

EFFECTS OF IRON(III) CHLORO-COMPLEXES ON THE POLYMERIZATION OF STYRENE—II

RETARDATION AND INHIBITION KINETICS IN DIMETHYL SULPHOXIDE

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Abstract—A kinetic study has been made of the polymerization of styrene in dimethyl sulphoxide (DMSO) at 60°, initiated by 2,2'-azobisisobutyronitrile in the presence of $\text{Fe}(\text{DMSO})_6^{3+}$ and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ complex ions. Velocity constants for polystyryl radical attack on $\text{Fe}(\text{DMSO})_6^{3+}$ and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ complex ions are 0.229 and $71.8 \text{ m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, respectively, at 60°.

INTRODUCTION

WHEN studying reactions in solution between polyvinyl radicals and transition metal salts, it is important to establish, when feasible, the precise nature of the ions subject to radical attack. One method of ion identification, previously described, involved the use of model complex compounds and spectroscopic studies.⁽¹⁾ In this way, the stability of the ions $\text{Fe}(\text{DMF})_6^{3+}$, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$, and FeCl_4^- in *N,N*-dimethylformamide (DMF) and DMF/styrene mixtures containing Cl^- ions has been established.⁽¹⁾ The reactivity of these complex ions towards polystyryl radicals was subsequently studied, and the presence of chloride ions in the iron(III) cations was shown to facilitate the radical-ion electron transfer process.⁽²⁾

The effect of changing the type of organic ligand on the reactivity of the complex iron(III) cations towards polystyryl radical attack led to a preliminary study of the polymerization of styrene in dimethylsulphoxide (DMSO) at 60° initiated by 2,2'-azobisisobutyronitrile, forming Part I of this series.⁽³⁾ The stability of the $\text{Fe}(\text{DMSO})_6^{3+}$ and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ complex ions in DMSO and DMSO/styrene mixtures was also established. This paper reports a kinetic study of the reactivity of the two latter iron(III) cations towards polystyryl radicals at 60°.

EXPERIMENTAL

Materials

2,2'-azobisisobutyronitrile (AIBN),⁽⁴⁾ *N,N*-dimethylformamide (DMF),⁽⁴⁾ and styrene⁽⁵⁾ were purified as described previously. DMSO (B.D.H.) was dried over Linde 4A molecular sieve, distilled under reduced pressure and the middle fraction collected. The final material was stored in the dark over oxygen-free nitrogen until required.

The model compound D, hexakis(dimethylsulphoxide) iron(III) tetrafluoroborate $\text{Fe}(\text{DMSO})_6(\text{BF}_4)_3$, was prepared by the reaction of anhydrous iron(III) chloride (Hopkin and Williams) and anhydrous silver boron tetrafluoride (Alfa Inorganic) in DMSO as previously described.⁽³⁾ The greenish-yellow solid D was recrystallized twice from a DMSO-absolute ethyl alcohol mixture, dried *in vacuo* and stored in the dark. Microanalytical figures have been reported elsewhere.⁽³⁾ The tetrafluoroborate salt was chosen for study since the BF_4^- ion shows little tendency to complex.

Lithium chloride (B.D.H.) was used directly without further purification.

Apparatus

Rates of polymerization of styrene in DMSO at 60°, initiated by AIBN in the presence and absence of added iron(III) salts, were measured gravimetrically or dilatometrically.^(4,5) Care was taken to degas the reactants thoroughly before sealing off the dilatometers. In certain experiments, dilatometers with a bulb capacity of about 30 cm³ and a capillary of 1.0 mm dia. were used to increase the accuracy of measuring low rates of polymerization. Literature values for the densities of styrene and polystyrene⁽⁴⁾ at 60°, and measured values for DMSO⁽³⁾ were used in calculations.

