Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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S. D. Hamann[a]; A. J. Murphy[a]; D. H. Solomon[a]; R. I. Willing[a]
[a] Division of Applied Chemistry, CSIRO, Melbourne, Victoria, Australia

To cite this Article Hamann, S. D. , Murphy, A. J. , Solomon, D. H. and Willing, R. I.(1972) 'The Mechanism of the Polymerization of Styrene by Perchloric Acid', Journal of Macromolecular Science, Part A, 6: 4, 771 — 787

To link to this Article: DOI: 10.1080/10601327208056874

URL: http://dx.doi.org/10.1080/10601327208056874

J. MACROMOL. SCI.—CHEM., A6(4), pp. 771-787 (1972)

The Mechanism of the Polymerization of Styrene by Perchloric Acid

S. D. HAMANN, A. J. MURPHY, D. H. SOLOMON, and R. I. WILLING

Division of Applied Chemistry
CSIRO
Melbourne, Victoria 3001
Australia

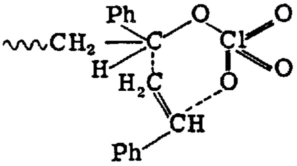
ABSTRACT

The kinetics of the polymerization of styrene, initiated by anhydrous perchloric acid in carbon tetrachloride solution and in mixtures of methylene chloride and carbon tetrachloride, have been studied by NMR and GLC methods. In carbon tetrachloride the reaction is zeroth order.
The kinetics, together with the known effects of dielectric constant and pressure on the reaction rate, suggest that the rate-determining step may be the formation of a carbonium perchlorate ion-pair, associated with neutral molecules of styrene.

INTRODUCTION

The nature of the propagating species in "cationic" polymerizations has been the subject of some controversy in recent years. The widely held view that the active propagating species is an ion, or an ion-pair, has been disputed by Plesch [1-5] who suggests that, in some systems at least, a neutral ester is the propagating entity. Plesch [1] has used the term pseudocationic polymerization to cover these systems.

Much of the discussion has centered on the styrene/perchloric acid system, which has been extensively studied by several groups [1-15]. In a series of detailed studies, Pepper et al. [6-9] have suggested that the propagation is by free ions under some conditions, and by free ions and some "nonsuppressible" species (unaffected by perchlorate ions) under other conditions [9]. In contrast Plesch [3] considers that the propagating entity is a formal perchlorate ester of the type (I). So far, esters of this type have not been isolated, their presence



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having been inferred from analysis of kinetic data and from spectral and conductivity measurements. However, as Bywater and Worsfold [12] and MacCarthy, Millrine, and Pepper [9] have pointed out, for certain values of the rate constants the kinetic and spectral data do not distinguish between chain propagation by esters and by free ions.

In an attempt to clarify the mechanism of the styrene/perchloric acid reaction we now report additional studies in carbon tetrachloride and carbon tetrachloride-methylene chloride solvent systems at normal temperatures.

EXPERIMENTAL

Preparation of Materials

Carbon tetrachloride (British Drug Houses Ltd., Analar grade) and methylene chloride (May and Baker Ltd., reagent grade) were dried, distilled from phosphorus pentoxide, and stored over dried molecular sieves (Union Carbide 4A).

Styrene (Monsanto Ltd., polymerization grade) was washed with aqueous potassium hydroxide, dried over anhydrous sodium sulfate, and distilled through copper turnings under a reduced pressure of nitrogen. It was stored below 0°C until required.

Anhydrous perchloric acid was prepared by distillation, under reduced pressure, of a mixture of 1 part by weight of potassium perchlorate and 4 parts by weight of concentrated, analytical grade, sulfuric acid. Because of the danger of handling pure perchloric acid, it was distilled directly into carbon tetrachloride and its concentration determined by titration with alkali.

Polymerizations

The polymerizations were followed by two techniques, NMR spectroscopy and GLC analysis.

NMR Method

The NMR spectra were measured on a Varian HA-100 Spectrosystem at a probe temperature of 30°C.

