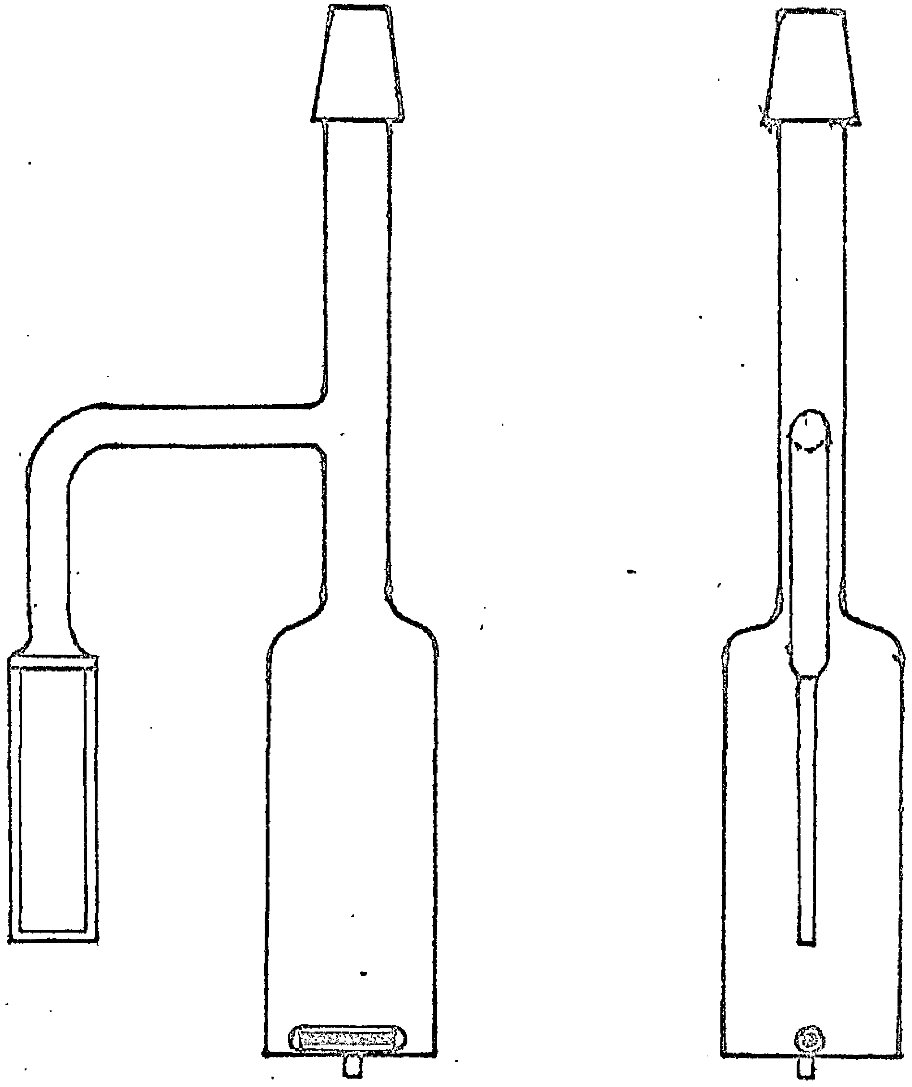


FIG 30 IRRADIATION VESSEL

An initial optical density reading was taken at 325 mμ and the vessel was then put into the bath and photolysis begun, times of irradiation being measured with a stopwatch. After given time intervals the vessel was withdrawn from the bath and further optical density readings taken. This latter was done by allowing the reaction mixture to run into the quartz cell from the photolysis vessel and fitting the vessel as a whole into the spectrophotometer. In this way a plot was obtained of optical density versus time of irradiation. Such a plot is given in Fig. 31.

A calibration curve of optical density at 325 mμ against ferric chloride concentration in DMF was drawn up. This is given in Fig. 32 for a 1 mm cell with the wire screen in the reference beam. The curve is linear over most of its length although a slight deviation occurs at the higher optical density values.

These two plots could then be combined to give a ferric chloride concentration versus time curve or alternatively a rate of production of ferrous iron plot.

Rates of photolysis by titration were estimated using the same vessel as in the above work. After irradiation the vessel was removed from the bath, an optical density reading taken as a check, and the contents of the vessel were quickly pored, after breaking open the stem, into