RESULTS AND DISCUSSION

Rate measurements with complex D; evaluation of k_p

On polymerizing styrene at 60° in the presence of AIBN, DMSO and complex D, Fe(DMSO)₆-(BF₄)₃, with a suitable choice of reactant concentrations, retarded rates of polymerization were recorded dilatometrically (see Fig. 1). The rate results were

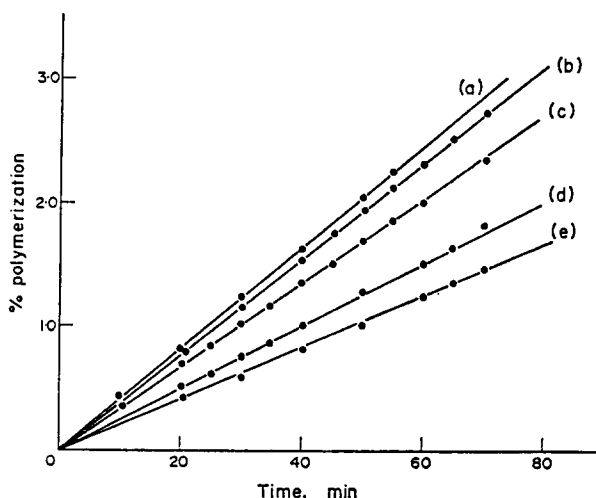


FIG. 1. Polymerization of styrene in DMSO at 60° in the presence of AIBN and complex D. [AIBN]₀ = 6.67×10^{-2} mol dm⁻³; [styrene] = 3.95 mol dm⁻³; [DMSO] = 7.17 mol dm⁻³. Concentrations of complex D: (a) 0.0 mol dm⁻³; (b) 2.5×10^{-3} mol dm⁻³; (c) 5.0×10^{-3} mol dm⁻³; (d) 14.7×10^{-3} mol dm⁻³; (e) 24.1×10^{-3} mol dm⁻³.

analysed by the method of Kice^(6,7) assuming that the equilibrium (1) was well over to the left hand side, and that the species Fe(DMSO)₆³⁺ of complex D was responsible for the retardation.



The kinetic scheme of Kice involves the three conventional steps,

Initiation:



where the velocity constant of (2a) is k_d and the overall rate of initiation is I ,

Propagation:



where the velocity constant is k_p , and

Mutual termination of polystyryl radicals by combination:



where the velocity constant k_t is defined by the equation

$$-d[R \cdot]/dt = 2k_t [R \cdot]^2. \quad (5)$$

In this scheme, I_n represents the initiator (AIBN), $R_c \cdot$ is a radical produced by direct decomposition of AIBN, $R_1 \cdot$, $R_r \cdot$ and $R_s \cdot$ are all growing polymer radicals, and M and P represent monomer and dead polymer molecules, respectively.

There are four other possible steps to be considered in the Kice-scheme,

Transfer to complex:



where the velocity constant will be designated k_y , and where $Z \cdot$ represents any species that could be formed by reaction between a polymer radical and complex D , which *a priori* might be a polymer radical,

Copolymerization:



where the velocity constant is k_o ,

Cross-termination:



where the velocity constant is k_z , and

Mutual termination of $Z \cdot$ species:



for which the velocity constant is k_z , defined by the equation:

$$-d[Z \cdot]/dt = 2k_z [Z \cdot]^2. \quad (10)$$

If ϕ is defined as the ratio of the retarded rate of polymerization at a retarder concentration $[D]$ to the rate in the absence of retarder D , c is a constant equal to $(4 k_t k_z/k_c^2)$, R_p is the fractional rate of polymerization, $-d[\ln[M]]/dt$, in sec^{-1} , and experiments are conducted at constant $[M]$ and $[\text{DMSO}]$, then

$$R_p \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} = \left(\frac{k_p k_y}{2k_t} \right) \frac{[D] \phi^2}{(1 - \phi^2)} \left[1 + \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} \right] - \frac{k_o k_p}{k_c} [M]. \quad (11)$$

Thus a plot of the left-hand side of (11) against

$$[\phi^2 [D]/(1 - \phi^2)] [1 + \sqrt{1 + \{c(1 - \phi^2)/\phi^2\}}]$$

at constant $[M]$ should give a slope of $(k_p k_y/2 k_t)$ and an intercept of $-[k_o k_p [M]/k_c]$ on the vertical axis.