The kinetic runs were carried out in NMR sample tubes mounted in situ in the instrument. In a typical experiment, 0.2 ml of styrene was placed in the tube, it was diluted with 0.5 ml of solvent, and then 0.2 ml of a solution of perchloric acid in carbon tetrachloride was added to initiate polymerization. The spectrum was measured as soon as possible after mixing and then at frequent intervals until the end of the reaction. The change in concentration of styrene was followed by measuring the relative areas of the monomer peak at δ 5.6 and of the peak δ 4.80 of a methylene bromide (British Drug Houses Ltd., Analar grade) internal integral reference, using the Varian V-3521A integrator. The concentration of perchloric acid, measured volumetrically in duplicate experiments, proved to be rather irreproducible because unavoidable losses occurred in handling the small quantities of solution. For that reason we did not attempt to measure absolute rate constants by the NMR method.

GLC Method

An F & M 402 all-glass system with a flame ionization detector was used throughout. The analytical results were obtained using a 1.8-m column, 8 mm in diameter, packed with 3% UC-W98 (Hewlett Packard) on 70-80 mesh Chromasorb W and operating at 80°C with a nitrogen flow of 0.7 $cm^3\ sec^{-1}$. For preparative separations, a 3-m column, 12 mm in diameter was packed with 4% UC-W98 on 70-80 mesh Chromasorb W and operated at 200°C with a nitrogen flow of 0.8 $cm^3\ sec^{-1}$.

The kinetic experiments were carried out in a 150-ml flask under an atmosphere of dry argon. Styrene (4 ml), solvent (100 ml), and an internal reference compound, toluene (1.5 ml), were mixed and equilibrated at 0° C, and 1.5 ml of a solution of perchloric acid in carbon tetrachloride was then added to start the polymerization. Samples of 5 ml were removed at intervals and quenched by vigorous shaking with 10 ml of water. The organic layer was removed, dried over sodium sulfate, and analyzed by GLC. The degree of reaction was calculated from the ratio of the integrated styrene and toluene peaks.

RESULTS

NMR Results

Figure 1 shows a set of NMR spectra measured during the polymerization of styrene in CCl_4 solution.

The progressive decrease in concentration of monomeric styrene is shown clearly by the weakening and final disappearance of the H_1-H_3 proton peaks. At the same time a number of new peaks appeared although these, too, vanished at the end of polymerization (cf. Figs. 1B and 1E). Comparison with Fig. 1F shows that they were due principally to the formation and subsequent reaction of the styrene dimer 1,3-diphenyl-1-butene.

Figure 2 shows a plot of the concentration of monomer [M] (expressed as a fraction of the initial concentration $[M]_0$) measured by integration of the δ 5.65 peak during a polymerization reaction in CCl_4. The linearity of the plot shows that the reaction was accurately of the zeroth order over the whole of its course. On the other hand, a reaction in a mixture of CCl_4 with 33% (vol) CH_2Cl_2 followed first-order kinetics, and reactions in solvents of intermediate compositions had fractional orders between zeroth and first.

There was no evidence in any of the NMR spectra of peaks that could be ascribed to the presence of the ester 1-phenylethyl perchlorate (I).

GLC Results

Figures 3 and 4 show zeroth-order and first-order kinetic plots for polymerizations in three solvent systems. The composition of the solvents and the reaction conditions are listed in Table 1. It is apparent from the diagrams that Reactions A and B are zeroth

