

719. *The Kinetics of Catalytic Polymerisations. Part X.* The Mechanism of the Polymerisation of Styrene catalysed by Chloroacetic Acids.*

By C. P. BROWN and A. R. MATHIESON.

A mechanism is suggested for the polymerisation of styrene catalysed by di- and tri-chloroacetic acid which is in agreement with the dependence of reaction rate and polymer molecular weight and constitution on reactant concentrations, dielectric constant, and temperature. Initiation involves the endothermic formation of a monomer-catalyst polarisation complex which is slowly and spontaneously converted into an ion-pair. The propagation step involves the catalyst, either as solvating the growing polymeric cation, or as addition of the monomer-catalyst complex to the growing cation. The necessity for this is diminished by increasing polarity of the medium. Termination involves spontaneous recombination of ions, and transfer to monomer also takes place. The formation of the monomer-catalyst complex explains the very rapid initial consumption of catalyst and the increase of activation energy with dielectric constant. The function of water as a cocatalyst for the polymerisation in absence of solvent is due to its dissociating effect on the dimeric forms of the acids, leading to more active monomeric forms. In media of higher dielectric constant this is unnecessary.

THE polymerisation of styrene catalysed by di- and tri-chloroacetic acid without solvent and in ethylene dichloride and nitromethane has been described in the preceding papers. Originally studied because it was felt that a hydrogen acid might prove to be a catalyst which functioned by a simpler mechanism, these reactions possess many complicated features which are not exhibited by the metal halide-catalysed polymerisations. Consequently the problem of devising a polymerisation mechanism is considerable.

The principal features requiring explanation are as follows :

The Rate of Monomer Consumption.—From kinetics determined from the initial rates of polymerisation,

$$-d[M]/dt = k [M]^2[C]^{3.5}[W] \text{ without solvent} \quad . \quad . \quad . \quad (1)$$

$$-d[M]/dt = k'[M]^2[C]^2 \text{ in ethylene dichloride} \quad . \quad . \quad . \quad (2)$$

$$-d[M]/dt = k''[M]^2[C] \text{ in nitromethane} \quad . \quad . \quad . \quad (3)$$

where $[M]$ = monomer concentration, $[C]$ = acid concentration, and $[W]$ = water concentration. The rate is always proportional to the square of the monomer concentration but the kinetic order with respect to the acid increases from unity to 3.5 as the dielectric constant of the medium is reduced from 31 to 2. Also, in the absence of solvent, water is an essential cocatalyst. The kinetics are the same for both acids but the overall rate constants are always much larger for trichloroacetic acid.

The Rate of Acid Consumption.—The initial rate of acid consumption is far too great to be accounted for by the acid incorporated in the polymer, and it is likely that some kind of complex is formed initially between the acid and the monomer. The Figure shows a plot of the mole ratio $y = (\text{monomer consumed})/(\text{acid consumed})$ against the extent of reaction (p) = (moles of monomer polymerised)/(moles of monomer originally present). A linear relation exists between these quantities which obeys the equations

$$y = 0.5 + 15.6p \text{ (dichloroacetic acid catalysis without solvent)} \quad . \quad . \quad (4)$$

$$y = 1.7 + 15.6p \text{ (dichloroacetic acid catalysis in ethylene dichloride)} \quad . \quad (5)$$

$$y = 0.5 + 1.6p \text{ (trichloroacetic acid catalysis without solvent)} \quad . \quad (6)$$

$$y = 2.3 + 0.9p \text{ (trichloroacetic acid catalysis in ethylene dichloride)} \quad . \quad (7)$$

* Parts VI—IX, preceding papers.

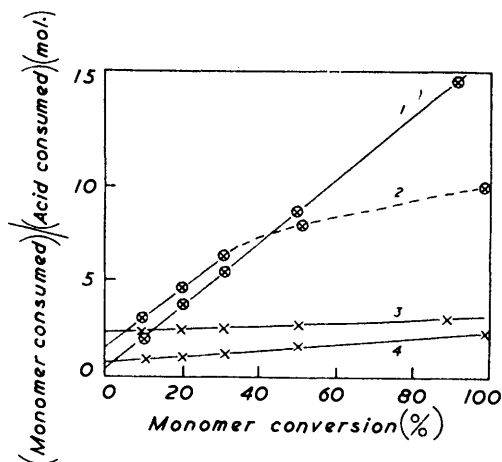
The values of y when $p = 0$ suggest the existence of a complex MC_2 in the absence of solvent and a complex M_2C in ethylene dichloride solution, or perhaps a series of complexes M_nC_y with MC_2 and M_2C as their stoichiometrical equivalents. The formation of polarisation complexes between these substances would not be surprising on chemical grounds.