A value of c equal to 1×10^{-6} was chosen to give the least deviation of the experimental points from a straight line and the results are shown in Fig. 2. The slope of the line is $0.5609 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$; using values of k_p and $2 k_t$ ⁽⁸⁾ equal to $0.176 \text{ m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ and $7.2 \times 10^4 \text{ m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ respectively, the value of k_y is

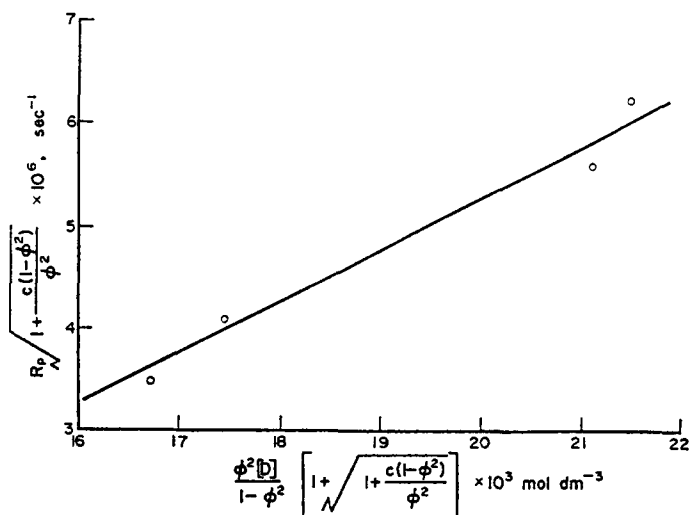
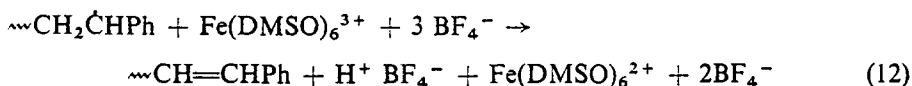


FIG. 2. Kice plot of retardation results with complex *D* alone. At 60°, [styrene] = 3.95 mol dm⁻³; [DMSO] = 7.17 mol dm⁻³; [AIBN]₀ = 6.67 × 10⁻² mol dm⁻³; value of *c* chosen = 1.0 × 10⁻⁶.

0.229 m³ mol⁻¹ sec⁻¹ at 60°. From the intercept, (*k*_o/*k*_c) was found to be 7.42 × 10⁻¹⁰, indicating an extremely low tendency of *Z'* species to attack monomer, which suggests that *Z'* is not a true radical but rather an inert product. Now the transfer constant to DMSO, *C*_s, in this system is only 2.4 × 10⁻⁵ at 60°⁽³⁾ and probably involves hydrogen atom abstraction from a CH₃ group. Therefore, unless the reactivity of a DMSO molecule is greatly altered when it is a ligand in the complex ion, another type of polymer radical-*D* reaction must occur to explain the high value of *k*_s. This reaction could be:

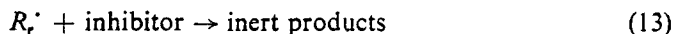


for which the products are completely inert. It was confirmed spectroscopically, using 1,10-phenanthroline,⁽¹⁾ that iron(III) species were produced, at least in part, by polystyryl radical attack on the iron(III) complex ions.

Effect of adding LiCl to D on rates of polymerization

On progressively adding LiCl to mixtures of constant composition containing styrene, DMSO and complex *D*, and measuring rates at 60°, definite induction periods were observed, at the end of which the rate always rapidly attained that expected in the absence of *D*. Some typical results are shown in Fig. 3.

A simple kinetic scheme of so-called "ideal" retardation has been developed by Bamford *et al.*^(9,10) which includes steps 2(a), 2(b), (3), (4) and, for this system, an additional step (13):



with velocity constant *k*₉, and giving products incapable of further reaction.