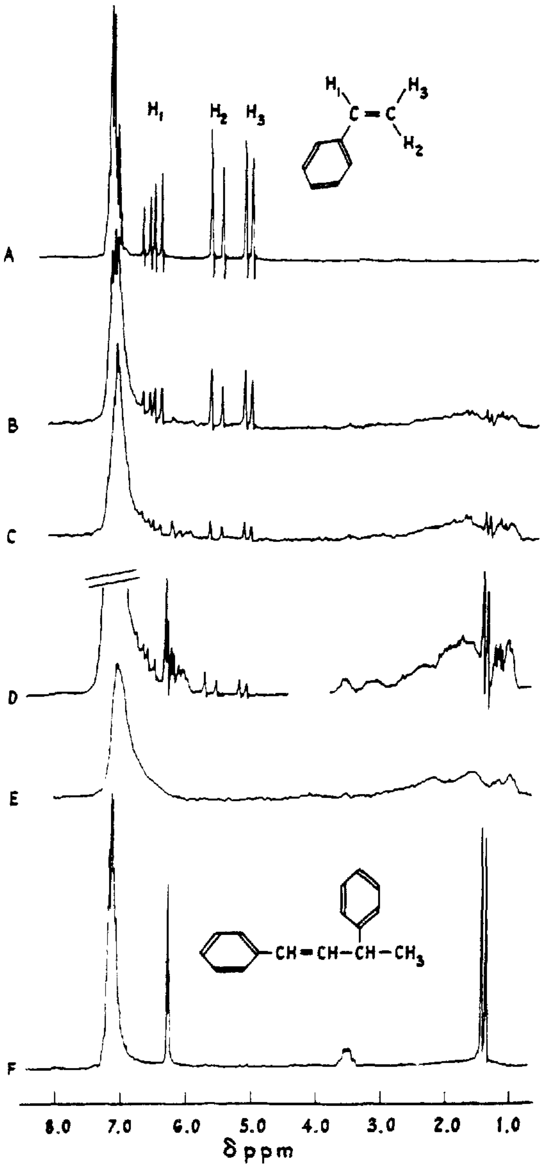

FIG. 1. 100 MHz NMR spectra in CCl_4. Spectra A to E were measured at different times t (sec) during the polymerization of styrene in CCl_4 at 30° C. The mixture initially contained 1.0 mole l^{-1} of styrene and ~ 0.05 mole l^{-1} of $HClO_4$. (A) t = 0, (B) t = 800, (C) t = 1250, (D) t = 1450 (spectrum measured at increased amplitude), and (E) t = 1750 sec (end of reaction). F is the spectrum of the styrene dimer 1,3-diphenyl-1-butene, measured in CCl_4.

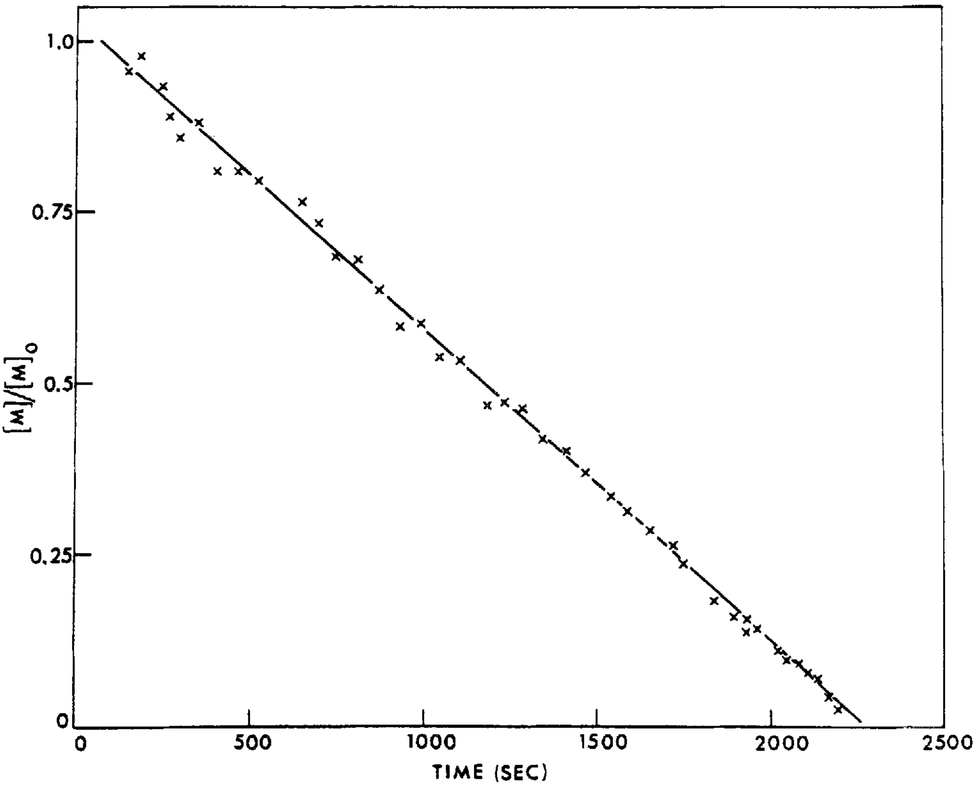

FIG. 2. A zeroth-order plot of NMR results for the polymerization of styrene in CCl_4 at 30°C. $[M]_0 = 1.9$ mole l^{-1}, $[HClO_4]_0 = \sim 0.07$ mole l^{-1}

order, but Reaction C is nearly first order; the deviation of its plot from linearity in Fig. 4 corresponds to an order of about 0.8.