FIG 31 OPTICAL DENSITY AT 325 mμ
Vs.
TIME OF IRRADIATION

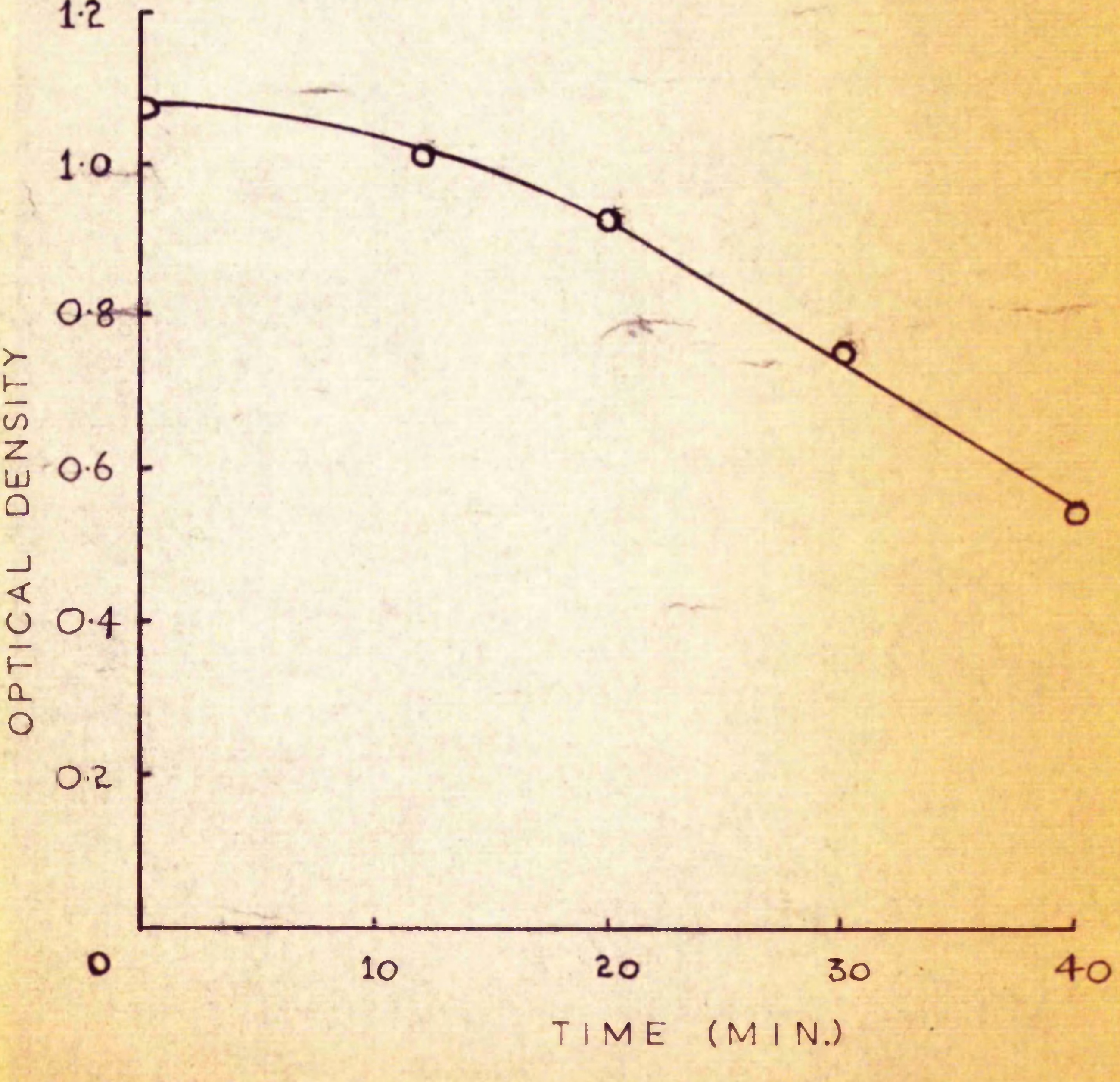
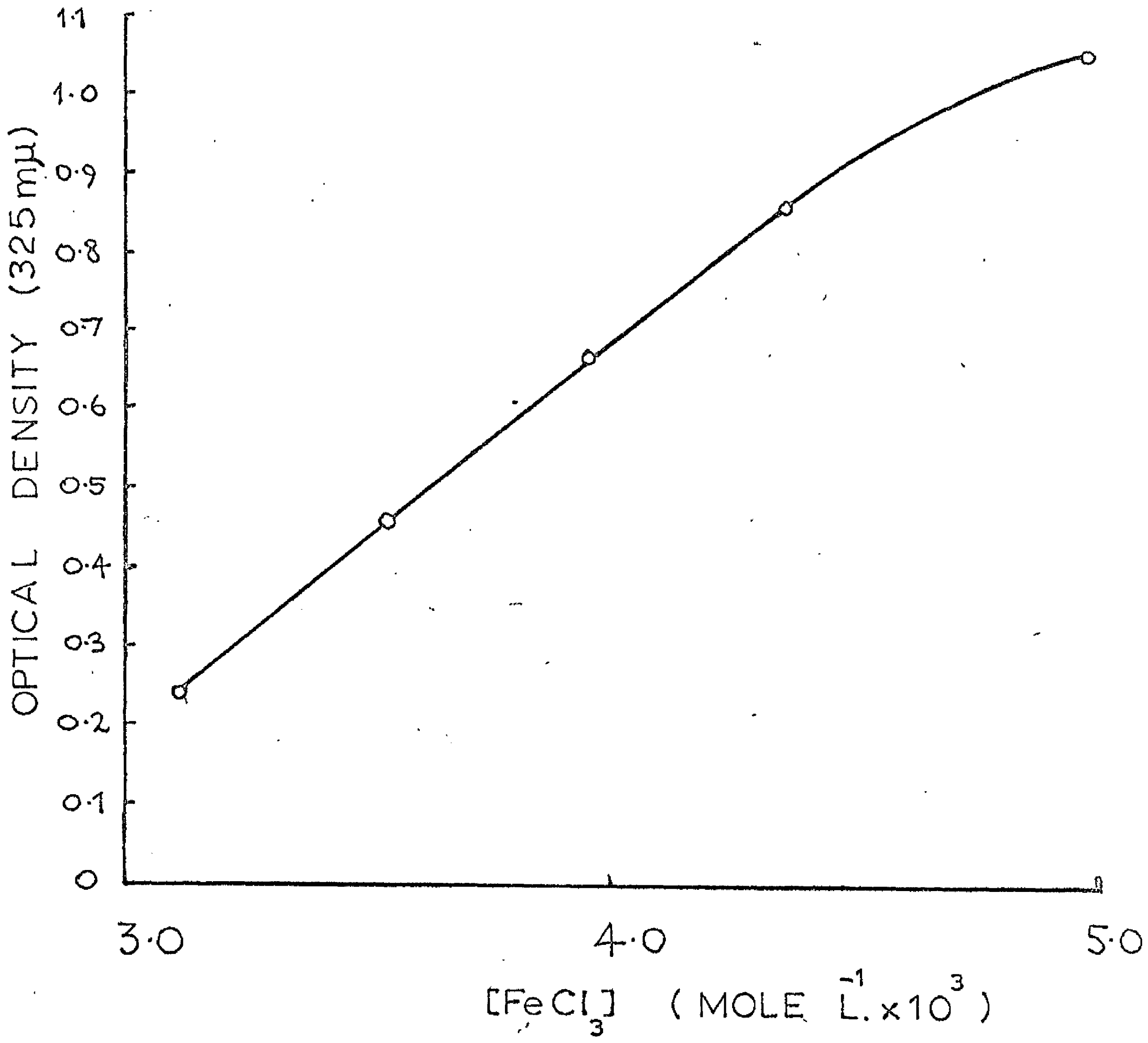


FIG. 32 OPTICAL DENSITY VS. [$FeCl_3$] PLOT



excess 2N sulphuric acid. Titration against the standard ceric solution was carried out with constant stirring of the the mixture. Blank determinations were carried out on non-irradiated samples.

In this way a plot of ferrous concentration against time was arrived at. This is given in Fig. 33 where comparison is made with that obtained spectrophotometrically.

5.2.2. Results and Discussion

It can be seen from the plots in Fig.33 that the rates of photolysis measured by spectrophotometry and by titration are effectively identical. The two curves are almost coincidental if account is taken of the blank titration values and the errors associated with the optical density readings.