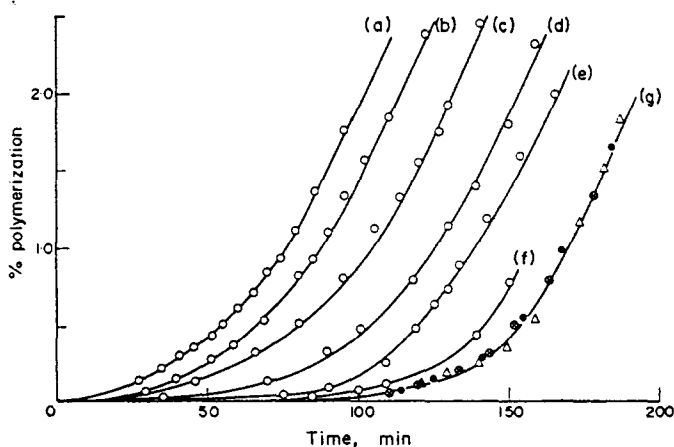


FIG. 3. Polymerization of styrene in DMSO at 60° initiated by AIBN in the presence of various iron(III) species, $[\text{styrene}] = 1.74 \text{ mol dm}^{-3}$; $[\text{DMSO}] = 10.75 \text{ mol dm}^{-3}$; $[\text{AIBN}]_0 = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; concentration of complex $D = [D] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$. Molar ratio $\text{LiCl}:D$ corresponding to curve (a) = 1:1; curve (b) = 1.5:1; curve (c) = 2:1; curve (d) = 2.6:1; curve (e) = 3:1; curve (f) = 4:1; and curve (g) \otimes —6.0:1; \bullet —8.0:1; Δ —9.3:1.

A stationary-state treatment leads to:

$$-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)] = k_9 [R']_s t + A^* \quad (14)$$

where ϕ_t is the reduced rate, equal to the ratio of the rate at any time t in the presence of ideal retarder to the final maximum rate, $[R']_s$ is the final maximum radical concentration in any experiment when all the retarder has disappeared and A^* is an arbitrary integration constant.

If τ is defined as the time when the rate of polymerization has attained a value 0.648 of the final maximum value,^(9,10)

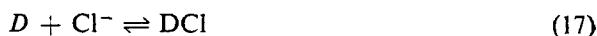
$$\tau = \frac{[\text{ideal retarder}]_0}{I} = \frac{[\text{ideal retarder}]_0}{2k_d f [\bar{I}n]} \quad (15)$$

where $[\text{ideal retarder}]_0$ represents the initial concentration of ideal retarder, $[\bar{I}n]$ is the mean initiator concentration, $[\text{AIBN}]$, in any experiment and f is the initiator efficiency.

A plot of τ , evaluated from the individual rate curves such as those shown in Fig. 3, against the concentration of lithium chloride added is shown in Fig. 4. It was found that LiCl alone did not affect the reaction rate of the above system in the absence of complex D . These results confirmed the spectroscopic conclusion⁽³⁾ that for this system all iron(III) species from complex D in the presence of a molar ratio of LiCl/D in excess of about 6:1 existed as $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ by virtue of the equilibrium,



which for convenience may be represented as:



which has an equilibrium constant, estimated from spectroscopic results, of about 10^3 .

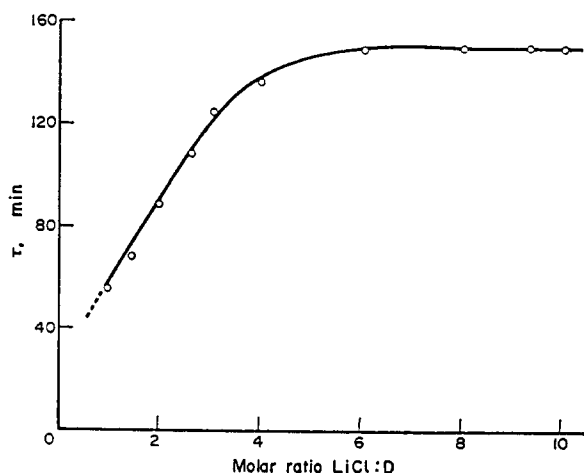
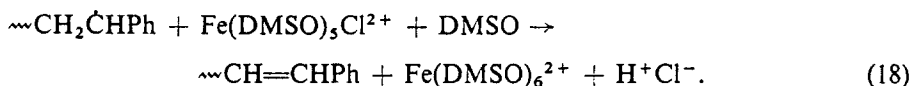


FIG. 4. τ as a function of added lithium chloride concentration. At 60° , $[\text{styrene}] = 1.74 \text{ mol dm}^{-3}$, $[\text{DMSO}] = 10.75 \text{ mol dm}^{-3}$, $[\text{AIBN}]_0 = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, and $[D] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

The $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ ions were much more reactive towards polystyryl radicals than $\text{Fe}(\text{DMSO})_6^{3+}$ ions, and the induction periods were presumably due to the overall process:



Thus in experiments for which the $\text{LiCl}:D$ molar ratio was always 10:1,

$$\tau = \frac{[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]}{I} = \frac{[\text{DCl}]_0}{2k_d f [\bar{I}n]} = \frac{[D]_0}{2k_d f [\bar{I}n]} \quad (19)$$

where $[\text{DCl}]_0$ represents the initial concentration of $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ ions, and $[D]_0$ is the initial concentration of complex D in the presence of the excess LiCl .