In addition to the quantitative measurements of monomer concentration, we made a number of qualitative GLC analyses of mixtures during polymerization. In CCl_4 solution these showed the presence of dimers, trimers, and tetramers and also adducts of toluene with styrene and its oligomers (toluene was used as a marker in the kinetic experiments). Three of the species were isolated by preparative GLC and shown to be:

(a) 1,3-Diphenyl-1-butene. This compound gave rise to the main dimer peak. Its structure was confirmed by both its NMR spectrum (Fig. 1F) and its mass spectrum, and by comparison of these with

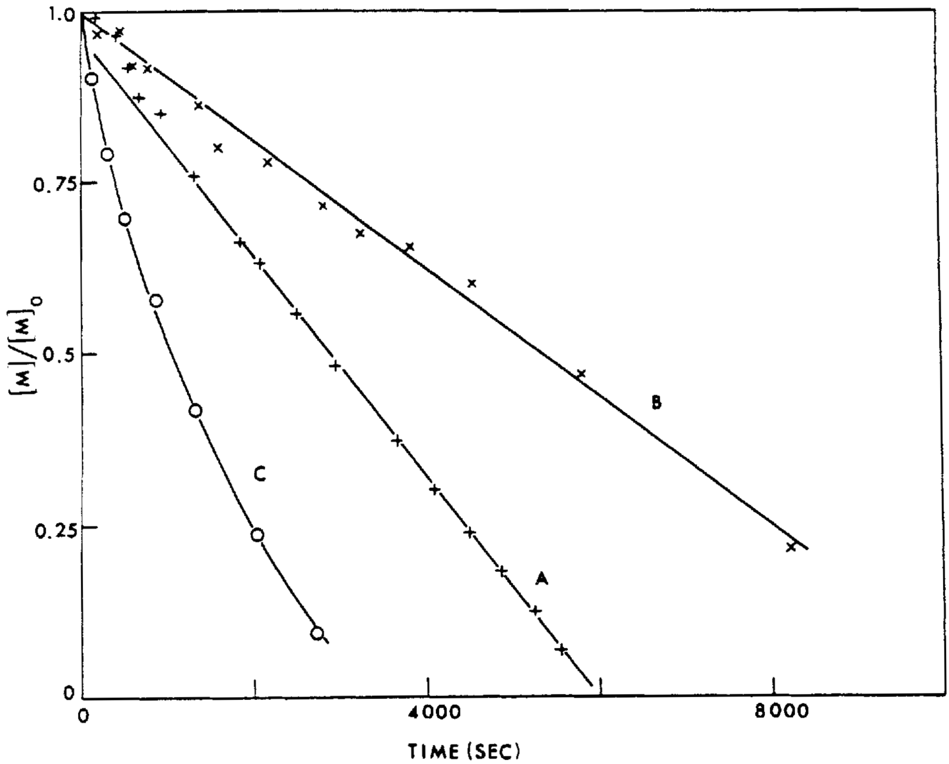

FIG. 3. Zeroth-order plots of gas-liquid chromatography results for the polymerization of styrene. The reaction conditions are listed in Table 1.

the spectra of an authentic specimen. The mass spectrum had m/e values 208(88), 193(84), 179(18), 178(25), 165(12), 130(22), 129(18), 115(100), 91(55), 89(4), 77(18).

(b) A styrene trimer. The composition of this product was deduced from the mass spectrum m/e values 312(3), 207(48), 206(17), 194(42), 193(100), 178(21) 129(41), 115(79), 106(52), 105(90), 103(21), 91(100), 77(31).

(c) 1-Phenylethyl toluene. This adduct of toluene and styrene was formed to the extent of about 0.5% of the amount of toluene present. Its structure was deduced from the mass spectrum m/e values 196(54), 182(21), 181(100), 179(8), 178(10), 166(24), 165(30), 119(5), 115(8), 104(7), 91(8), 89(10), 83(8), 78(10).