The method of taking optical density readings, viz., by pouring from the main vessel into the cell, would tend to give an inflated ferric chloride value for all save the initial reading (because of solution from a previous determination adhering to the walls of the cell). The initial increasing rate of ferrous ion formation is presumably due to incomplete degassing of the system.

From the slopes in Fig.33 the rates of photolysis are 5.61×10^{-7} mole l^{-1} sec^{-1} by titration and 5.45×10^{-7} mole l^{-1} sec^{-1} by spectrophotometry.

Three determinations of the rates were carried out

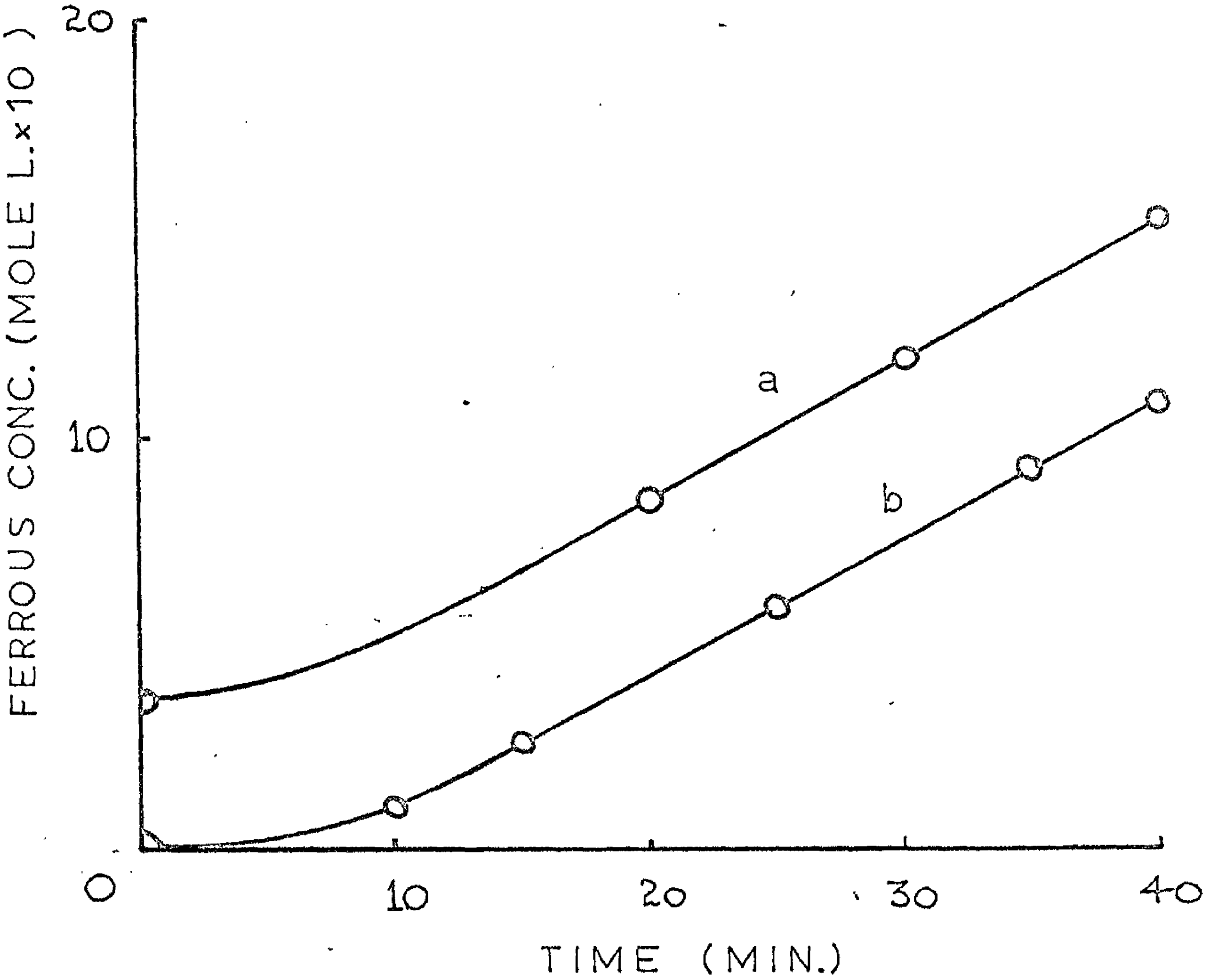
FIG 33 FERROUS CONCENTRATION

Vs.

TIME OF IRRADIATION

a BY TITRATION

b BY SPECTROPHOTOMETRY



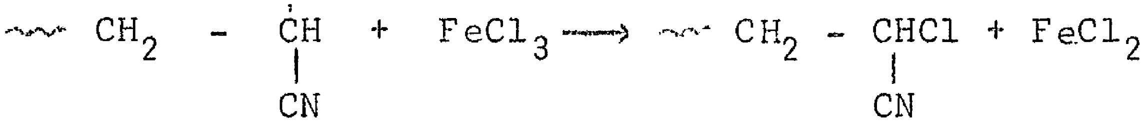
giving mean values of 6.62×10^{-7} and 5.99×10^{-7} mole l^{-1} sec^{-1} by titration and spectrophotometry respectively. The lower value obtained from the spectral work is probably partly attributable to the effect, mentioned above, of the solution remaining on the walls of the cell from one optical density determination to the next.

It is difficult to explain the discrepancy found by Ross in his work. It was thought possible that the difference be caused by a spectral shift to shorter wavelengths during the reaction, but there was no evidence of this effect in the present work.

5.3 Polymerization of Acrylonitrile in DMF in the presence of Chlorine-36 labelled Ferric Chloride.

The polymerization of the monomer in the presence of ferric chloride labelled with a radioactive chlorine isotope has been studied in order to get some information on the mechanism of the initiation and termination reactions.

This work was undertaken in extension of a qualitative study of the system by Ross[40] who found that effectively no chlorine entered the polymer during initiation whereas a significant contribution to termination seemed to be made by the reaction



$$\sim\sim CH_2 - \underset{\underset{CN}{|}}{CH} + FeCl_3 \longrightarrow \sim\sim CH_2 - \underset{\underset{CN}{|}}{CHCl} + FeCl_2$$

Thus it was hoped that by using scintillation counting techniques on polymer prepared photochemically under conditions of high and low ferric chloride concentration the role of chlorine in the mechanism could be elucidated.