In confirmation of Eqn. (19), the results of further experiments at constant $[M]$, $[\text{DMSO}]$ and $[D]$ with a molar ratio of $\text{LiCl}:D$ of 10:1 showed a linear relationship between τ^{-1} and $[\bar{I}n]$ as indicated in Fig. 5. Again, for a series of experiments in which the initial initiator concentration, $(\text{AIBN})_0$, was maintained constant but $[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]$, prepared *in situ*, was varied, there was a linear relationship between $\tau[\text{AIBN}]$ and $[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]$ as shown in Fig. 6. The mean value of f deduced from these two plots using the previously measured value⁽³⁾ of k_d of $0.94 \times 10^{-5} \text{ sec}^{-1}$ was 0.61, which is close to other literature values.⁽¹¹⁾

A more detailed analysis of a single rate curve, measured with a 10:1 molar ratio of $\text{LiCl}:D$, was then made as previously described⁽²⁾ and gave a plot of ϕ_t vs. $k_9 [R']_t + A^*$ illustrated in Fig. 7. Reasonable agreement was found between the experimental and theoretical plots when $k_9 [R']_t$ was $2.9 \times 10^{-3} \text{ sec}^{-1}$ and A^* was -27.2 . This method is termed Method I, later.

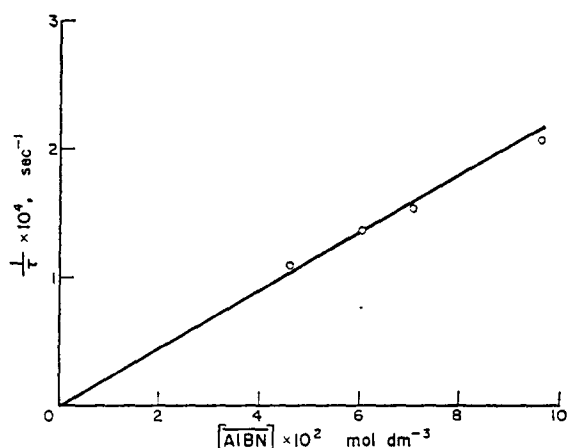


FIG. 5. τ as a function of mean initiator concentration. At 60° , [styrene] = 1.74 mol dm^{-3} ; [DMSO] = $10.75 \text{ mol dm}^{-3}$; and $[D] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$. Molar ratio of LiCl:D = 10:1.

Since the final maximum rate of polymerization $(R_p)_s$ is given by:

$$(R_p)_s = \frac{-d[M]}{dt} = k_p[M][R']_s \quad (20)$$

it follows that

$$\frac{k_9[R']_s[M]}{(R_p)_s} = \frac{k_9}{k_p} \quad (21)$$

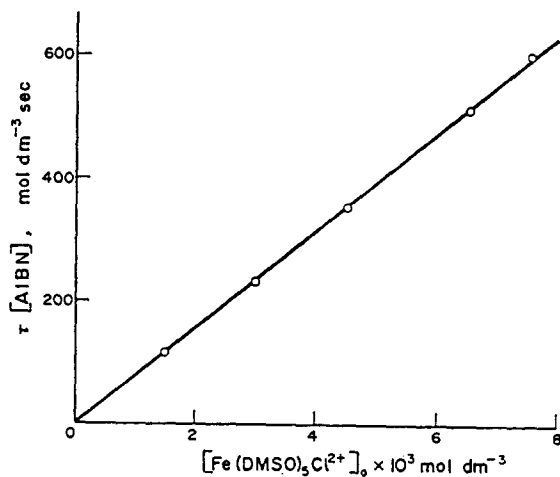


FIG. 6. Dependence of τ on the initial concentration of $\text{Fe}(\text{DMSO})_3\text{Cl}^{2+}$ prepared *in situ* using a molar ratio of LiCl:D = 10:1. At 60° , [styrene] = 1.74 mol dm^{-3} ; [DMSO] = $10.75 \text{ mol dm}^{-3}$; and $[\text{AIBN}]_0 = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$. Complete conversion of iron(III) material to the iron(III) chloro-complex is assumed to occur in the presence of the excess LiCl.