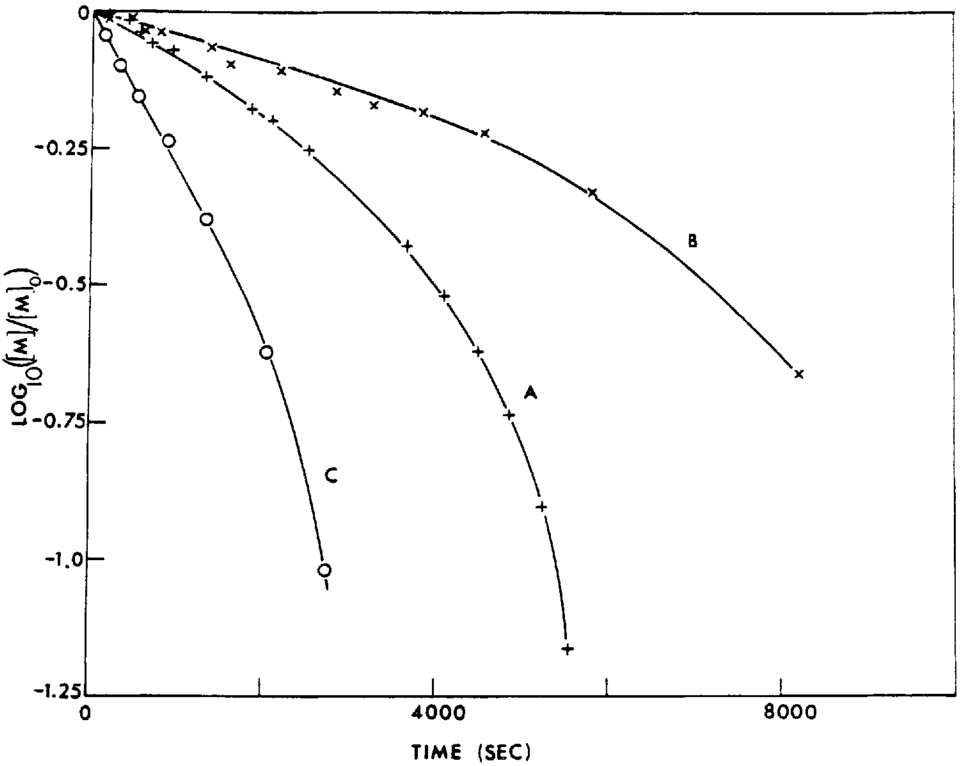

FIG. 4. First-order plots of gas-liquid chromatography results for the polymerization of styrene. The reaction conditions are listed in Table 1.

DISCUSSION

Kinetics

Previous investigations of this reaction have established that, in the solvents methylene chloride [3], ethylene dichloride [7], and chlorobenzene [10], its kinetics are of the first-order internally (Eq. 1) and of the second-order over-all (Eq. 2), where $[HClO_4]_0$

$$-\,d[M]/dt = \text{constant} \times [M] \qquad (1)$$

TABLE 1. Reaction Conditions and Rate Constants

Reaction	Solvent (vol. %)		Temp. (°C)	$[M]_0$ (mole l^{-1})	$[HClO_4]_0$ (mole l^{-1})	k_1 (sec^{-1})	k_2 (liter $mole^{-1}$ sec^{-1})
	CCl_4	CH_2Cl_2					
A	100	0	30	0.33	0.049	1.1×10^{-3}	
B	85	15	0	0.35	0.052	1.8×10^{-3}	
C	65	35	0	0.33	0.046		(4.9×10^{-3})[a]

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[a] This rate constant is an apparent value calculated from Eq. (2), which is not strictly applicable since the internal reaction order is about 0.8, not 1.

$$-d[M]/dt = k_2[M][HClO_4]_0 \tag{2}$$

denotes the concentration of the catalyst, which is assumed to be unchanged during reaction, and k_2 is a second-order rate constant.

A remarkable result of our measurements by both the NMR and GLC methods is the finding that, in CCl_4 solution, the reaction is of the zeroth-order internally (Eq. 3) and of the first-order over-

$$-d[M]/dt = \text{constant} \tag{3}$$

all (Eq. 4), where k_1 is a first-order rate constant. This result is in

$$-d[M]/dt = k_1[HClO_4]_0 \tag{4}$$

apparent conflict with the work of Pepper and Reilly [7] who reported an over-all second-order rate constant for the reaction in CCl_4. However, Dr. Pepper has told us that in his experiments, which were carried out at a lower temperature than ours, the amount of conversion may have been too small to distinguish between the two reaction orders. If Pepper and Reilly's second-order rate constant is converted to a first-order one, it becomes $k_1 = 5.2 \times 10^{-4}$ sec^{-1} at 20°C, which agrees satisfactorily with our value $k_1 = 1.1 \times 10^{-3}$ sec^{-1} at 30°C.