5.3.1. Preparation of Radioactive Ferric Chloride

The radioactive material was prepared from the elements as follows.

I.C.I. cylinder chlorine was washed with water and dried by bubbling through concentrated sulphuric acid and storing over magnesium perchlorate granules (Anhydrone). This material was then admitted to the vacuum line and all air removed by distilling under vacuum between traps at -78° and ca. -196°C. The purified gas was then stored over Anhydrone granules at a pressure of almost $\frac{3}{4}$ atmospheric.

This gas was used to dilute a sample of chlorine-36 (supplied by The Radiochemical Centre, Amersham) of total activity 27.4 μc, volume at N.T.P. 13.9 ml. The radioactive isotope was supplied in a glass break seal vial which was fitted to the vacuum line and the space above the seal evacuated. The seal was then broken and the chlorine-36 thoroughly mixed with the natural gas by condensing both in a vessel at -78°C and then letting the mxiture, in contact with a cold trap at -40°C, stand over granulated Anhydrone at a pressure somewhat below atmospheric.

The isotopic mixture was thencycled over heated iron powder (B.D.H. Hydrogen Reduced Grade) and the resulting ferric chloride crystals were carried in a stream of chlorine into a receiving vessel where the product was several times resublimed in a chlorine atmosphere. The receiving vial was then flame sealed and the radioactive material stored for use in the preparation of stock DMF solutions for the preparation of polymer.

5.3.2 Experimental

Activities of samples were measured by liquid scintillation counting techniques. This method of radioactive assay depends on the generation of photons occurring when a luminescent material is excited by ionizing radiation. Such photons may be collected at a photocell cathode where they create a small current which is amplified in a photomultiplier tube. The amplified current gives rise to an electrical pulse which may be recorded. The use of a scaler and timing unit to record such pulses provides a means of estimating the activity of the source of the ionizing radiation.

The counting equipment used in the present work (supplied by Nuclear Enterprises Ltd.) consisted of a lead lined 'castle' incorporating the P.M. tube which housed the cells used to contain the sample and liquid scintillator. The high voltage supply to the P.M.

tube was provided by an E.H.T. unit and the output of the former was amplified by a linear pulse amplifier. A pulse height and gate width selector was incorporated for filtering purposes.

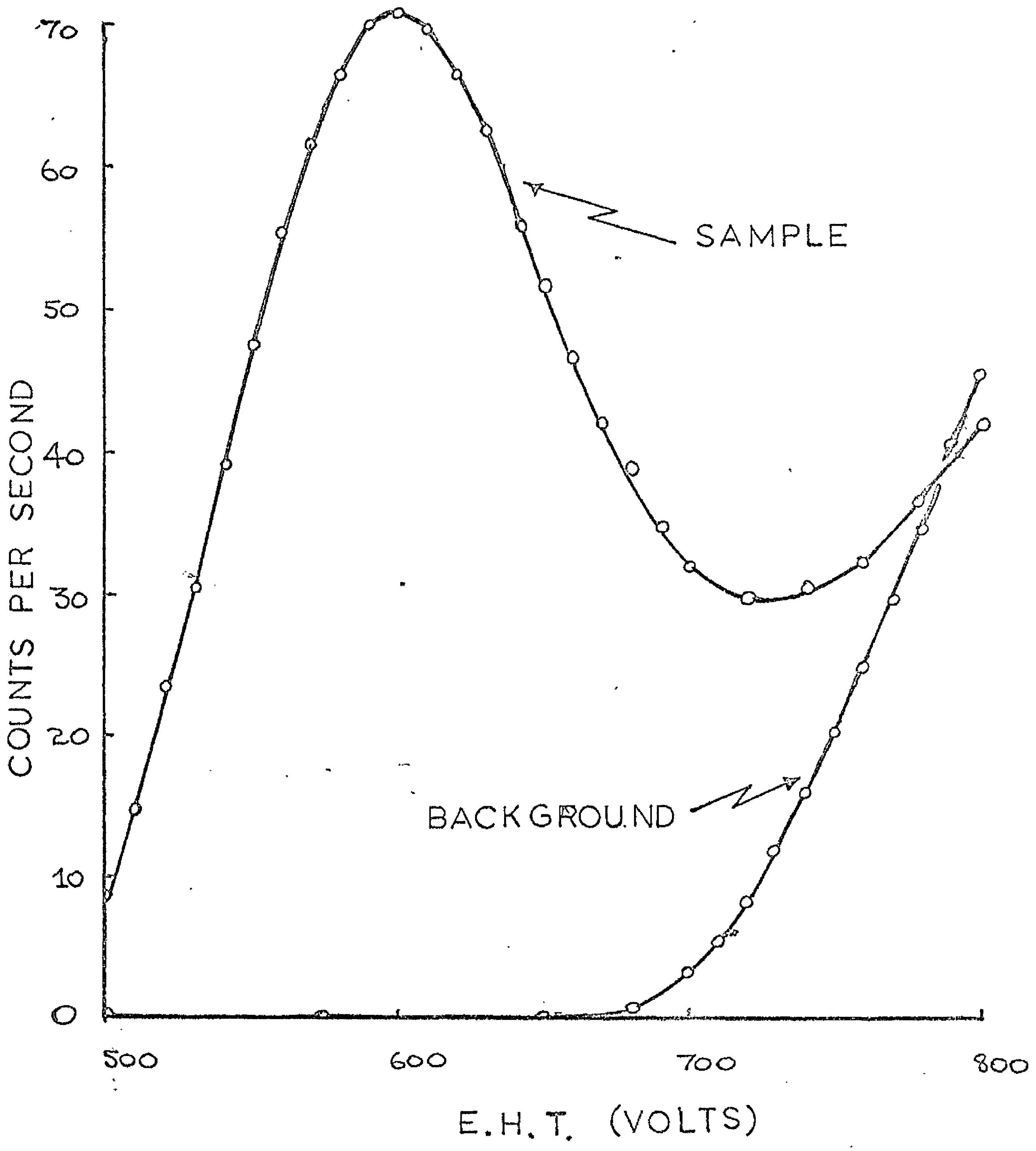
The liquid scintillator used (also obtained from Nuclear Enterprises Ltd.) was made up of a toluene solution containing 3g per litre 2,5 diphenyloxazole and 0.1 g per litre diphenyloxazolylbenzene.