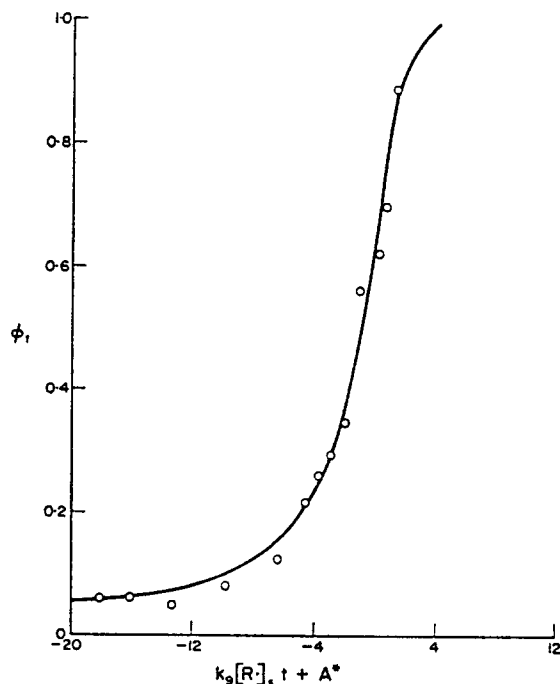


FIG. 7. Reduced rate ϕ_t as a function of reaction time t . (○) experimental points; (—) calculated curve. Molar ratio of $\text{LiCl}:D = 9.3:1$ at 60° . $[\text{Styrene}] = 1.74 \text{ mol dm}^{-3}$; $[\text{AIBN}]_0 = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{DMSO}] = 10.75 \text{ mol dm}^{-3}$ and $[D] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

For the experiment corresponding to Fig. 7, $(R_p)_s$ was $1.21 \times 10^{-2} \text{ mol m}^{-3} \text{ sec}^{-1}$ and, since $[M]$ was $1.74 \times 10^3 \text{ mol m}^{-3}$, k_9 was equal to $73.3 \text{ m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$.

Bengough *et al.*⁽¹²⁾ have suggested other methods of analysing results for retardation caused by a single ideal retarding species. For example, a plot of the left-hand side of Eqn. (14) against time t gives a straight line of slope $k_9 [R]_s$, and k_9 can be determined using Eqn. (21) with a measured value of $(R_p)_s$ at a known monomer concentration $[M]$. Alternatively the Bengough treatment,⁽¹²⁾ modified to apply to equilibrium (17) gives, where F is the fractional conversion:

$$\log_{10} \left[\frac{(1 - \phi_t^2)}{\phi_t} \right] = \log_{10} \left[\frac{k_9 (D\text{Cl})_0}{(2Ik_t)^{\frac{1}{2}}} \right] + \left(\frac{k_9}{k_p} \right) \log_{10} (1 - F) \quad (22)$$

as long as the equilibrium is well over to the right-hand side and $k_9 > k_p$.

Thus for I and $[D\text{Cl}]_0$ fixed, a plot of

$$\log_{10} \left[\frac{(1 - \phi_t^2)}{\phi_t} \right]$$

against $\log_{10} (1 - F)$ gives a straight line of slope (k_9/k_p) . These methods, referred to later as Method II and Method III respectively, were applied to analyse smoothed-out plots of percentage polymerization against time for a range of ϕ_t values equal to 0.15–0.80. One of the typical plots is shown in Fig. 8 and the values of k_9 obtained

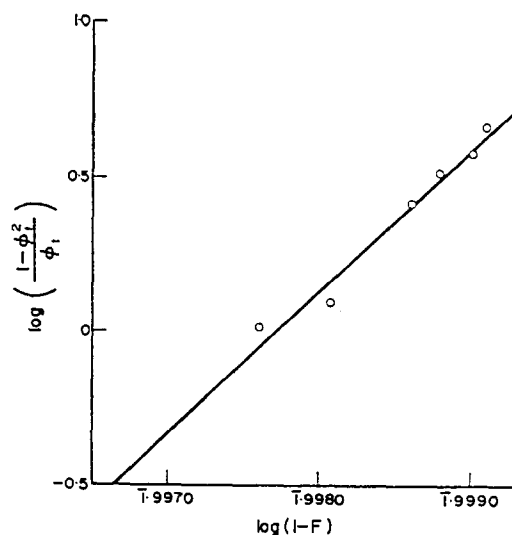


FIG. 8. $\log_{10} ([1-\phi_t^2]/\phi_t)$ as a function of $\log_{10} (1-F)$ for the polymerization of styrene initiated by AIBN at 60°, inhibited by $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$, prepared *in situ*. Molar ratio of $\text{LiCl}:D = 9.3:1$ at 60°; $[\text{styrene}] = 1.74 \text{ mol dm}^{-3}$; $[\text{DMSO}] = 10.75 \text{ mol dm}^{-3}$ and $[D] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