Influence of Monomer and Catalyst Concentrations on the Molecular Weight (M) of the Polymer.—The two catalysts produce polymers of almost the same molecular weight under the same conditions, and the following relations are obeyed:

$$M = 1100 + 200[M] = 1100 + 120[C] \text{ (ethylene dichloride solution)} \quad (8)$$

$$M = 975 + 70[M] = 1000 + 190[C] \text{ (nitromethane solution)} \quad (9)$$

The form of these expressions suggests that a chain-transfer mechanism is operating.



Ratios of monomer and acid consumed: 1, dichloroacetic acid without solvent; 2, dichloroacetic acid in ethylene dichloride; 3, trichloroacetic acid in ethylene dichloride; 4, trichloroacetic acid without solvent.

Effect of Dielectric Constant.—This is described by

$$-d[M]/dt = Ke^{aD} \quad (10)$$

$$\log M = B + C(D - 1)/(2D + 1) \quad (11)$$

The molecular weight increases only slightly with increased dielectric constant, but the reaction rate is greatly increased, which is a recognised feature of cationic polymerisations.

The Constitution of the Polymer.—The polymer incorporates one catalyst fragment per polymer molecule under all conditions. The very small amount of residual unsaturation indicated by infrared analysis is unlikely to be kinetically significant. No solvent fragments are incorporated, and neither is the water cocatalyst.

The Overall Energies of Activation (E_0).—These increase with the dielectric constant and hence with the rate of polymerisation. This feature has been observed before in cationic polymerisations.

Conductance.—An increase of conductance is associated with a decrease in reaction rate.

Dimerisation and Hydration.—The acid catalysts are dimersed and hydrated.

Retardation.—The polymerisation is retarded and the molecular weight reduced by quinones. A complete explanation for this has already been given (Part VII).

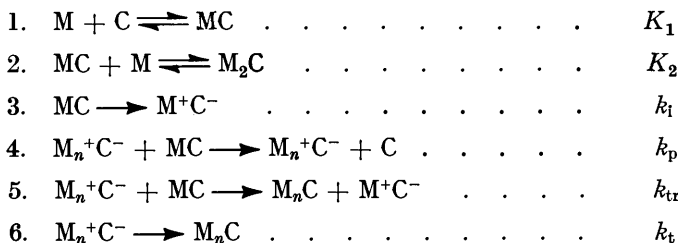
Any explanation of these phenomena must be based on the known chemical species present. It has been shown (Part IX) that the acid exists in four forms, *i.e.*, monomer and dimer and their hydrates, which can be represented as C, C_2 , CW, and C_2W_2 . The last three can be considered to be hydrogen-bonded complexes, or alternatively ion-pairs.

Complex-formation occurs between styrene and the acids, and complexes MC_2 (without solvent) and M_2C (in ethylene dichloride) have been postulated. An intermediate complex MC seems likely to occur in each case also and is required to explain the kinetics.

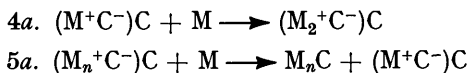
The Polymerisation Mechanism

It is proposed to interpret the kinetics in terms of a stationary-chain mechanism, since this type of mechanism has proved very successful in explaining cationic polymerisation. The reactions showed no sign of non-stationary conditions and the chain lengths were sufficiently great to make the stationary-chain mechanism feasible. Nevertheless the possibility must be borne in mind that the reactions proceed by a stepwise addition process.

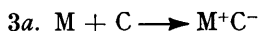
The Polymerisation in Ethylene Dichloride Solution.—The sequence of reactions which represents the results for this system can be written as follows :



The first two equilibria lead to the formation of monomer-catalyst complexes and are responsible for the initial rapid consumption of catalyst. Step 2 plays no part in the polymerisation. Initiation (step 3) is envisaged as a conversion of the complex MC into an ionised complex M^+C^- , and propagation (step 4) results in the growth of the M^+ ion with the C^- ion in attendance to form an ion-pair. This growth suffers spontaneous termination (step 6) with recombination of the ions. An alternative to propagation is monomer transfer (step 5). Propagation and transfer are written as requiring reaction with the monomer-catalyst complex MC rather than with free monomer. An alternative formulation could be made in terms of solvation by the catalyst of the polymerising ion, and reaction with pure monomer, *i.e.*,