Counting was carried out on samples dissolved in 5 ml DMF which were added to 5 ml scintillator solution in the silica counting cells. Background counts were taken using 5 ml pure DMF and 5 ml scintillator solution only.

Prior to any work on polymer samples it was necessary to find satisfactory counting conditions for this isotope and to draw up a calibration curve of activity as counts per second under the optimum conditions against ferric chloride concentration for use in the later work.

Satisfactory counting conditions were found by varying the E.H.T. voltage for constant amplifier gain, pulse height and gate width settings and taking measurements of the registered activity of a radio-active sample and of background. The result of this work is shown in Fig.34 for a sample of ferric chloride concentration of 1.76×10^{-4} mole l^{-1}. The other variables were held at the following constant values:-

FIG. 34 COUNT VS. E.H.T.



Amplification	20 x 1
Pulse Height	10 volts
Gate Width	30 volts

On the basis of these results counting was carried out at an E.H.T. setting of 600 volts at the above values of amplifier gain, gate width and pulse height.

The calibration curve shown in Fig.35 was arrived at by counting on 5 ml samples of DMF solutions of increasing concentrations of the radioactive salt.

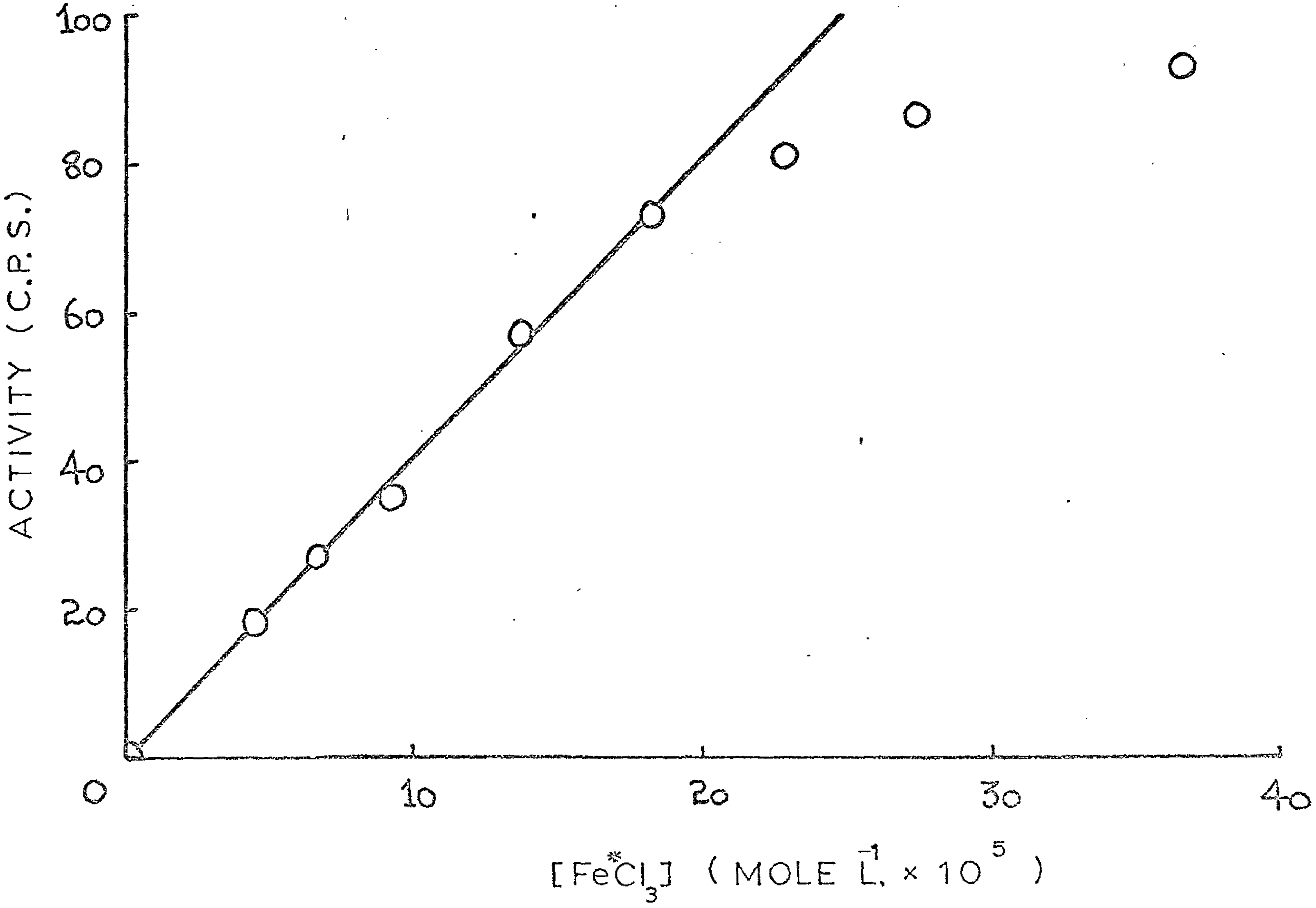
It may be seen that as the concentration of the ferric chloride is increased there develops a marked deviation from linearity. This is caused by absorption or 'quenching' by ferric chloride of the luminescence produced by excitation of the scintillating liquid. The linearity at low concentrations of the salt is good, however, and it may be assumed that in this region no self-quenching occurs.

5.3.3 Results and Discussion

Runs were carried out initially to examine for the formation of any volatile compounds containing chlorine-36 in the initiation and termination reactions.

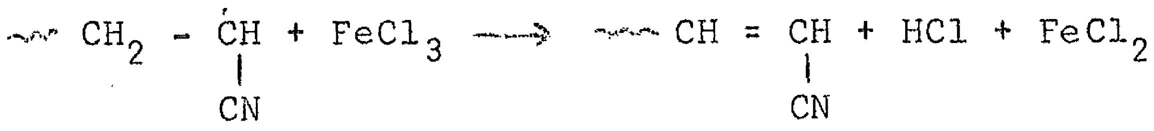
If initiation in this system does not occur by direct attack on the monomer by the photochemically produced chlorine atom, but rather by attack by this radical on the solvent DMF then there is a possibility that such

FIG 35. RADIOACTIVITY CALIBRATION CURVE



chlorinated compounds as HCl, HCOCl, $ClCONMe_2$ etc., be formed.