by the Methods I–III agreed reasonably well, with a mean k_9 value of $71.8 \text{ m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ at 60°.

A comparison of the velocity constants for reaction of different species of $\text{Fe}(\text{III})$ with polystyryl radicals, evaluated by these methods is given in Table 1.

From the results of Table 1, it is apparent that the presence of coordinated chloride ions in the complexes of iron(III) facilitates the electron transfer process in a way that is relatively unaffected by the number of coordinated chloride ions present, even if a statistical correction is applied, by the net charge carried by the ion, or by the geometry of the complex, octahedral $\{\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}\}$ or tetrahedral $\{\text{FeCl}_4^-\}$. The accelerative effects of added chloride, and other ions, with respect to electron transfer between iron(III) and iron(II) species, is already well

TABLE 1. VELOCITY CONSTANTS FOR REACTION OF POLYSTYRYL RADICALS WITH VARIOUS $\text{Fe}(\text{III})$ SPECIES AT 60°

Fe(III) species	Symbol for velocity constant	Value of velocity constant at 60° ($\text{m}^3 \text{ mol}^{-1} \text{ sec}^{-1}$)				Ref.
		Method I	Method II	Method III	Mean value	
$\text{Fe}(\text{DMF})_6^{3+}$	k_x				0.847	(2)
$\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$	k_6	41.5	47.9	46.5	45.3	(2)
$\text{Fe}(\text{DMF})_4\text{Cl}_2^+$	k_7	65.5	62.5	63.9	64.0	(2)
FeCl_4^-	k_8	31.4	28.4	29.0	29.6	(2)
$\text{Fe}(\text{DMSO})_6^{3+}$	k_y				0.229	
$\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$	k_9	73.3	67.4	74.7	71.8	

established both in aqueous and non-aqueous solutions.^(13,14) If the Cl^- ions form inner sphere complexes on coordination, electron transfer between two metal ions may be facilitated by a bridged activated-complex mechanism. The coordinated Cl^- ion may be regarded as acting as an electron "conductor" during the electron transfer process, but precise mechanisms still remain obscure. In the termination of polyacryl amide radicals in aqueous solution by iron(III) species, the presence of coordinated ions such as Cl^- and SO_4^{2-} within the complex causes an accelerative effect.^(15,16)

The velocity constant for polystyryl radical attack on $\text{Fe}(\text{DMF})_6^{3+}$ is greater than the corresponding value for $\text{Fe}(\text{DMSO})_6^{3+}$. Infra-red spectroscopy suggests that the Fe(III) ion in the complex *A*, $\text{Fe}(\text{DMF})_6(\text{BF}_4)_3$, is coordinated through the oxygen atoms⁽¹⁾ and the Fe(III) ion in the complex *D* is also likely to be coordinated through oxygen atoms since $\text{Fe}(\text{DMSO})_6^{2+}$ is reported to be a strongly oxygen-bonded complex.⁽¹⁷⁾ So the nature of coordination in both these complexes is likely to be the same, although the strengths of the ligand-ion bonds, which may involve both σ - and π -bonding, are different. In particular, the DMSO-Fe(III) ion bond is stronger than that for DMF-Fe(III) . Oxidation of the polystyryl radical probably involves interaction of the $2p$ orbital of the radical end carbon-atom with the vacant d -orbitals of the cation in the transition state.⁽¹⁸⁾ Electron transfer occurs in the transition state followed by proton expulsion from the polymer radical. The polystyryl radical is more reactive towards the $\text{Fe}(\text{DMF})_6^{3+}$ species, in which the net σ - and π -bonding is weaker, than towards the corresponding $\text{Fe}(\text{DMSO})_6^{3+}$ species.