Initiation is given as the rearrangement of the complex MC to give an ion-pair, but the ion-pair could arise directly from a monomer-catalyst collision :



Reactions 3a, 4a, and 5a are kinetically indistinguishable from reactions 3, 4, and 5 and probably represent merely alternative ways of writing essentially the same processes. The monomeric form of the catalyst is shown as the active catalytic species; this is likely on chemical grounds since the dimeric form is more stable, and is further suggested by a comparison of the kinetics in the absence of solvent and in ethylene dichloride and nitromethane solution and the interpretation of the function of water in the reaction without solvent. The true catalytic species may actually be the hydrate CW but there is no direct evidence for this as in the polymerisation without solvent.

Application of the stationary-state hypothesis leads kinetically to

$$V_i = V_t \text{ and so } [M_n^+C^-] = k_i K_1 [M][C] / k_t$$

The rate of polymerisation is then

$$V_p = -d[M]/dt = k_p [M_n^+C^-][MC] = k_p k_i K_1 [M]^2 [C]^2 / k_t \quad \dots \quad (12)$$

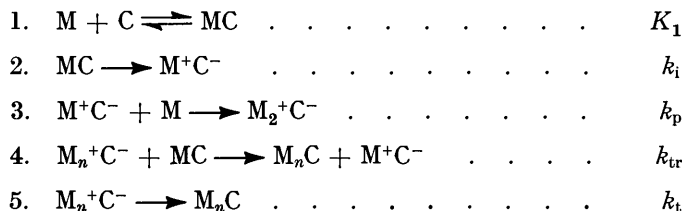
in agreement with observation. The chain length of the polymer (n) is $V_p/(V_t + V_{tr})$ and hence

$$1/n = k_{tr}/k_p + k_t/k_p K_1[M][C] \quad . \quad . \quad . \quad . \quad . \quad (13)$$

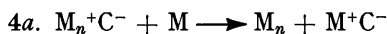
Thus $1/n \propto 1/[M]$ and $1/n \propto 1/[C]$. These relations are obeyed and a value of $k_p/k_{tr} = 21$ is obtained. Incorporation of one catalyst fragment in each polymer molecule is demanded by steps 5 and 6.

The detailed molecular and electronic processes involved in the various steps of the polymerisation will be considered later.

The Polymerisation in Nitromethane Solution.—No evidence was obtained for monomer-catalyst complex formation in this system because the consumption of the acid catalyst could not be studied, but by analogy with the other systems, and by the interpretation given to the energies of activation it may be assumed to occur. The best reaction scheme is

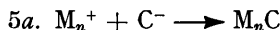


Propagation (step 3) involves the free monomer; alternatively, catalyst solvation of the polymerising ion may be unnecessary, the dielectric constant of the medium being so much higher. The transfer process (step 4), however, needs the participation of catalyst either as the complex MC or as a solvate if all the polymer molecules are to contain one catalyst fragment. It may be, however, that only a relatively small number of growing polymer chains are terminated by monomer transfer in which case this could occur as

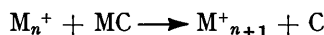


and the small number of polymer molecules free from catalyst fragments might be overlooked.

There is some doubt in this system whether the polymerising ion-pair $M_n^+C^-$ should be looked upon as a single kinetic unit or whether the ions become independent. An alternative formulation for the step 5 is therefore



This requires that propagation should involve direct catalyst participation as in ethylene dichloride (cf. 3a):



in order to preserve agreement with the observed kinetics.

The stationary-state hypothesis leads to

$$[M_n^+C^-] = k_i K_1 [M][C] / k_t$$

and

$$V_p = -d[M]/dt = k_p k_i K_1 [M]^2 [C] / k_t \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in agreement with experiment.