Similarly if termination occurs by the reaction



$$\sim\!\sim CH_2 - \underset{\displaystyle CN}{\underset{|}{\dot{C}H}} + FeCl_3 \longrightarrow \sim\!\sim CH = \underset{\displaystyle CN}{\underset{|}{CH}} + HCl + FeCl_2$$

it should be possible to isolate and detect the HCl produced using chlorine-36 labelled ferric chloride.

Polymerizations were therefore carried out at a monomer, solvent ratio of 4:1 using initial salt concentrations of 6.5×10^{-3} and 6.5×10^{-4} mole l^{-1}.

The reactions were taken to completion, i.e. irradiated until the yellow ferric colour had been discharged after which all residual volatile material was collected by distillation into a trap cooled by liquid nitrogen. A 5 ml sample of this distillate was then taken and examined for radioactivity.

The residual solid material containing polymer, ferric and ferrous chloride was taken up in DMF and its activity counted as a check against loss of radioactive material.

Results of this work are given below:

[M] = 3.02 mole l^{-1} background count 0.154 c.p.s.

Initial Salt concentration (mole l^{-1})	6.5×10^{-3}	6.5×10^{-4}
Total Salt Activity (c.p.s.)	2453.1	239.4
Total Residue Activity (c.p.s.)	2353.7	234.1
Total Distillate Activity (c.p.s.) . .	2.742	0.074
% Original Activity in Distillate	0.11%	0.03%
% Loss in Activity	4.0%	2.2%

It would appear from these results that there is no significant quantity of chlorine-containing volatile material produced during the reaction.

As far as the initiation reaction is concerned, this result would imply that initiation occurs either by direct attack by atomic chlorine on the monomer, or by attack on the solvent with production of either a chlorine containing radical which initiates or a chlorine-free initiating radical and a non-volatile chlorinated compound.

The termination reaction would appear not to proceed by hydrogen abstraction from the growing radical unless the resulting hydrogen chloride is bound in some way that renders it non-volatile.

These comments are based on the assumptions, firstly that the liquid nitrogen trap is effective in condensing out all volatile material and, secondly, that such volatile material remains in solution during counting. It may be noted in respect of this last consideration that constant counts were obtained with the distillate, there being no diminution in activity with time as would be expected if a volatile active solute were escaping from solution

Some runs were carried out for the preparation of polymer under conditions of first and of second order termination.

The polymer produced was isolated by precipitation in excess water and washed with dilute aqueous hydrochloric acid to remove residual ferric chloride. The polymer sample was then washed with water and methanol, dried and weighed.

A weighed sample of this polymer in DMF solution was used for radioactive assay.

Results of this work are given in Table 20 for three runs of initial ferric chloride concentrations of 1.86×10^{-4}, 5.35×10^{-3} and 5.45×10^{-3} mole l^{-1}.

The following comments may be made on the data given in this table.

The rate of photolysis of the radioactive ferric chloride in solution was assumed to be that measured with the natural salt in section 5.2. A value of 3.35×10^{-5} mole l^{-1} min^{-1} was taken for the calculation of the salt concentration photolysed in columns 2 and 3 where the photolyses were not taken to completion.

TABLE 20 Experimental Data for Photolyses of Radioactive Ferric Chloride in DMF in Presence of Acrylonitrile

	1	2	3
Initial Ferric Chloride Concentration (mole $l^{-1} \times 10^4$)	1.86	54.5	53.5
Irradiation Time (min)	190	133	124
Concentration Photolysed (mole $l^{-1} \times 10^4$)	1.86	44.5	41.5
Weight Polymer Formed (g)	0.195	0.138	0.129
Weight Polymer Sample (g)	0.034	0.036	0.012
Activity of Polymer Sample (c.p.s.)	0.316	9.043	4.360
Background Count (c.p.s.)	0.154	0.154	0.154
Total Activity of Polymer (c.p.s.)	0.939	33.880	44.101
+ Equivalent $[Fe^*Cl_3]$ Reacted (mole $l^{-1} \times 10^6$)	7.02	255	333
Ratio: Equivalent $[Fe^*Cl_3]$ Reacted to $[Fe^*Cl_3]$ Photolysed (%)	3.8	5.7	8.0

+ Fe^*Cl_3 represents chlorine-36 labelled ferric chloride.

The reacted ferric chloride concentration equivalent to the total activity in the polymer was found from the calibration curve as follows for the run in column 2:

The total activity in the polymer produced is equivalent to 33.880 counts per second (c.p.s.). From the calibration curve this is seen to correspond to a radioactive ferric chloride concentration of 8.5×10^{-5} mole l^{-1}. The chlorine-36 in the polymer, counted as ferric chloride in this way, is equivalent, therefore,to that introduced by reaction of three times this concentration i.e., 2.55×10^{-4} mole l^{-1} of the ferric salt.

The results obtained in Table 20 are rather difficult to interpret in the light of those obtained in the first part of this section. In columns 2 and 3 where termination occurs exclusively by interaction of the salt with growing polymer radicals it appears that less than 10% of the chlorine abstracted from the salt combines with the polymer. From the earlier results the proportion of this chlorine which appears as a volatile product is quite negligible.

The problem arises of what happens to the chlorine removed from the salt during initiation and termination.

The result given in column 1 of Table 20 indicates that under conditions where the salt is behaving only as an initiator there is again very little chlorine in the polymer.

Even taking into account possible sources of error such as incomplete dissolution of the sample in the counting medium or a lower rate of photolysis than that assumed, it appears that very little chlorine enters the polymer chain during the reaction, and that the chlorine produced on reduction of the salt by photolysis and by radical oxidation is in some way bound in a non-volatile form.

The situation in the literature regarding the product of the radical-salt reaction is to some extent confused. Bamford and co-workers[19] find no trace of chlorine in polyacrylonitrile from the ferric chloride retarded polymerization at 60°C, whereas Dainton et al[21] assume that termination occurs by chlorine atom transfer in work done on the scavenging of cyanoisopropyl radicals by ferric chloride. It appears that radical properties have a great effect on the mechanism of the reaction since, for example, Entwistle[25] finds that termination of styrene and methylmethacrylate polymerizations by ferric chloride proceeds almost exclusively by chlorine transfer to give saturated polymer.

An attempt was made to study the termination reaction in isolation by using labelled ferric chloride as a retarder in the AIBN initiated thermal polymerization of acrylonitrile in DMF.