The octahedral $\text{Fe}(\text{DMF})_6^{3+}$ and $\text{Fe}(\text{DMSO})_6^{3+}$ ions are of high spin $\{t_{2g}^3 (d_{xy}, d_{xz}, d_{yz}), \text{low energy}; e_g^2 (d_{x^2-y^2}, d_{z^2}), \text{high energy}\}$, and their various chloride coordinated complexes are also probably of high spin since Cl^- ligands provide a relatively weak field. The tetrahedral ion $\text{FeCl}_4^- \{e_g^2 (d_{x^2-y^2}, d_{z^2}), \text{low energy}; t_{2g}^3 (d_{xy}, d_{xz}, d_{yz}), \text{high energy}\}$ is also of high spin for similar reasons. Hence differences in reactivity between the pure DMF- and DMSO-coordinated octahedral complexes and the various Cl^- coordinated complexes cannot be due to a mere difference in spin states.

However, the coordinated Cl^- ligands can engage not only in σ -bonding but also in π -bonding with some of the metal orbitals of iron(III). The π -bonding between the more compact Cl^- ligand will be more extensive than that between the larger DMF- and DMSO-ligands. In the octahedral complexes, π -orbitals are formed by interaction of the filled $3p$ -orbitals of coordinated Cl^- ions and the partly filled t_{2g} orbitals of the central metal ion. Back-donation of the metal t_{2g} orbital electrons to the empty $3d$ and $4p$ orbitals of coordinated Cl^- may also occur. An extended π -bond may be formed between a coordinated Cl^- ion in an octahedral complex and a polystyryl radical by interaction of the appropriate t_{2g} metal orbitals, the filled $2p$ or empty $3d$ or $4p$ orbitals of a coordinated Cl^- ion and a $2p$ orbital on the polymer radical end C-atom. An extended π -bond system of this type in the transition state would facilitate electron transfer markedly. For FeCl_4^- , the t_{2g} and e_g metal orbitals can all be involved in the formation of π -bonds with coordinated Cl^- ions, and extended π -bond systems with a polymer radical can be formed. The coordinated Cl^- ions may also facilitate electron transfer by causing d -electron cloud expansion (the "nephelauxetic" effect) to a greater extent than DMF or DMSO ligands. The effect of π -orbital formation, involving coordinated Cl^- ions, on the lower energy levels of the metal d -orbitals is difficult to assess.

Further investigations will be made into the temperature dependence of these velocity constants, and of the effects of other ligands, in an attempt to elucidate further the precise mechanism of these polymer radical-complex reactions.

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Résumé—On a effectué une étude cinétique de la polymérisation du styrène dans le diméthylsulfoxyde (DMSO) à 60°, amorcée par l'azobisisobutyronitrile en présence des ions complexes $\text{Fe}(\text{DMSO})_6^{3+}$ et $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$. A 60°, les constantes des vitesses d'attaque du radical polystyrène sur les ions complexes $\text{Fe}(\text{DMSO})_6^{3+}$ et de $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ sont respectivement de 0,229 et 71,8 $\text{m}^3 \text{mole}^{-1} \text{sec}^{-1}$.

Sommario—Si è effettuata un'indagine cinetica della polimerizzazione a 60° di stirolo in dimetilsolfossido (DMSO) con 2,2'-azobisisobutyronitrile come iniziatore e in presenza di ioni complessi $\text{Fe}(\text{DMSO})_6^{3+}$ e $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$. A 60° le costanti di velocità per l'attacco dei polistirilradicali su $\text{Fe}(\text{DMSO})_6^{3+}$ e $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ sono pari rispettivamente a 0,229 e 71,8 $\text{m}^3 \text{Mol}^{-1} \text{sec}^{-1}$.

Zusammenfassung—Es wurde eine kinetische Untersuchung der Polymerisation von Styrol in Dimeethylsulfoxid (DMSO) bei 60° durchgeführt mit 2,2'-Azobisisobutyronitril als Initiator und in Gegenwart von $\text{Fe}(\text{DMSO})_6^{3+}$ und $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ Komplex Ionen. Die Geschwindigkeitskonstanten bei 60° für den Angriff der Polystyryl-Radikale auf $\text{Fe}(\text{DMSO})_6^{3+}$ und $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ sind 0,229 bzw. 71,8 $\text{m}^3 \text{Mol}^{-1} \text{sec}^{-1}$.