General Mechanism of Reaction

The zeroth-order internal kinetics for polymerization in CCl_4 mean that the rate-determining step cannot be the attack of an active species on a free monomer molecule in solution, as it is assumed to be in the more polar solvents [7]. It must be the rearrangement of a molecular complex which already has one or more monomer molecules built into it, essentially as a separate "phase" from the solution. Fontana and Kidder [16] used this kind of model to explain the unusual kinetics of the cationic polymerization of propylene initiated by $AlBr_3.HBr$.

To apply the model here, we shall first assume that all the $HClO_4$ is bound in an unspecified way to monomer molecules M or to growing polymer molecules M_n. (Bywater and Worsfold [12] have produced very strong evidence that this is so.) We also assume that each catalyst complex may be associated with, or "solvated" by, an additional x monomer molecules (Plesch [1, 3, 5] has previously suggested that this kind of association occurs, with x = 4) according to the equilibrium of Eq. (5), and that the rate-determining step in

$$M_n.HClO_4 + xM \overset{\text{fast}}{\rightleftharpoons} M_n.HClO_4.xM \tag{5}$$

$$K = \frac{[M_n.HClO_4.xM]}{[M_n.HClO_4][M]^x} \tag{6}$$

polymerization is the reaction of Eq. (7), followed by fast incorporation

$$M_n.HClO_4.xM \xrightarrow{\text{slow}} M_{n+1}.HClO_4.(x - 1)M \tag{7}$$

of another monomer molecule from the solution into the complex. The rate of disappearance of monomer is then as shown in Eq. (18). From

$$-d[M]/dt = k[M_n.HClO_4.xM] \tag{8}$$

Eq. (6) and from the mass balance equation (Eq. 9), Eq. (10) follows.

$$[HClO_4]_0 = [M_n.HClO_4] + [M_n.HClO_4.xM] \tag{9}$$

$$-\frac{d[M]}{dt} = \frac{k\,K\,[HClO_4]_0[M]^x}{1 + K[M]^x} \tag{10}$$

When K is large, Eq. (10) reduces to Eq. (4) and the kinetics are zeroth-order internally; when K is small, it reduces to the numerator and the kinetics are xth-order internally. The integrated form of Eq. (10) is Eq. (11) or, if $x = 1$, Eq. (12). To illustrate the forms of

$$k[HClO_4]_0t = \frac{[M]^{1-x} - [M]_0^{1-x}}{K(x - 1)} + [M]_0 - [M] \tag{11}$$

$$k[HClO_4]_0t = \frac{\ln([M]_0/[M])}{K} + [M]_0 - [M] \tag{12}$$

these relationships generally, it is convenient to rewrite them in dimensionless terms as in Eqs. (13) and (14), where α and K' are

$$t^* = \frac{K'(1-\alpha) + (\alpha^{1-x} - 1)(x-1)^{-1}}{1+K'}, \qquad \text{for } x \neq 1 \qquad (13)$$

$$t^* = \frac{K'(1-\alpha) - \ln \alpha}{1+K'}, \qquad \text{for } x = 1 \qquad (14)$$

the dimensionless quantities $\alpha = [M]/[M]_0$, $K' = [M]_0^x K$, and t^* is a dimensionless quantity proportional to the time and scaled to make the initial slopes of the reaction curves all equal to unity, i.e., $-d\alpha/dt^* = 1$. It is related to the real time t as in Eq. (15).

$$t^* = \frac{k K' [HClO_4]_0}{(1+K')[M]_0} t \qquad (15)$$

Figure 5 illustrates some reaction curves for the particular case x = 1, plotted as if they were first-order reactions D and zeroth-order reactions E. As K' increases, they change from one extreme to the other and show intermediate order kinetics of the kind that we have found experimentally for Reaction C (Figs. 3 and 4).

On this basis, we interpret the trend towards zeroth-order kinetics with increasing CCl_4 content in CH_2Cl_2/CCl_4 mixtures as arising from increasing association of monomer molecules with the catalyst complex. We suggest that the complex is polar and that in CCl_4 solutions it is preferentially "solvated" by polarizable styrene monomer molecules, whereas in CH_2Cl_2 it is solvated by the more polar solvent molecules.