Runs were therefore carried out at 60°C at ferric chloride concentrations of 5 x 10^{-3} mole l^{-1} and AIBN concentrations between 5 x 10^{-2} and 5 x 10^{-3} mole l^{-1}.

During these runs it was found, however, that the yellow colour of the ferric salt although fading somewhat initially, was not discharged but rather displaced by a red coloration which remained throughout the reaction.

This effect could not be explained. It is unlikely to be due to impurity in the chlorine-36 labelled salt since this behaved normally in the photolysis runs and had a u.v. spectrum essentially similar to the ordinary salt in solution. The unusual behaviour could be due to other adventitious impurities in the system. There was, however, no opportunity of pursuing the problem and it was left at this stage.

CHAPTER VI

GENERAL DISCUSSION

The results reported in Chapters II, III, and IV indicate in agreement with previously recorded work[22-24] that cupric chloride in DMF solution is a more efficient terminator of free radical chains than is ferric chloride.

From considerations of the ease of oxidation of cuprous salts and the higher strength apparently possessed by a Cu-Cl relative to a Fe-Cl bond[42], it could perhaps be anticipated that the cupric salt be more resistant than the ferric to reduction by a free radical. It is possible that differences in ionisation potential are important here, but an understanding of the process is impeded by the existence of the cupric and ferric salts in solution as complexed molecules. Such complexing with monomer or solvent will have an effect on the oxidation-reduction potentials of the processes and on the ionization potentials of the metal species, an effect which at present remains indeterminate.

Steric factors may also exert a considerable influence on the rates of these reactions. It is again impossible to estimate this influence as the structures of the oxidizing species are unknown.

The reactivities at 60°C of polystyryl and polymethacrylonitrile radicals towards cupric chloride in dimethyl formamide solution, as estimated in Chapters III and IV, are of interest when compared with data determined by Bamford and co-workers[43] on the reactivities of polymer radicals towards ferric chloride in this solvent.

These workers have compared the reactivities of the radicals corresponding to the monomers, styrene (St), methacrylonitrile (MAN), acrylonitrile (AN), methylmethacrylate (MMA), methyl acrylate (MA), and vinyl acetate (VA) towards ferric chloride in DMF with their (general) reactivities towards a non-polar transfer agent such as toluene.

These general reactivities are arranged below in decreasing order of reactivity:

$$\text{VA} > \text{AN} > \text{MA} > \text{MAN} > \text{MMA} > \text{St} \qquad (1)$$

whereas, in the radical-salt interaction the following sequence is observed

$$\text{VA} > \text{St} > \text{AN} > \text{MA} > \text{MMA} > \text{MAN} \qquad (2)$$

Thus, in their reaction with ferric chloride the growing polymer radicals derived from the monomers, AN, MA, MMA, and MAN are less reactive than might be expected on the basis of their general reactivities, whereas the polystyryl radical shows a much enhanced reactivity.

Similar but non-identical patterns of behaviour exhibited in transfer reactions with carbon tetrabromide and n-butyl mercaptan are shown below in sequences (3) and (4) respectively

CBr_4: VA > MA > St > MMA ÷ AN > MAN (3)

n-BuSH: VA > St > MA > AN > MMA (4)

In contrast to the above, transfer reactions by these polymer radicals with the tertiary amine, triethylamine, are characterized by the following reactivity sequence:

AN > VA > MA > MAN > MMA > St (5)

in which the poly- AN, MA and MAN radicals are more reactive than expected from their general, non-polar reactivities.

The behaviour typified by sequences (2) - (5) has been explained as due to the existence of polar contributions to the transition state in the transfer reactions. The importance of such contributions will be influenced by the polar properties of the substituent groups in the radical.

Thus in sequence (2) the transition state is thought to have contributing structures of the type $R\cdot Fe^{3+} \longleftrightarrow R^{+}Fe^{2+}$. The very high reactivity of polystyryl radicals may be understood on this basis since the substituent terminal phenyl group will not oppose polarization in the sense indicated. Such polarization would, however, be resisted by electron-withdrawing substituents such as -CN and - $COOCH_3$.

Similarly the reactivities observed in the transfer reactions with carbon tetrabromide and n-butyl mercaptan are explained by postulating a transition state involving contributions of the type

$$R^{+}Br^{-}\ \cdot CBr_3 \longleftrightarrow R^{+}Br^{\cdot}\ {}^{-}\cdot CBr_3$$

and $$R^{+}H^{\cdot}\ {}^{-}SBu \longleftrightarrow R^{+}HS^{-}Bu^{\cdot} \longleftrightarrow R^{+}HS^{\cdot}Bu^{-}$$

respectively.

On the other hand sequence (5) for the reaction with triethylamine has been explained on the basis of a transfer reaction mechanism involving electron transfer from amine to radical[44], a process which would be favoured by electron-withdrawing groups.

Bamford and co-workers have treated the above data in a semi-quantitative way to develop a more satisfactory approach to the determination of radical reactivity than is offered by the Q-e scheme. It has been possible to express the rate of reaction between a radical and a given substrate in terms of the general radical reactivity, substrate bond energy and the Hammett substituent function, σ, representing the effect of radical substituents on polarization of the transition state.

The sequence of radical reactivity towards cupric chloride in DMF given below is based on the results reported here and in the literature[24]. In decreasing order of reactivity this is

$$St > MAN > MMA \qquad (6)$$

Although the sequence is incomplete in comparison with (1) - (5), it may be noted that the higher reactivity of radicals from styrene relative to poly-MAN and poly-MMA radicals is in keeping with the above considerations.

The precedence of MAN over MMA is unexpected on the basis of the polar factors likely to be involved. It is possible that the importance of general reactivity is higher in this case, although the behaviour of styrene would suggest otherwise.

A possible explanation of these results and a consideration that should be borne in mind throughout this work is that the termination reaction is less simple than has been assumed.

It is possible that from one monomer system to another there is a change in the effective terminating species, so that in the styrene system the radical scavenger is a $CuCl_2$ - DMF complex, whereas with methacrylonitrile, for example, the monomer itself may complex with the salt to an extent which affects measured values of k_x.

This consideration is very important in the determination of the energy of activation of the radical-salt termination reaction from measurements of k_x/k_p at different temperatures. It has recently been found[45], for example, that in a system consisting of cupric chloride, acrylonitrile and 10% DMF, the absorption spectrum in the visible at 30°C corresponds to that of a cupric chloride - DMF complex, whereas at 60°C the equilibrium has been displaced to give a spectrum corresponding to the species existing in acrylonitrile solutions of the salt at the corresponding concentration.

In the light of this effect the results presented in this thesis on the activation energies of the termination reactions for styrene and methacrylonitrile may require revision.

The values for rates of initiation found in Chapters III and IV may possibly be inflated by the occurrence of primary radical termination with the cupric salt.

Bamford and co-workers have found this effect to be significant in the AIBN initiated polymerization at 60°C of several monomers in the presence of ferric chloride in DMF[32]. They have reported a $2k_i$ value for acrylonitrile and methacrylonitrile of 1.90×10^{-5} sec^{-1} which, on correction for the participation of primary radicals, give mean $2k_i$ values of 1.43×10^{-5} and 1.45×10^{-5} sec^{-1} respectively for the two monomers.

On the other hand, correction for the primary radical effect causes no change in the $2k_i$ value in styrene of 1.40×10^{-5} sec^{-1}, a result which has been explained as due to the high reactivities of styrene towards radicals and the styryl radical towards the salt.

Although parallel behaviour would be expected in the styrene, cupric chloride system, it may be that with methacrylonitrile and the cupric salt primary radical termination is more important. This would be expected if cyanoisopropyl radicals exhibit a much higher reactivity than the polymer radicals towards cupric chloride in DMF i.e. if their behaviour with the ferric salt[21] is reproduced here.

It has been seen in Chapters III and IV that the treatments of Bengough and Bamford are applicable to the systems studied, so that the simple kinetic scheme on which they are based would appear to describe these systems. Limitations on the applicability of the methods have been discussed previously.

A comparison is made below of the inhibition periods obtained by extrapolation and by Bamford's method, viz., the reaction time at which $\phi = 0.648$ for runs, the acceleration periods of which have been plotted earlier.

Monomer	Temperature (°C)	t by extrapolation (min.,sec)	t at ϕ = 0.648 (min.,sec)
Styrene	50 (Fig.10)	126 : 56	126 : 25
	60 (Fig.4)	72 : 40	73 : 11
	70 (Fig.12)	57 : 18	57 : 40
MAN	50 (Fig.22)	89 : 10	90 : 40
	60 (Fig.18)	63 : 30	65 : 40
	70 (Fig.24)	65 : 00	66 : 50

The difference in values obtained is small in all cases, although it is consistently greater for the methacrylonitrile than for the styrene system. These small differences, however, together with the difficulty involved in estimating the point on the curve where ϕ = 0.648 deprive Bamford's method of any practical importance in the estimation of rates of initiation.

A possible explanation may be found in the work of Palit and co-workers[46] of the puzzling results obtained in section 5.3 regarding the role of chlorine in the ferric chloride, AN, DMF system and the apparent loss from the system of the chlorine-36 liberated during photolysis.

These workers maintain in explanation of the low transfer constants obtained between acrylonitrile and various chlorinated compounds that a chlorine situated alpha to a nitrile group is labile and may readily be removed by hydrolysis. If this were the case then in the present work the polymer formed by any chlorine transfer to the radical from ferric chloride would have the the end group - $CH_2CHClCN$. The chlorine in this group could then perhaps be hydrolysed off by the water - precipitation and dilute acid washing of the polymer with subsequent loss from the system.

This possibility would explain the difference in results obtained in this work from those reported by Ross[40] since the latter work was done in the absence of any likely hydrolytic agents.

The assertion of Palit and co-workers as to the lability of such chlorine substituents is not borne out by the experience of some workers in the hydrolysis of such compounds as $CHCl_2CH_2CHClCN$ and $CCl_3CH_2CHClCN$[47]. These compounds yield the acids, $CHCl_2CH_2CHClCOOH$ and $CCl_3CH_2CHClCOOH$ with no apparent hydrolysis of the α-chlorine.

One observation by Palit and co-workers[48] which has been verified in the present work is that it is possible in the course of precipitation of polyacrylonitrile with water to prepare polymer which is sparingly soluble in DMF. Such polymer was often prepared in small amounts in the course of precipitations, but the cause of its low solubility is unknown. It is suggested by Palit and co-workers that terminal hydroxyl groups play some part since polyacrylonitrile prepared from solutions of the monomer in acetic acid is found to be insoluble in DMF. If this is so, then it may indeed be that hydrolysis of the terminal chlorine is occurring in this system.

The direction taken by future study of metal salts as terminators in free radical polymerizations must be strongly influenced by recognition of the complex nature of these compounds in non-aqueous media.

Thus, rather than extend to other monomer and salt systems the work reported here, advantage would probably be had by a preliminary, more intensive study of past systems.

Spectrophotometric analysis, for example, should enable examination to be made for changes in terminator composition from one run to another. It may then be possible, for example, by manipulation of concentrations to ensure that the same species is being studied at different temperatures.

Isolation and structural analysis of the complexes involved would, if possible, provide invaluable information on the systems and perhaps lead to an understanding of the steric factors influencing these reactions.

Study of changes in oxidation-reduction potentials of the metal species with change in complex composition and of changes in ionization potentials from electron transfer spectra should help to elucidate the termination mechanism in a given system. A further necessary stage in this work would be an examination of the products of the termination reaction by tracer methods, analysis of the polymer and conductivity measurements.

When work of this nature has been done and an understanding reached of the factors involved in a given system, the work could then be extended with profit to other monomer, solvent and salt systems.

Tracer studies of the ferric chloride, acrylonitrile, DMF system could be continued by examining for the possible hydrolysis of chlorine in the polymer as mentioned above. Assuming that an understanding of the role of chlorine in the mechanism can be arrived at, it would be of interest to study any changes brought about by change in temperature.

The mechanism of initiation could be looked at from the point of view of participation by solvent. Carbon-14 labelled dimethylformamide could be used in such an investigation. A study of initiation in a system without DMF, either as a bulk heterogeneous system or in the presence of other solvents such as ethylene carbonate or 4-butyrolactone could also be carried out using chlorine-36 labelled ferric chloride.;

Although there appears to be no change in complex composition in this system[19] at 60°C over the monomer concentration range from zero to 5 mole 1^{-1}, it would be worthwhile to study the effect of temperature. The importance of complex composition could perhaps be brought out by a comparative study of the behaviour of chelates with different ligand groups in these radical-salt processes.

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