The fact that the polymerization has internal first-order kinetics in polar systems could be taken to mean that, in Eq. (10), x = 1 and $K \rightarrow 0$ for these solvents. Or, what is almost equivalent, that the slow step is the collision and reaction of the $HClO_4$ complex with a monomer molecule in solution, as proposed by Pepper and Reilly [7].

Detailed Mechanism

So far we have not considered the detailed structure of the catalyst complex or of the transition state.

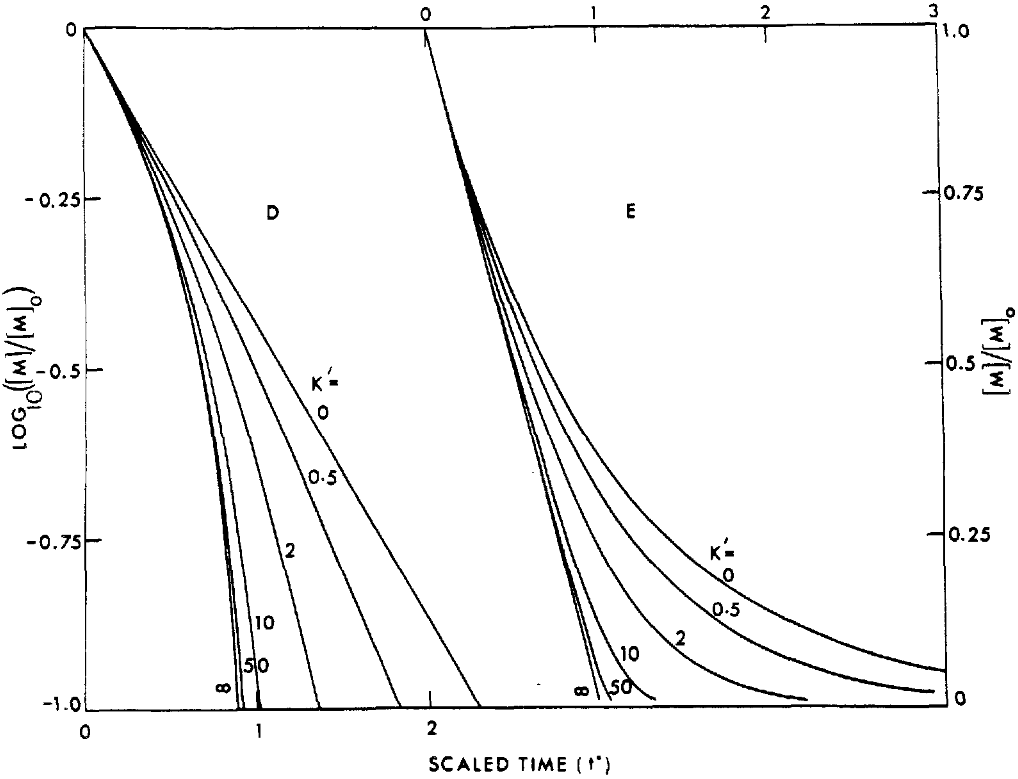
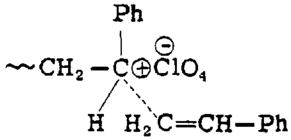


FIG. 5. Theoretical first-order D and zeroth-order E plots for reactions obeying the kinetic equation (12).

Plesch [3] considers that the complex is an ester molecule, 1-phenylethyl perchlorate (I) or its oligomers; Bywater and Worsfold [12] have suggested that it might be a π-complex, and Reilly and Pepper [7] have considered the possibility that it is an ion-pair, but on the whole are noncommittal. Our only new evidence on the question is that we have been unable to detect any ester peaks in the NMR spectra during polymerization. Although this does not prove the complete absence of styryl perchlorate esters, we think it significant, particularly since the esters have never been detected by other spectroscopic means and have never been isolated.

Whatever the nature of the $HClO_4$ complex, it is generally agreed that the transition state is polar, and the main difference between Plesch's pseudocationic mechanism (I) and a mechanism



(II)

involving ion-pairs (II) lies in the degree of polarity. We are inclined to favor the ion-pair transition state for the following reasons:

Effect of Dielectric Constant

Pepper and Reilly [7] made a quantitative study of the rate of polymerization as a function of the dielectric constant ϵ in $(CH_2Cl)_2/CCl_4$ mixtures. It is informative to analyze their results in terms of Laidler and Eyring's theory [17] of dielectric effects, which gives Eq. (16) for a bimolecular reaction, where $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$; k denotes Boltzmann's constant, T is the absolute

$$\left(\frac{\partial \ln k}{\partial f(\epsilon)}\right)_{P,T} = -\frac{1}{kT}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu^{\ddagger 2}}{r^{\ddagger 3}}\right) \tag{16}$$

temperature; μ_A, μ_B, and $\mu^\ddagger$ are the dipole moments of the two reacting species and the transition state; and r_A, r_B, and $r^\ddagger$ are the corresponding effective radii of the species. Of the three terms in Eq. (16), the first two must lead to a decrease of k with increasing ϵ, and the last to an increase. Experimentally, Pepper and Reilly [7] found a very marked increase, the derivative $\partial \ln k/\partial f(\epsilon)$ being equal to +62 and constant over a considerable range of composition. If this change is equated simply to the last term in Eq. (16), it yields the value $\mu^{\ddagger 2}/r^{\ddagger 3} = 2.55 \times 10^{-12}$ erg (which is a lower limit since the first two terms are negative). The values of $r^\ddagger$ is uncertain, but it is unlikely that it is less than 3 Å and a more reasonable value is 5 Å. The derived values of $\mu^\ddagger$ for these radii are 8.3 and 17.8 D, respectively, corresponding to full positive and negative charges separated by 1.8 and 3.8 Å. Although these figures should not be taken too seriously, they do show that the effect of dielectric constant is great enough to be consistent with the idea that the transition state is a fully developed ion-pair. As a corollary, the initial species must be relatively nonpolar, which implies that the $HClO_4$ complex is an ester or a π-complex, not an ion-pair.

Effect of Pressure

Zharov et al. [10, 14] have measured the effect of pressure on the polymerization of styrene initiated by $HClO_4$ in chlorobenzene. They expressed their results as activation volumes $\Delta V^{\ddagger}$, defined as in Eq. (17), and found that $\Delta V^{\ddagger}$ was in the range -20 to -25 cm^3

$$\Delta V^{\ddagger} = -RT \frac{\partial \ln k}{\partial P} \tag{17}$$

mole^{-1}, which is remarkably close to the values -22 and -25 cm^3 mole^{-1} given by Hamann and Teplitzky's [18] high-pressure measurements on the cationic polymerization of isoamyl vinyl ether, initiated by iodine. If the transition state is more polar than the initial state, part, at least, of this contraction must arise from increased electrostriction $\Delta V_{el}^{\ddagger}$ of the surrounding medium. We can estimate the magnitude of $\Delta V_{el}^{\ddagger}$ by differentiating the electrostatic free energy and obtaining the relationship of Eq. (18). Using Pepper and Reilly's value of +62 for the first

$$\Delta V_{el}^{\ddagger} = -\frac{3RT}{(2\epsilon + 1)^2} \left(\frac{\partial \ln k}{\partial f(\epsilon)}\right)_{P,T} \left(\frac{\partial \epsilon}{\partial P}\right)_{T,\mathrm{comp}} \tag{18}$$

derivative and Schornack and Eckert's [19] value of $+5.83 \times 10^{-4}$ bar^{-1} for the second derivative for chlorobenzene, we find $\Delta V_{el}^{\ddagger}$ = -18.7 cm^3 mole^{-1}. The major part of $\Delta V^{\ddagger}$ therefore arises from strong electrostriction around the highly polar transition state and the remainder is probably associated with the approach of the styrene molecule which is being attacked [20].

Reaction Products in the Presence of Toluene

We mentioned, in the section on Results, that reactions in the presence of toluene yielded measurable amounts of 1-phenylethyl toluene. We think that this is good direct evidence that 1-phenylethyl carbonium ions are formed and that a small proportion of them attack toluene molecules by an electrophilic substitution reaction in competition with their addition reaction with styrene. The ions may, of course, be present as ion-pairs.

To summarize, a mechanism which fits all the facts is one in which $HClO_4$ rapidly forms a π-complex with one or more styrene molecules or oligomers. The complex then undergoes slow ionization to an ion-pair state and in that form attacks a styrene molecule in solution or one already associated with the complex, by first- or zeroth-order kinetics, respectively.

ACKNOWLEDGMENTS

We are grateful to Dr. S. R. Johns for advice in the use of NMR, and we appreciate the exchange of views we have had with Drs. D. C. Pepper and P. H. Plesch.

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Received for publication February 7, 1972