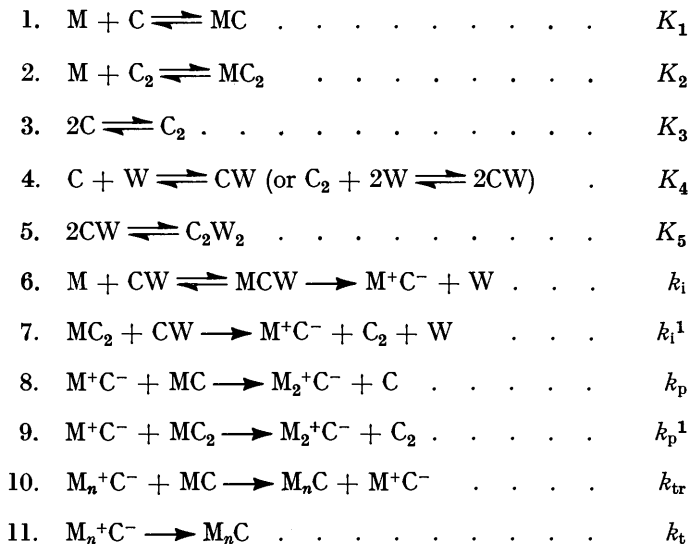
The chain length of the polymer (n) is given by

$$1/n = k_t / (k_p [M]) + k_{tr} K_1 [C] / k_p \quad . \quad . \quad . \quad . \quad . \quad (15)$$

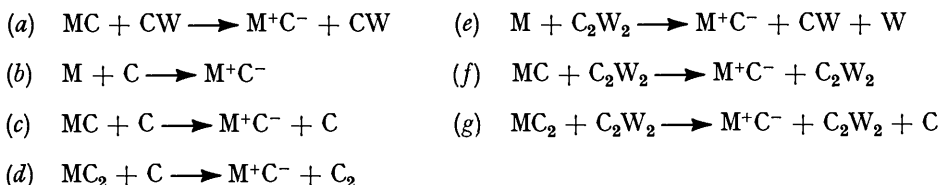
which gives the correct dependence on monomer concentration but not for the catalyst concentration. No explanation has been found for this discrepancy, and no reaction

scheme has been discovered which will explain the increase of n with $[C]$. Again the true catalytic species may be CW.

The Polymerisation in Absence of Solvent.—The polymerisations are more complex under these conditions, additional features being the extraordinarily high dependence of the rate of polymerisation upon catalyst concentration, and the proved necessity for water. The function of the water seems most likely to be to cause dissociation of the dimeric acid C_2 and formation of the monomeric hydrate CW which is the active catalytic species. This agrees with the observed effect of water on the degree of dimerisation of the acids. The rate of consumption of acid suggests the formation of a complex MC_2 , and if this participates in the polymerisation as well as MC, the observed kinetic order can be derived. The reaction scheme is

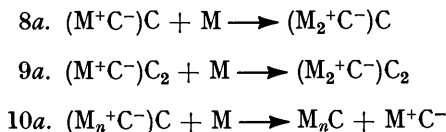


Possible steps which have been omitted are



(a) and (f) are omitted because the function of the catalyst is not clear; (b), (c), and (d) because water is a necessary cocatalyst; (e), (f), and (g) because they lead to a dependence of the rate on $[W]^2$ which is not observed.

Steps 1 and 2 represent monomer-catalyst complex formation, and steps 3, 4, and 5 the dimerisation and hydration of the acids already established. Steps 6 and 7 are both initiation reactions and steps 8 and 9 are alternative propagations. Steps 10 and 11 are transfer and termination as already given for the solution reactions. Steps 8, 9, and 10 can be given the alternative formulation in terms of catalyst solvation of the polymerising ion, and so become



Application of the stationary-state hypothesis leads to

$$\begin{aligned} k_t(M_n^+C^-) &= k_i[M][CW] + k_i^{-1}[MC_2][CW] \\ &= K_4[M][C][W] \{k_i + k_i^{-1}K_2K_3[C]^2\} \end{aligned}$$

$$\begin{aligned} \text{Hence } -d[M]/dt &= k_p[M_n^+C^-][MC] + k_p^{-1}[M_n^+C^-][MC_2] \\ &= (K_4/k_t)[M]^2[C]^2[W] \{k_i + k_i^{-1}K_2K_3[C]^2\} \{k_pK_1 + k_p^{-1}K_2K_3[C]\} . \quad (16) \end{aligned}$$

which, depending on the relative values of the constants, gives a dependence of rate on catalyst concentration between $[C]^2$ and $[C]^5$. Examination of this equation shows that if K_2 or $K_3 \rightarrow 0$, $k_i^{-1} \rightarrow 0$ and $k_p^{-1} \rightarrow 0$ and $-d[M]/dt \propto [C]^2$. Also if $k_i \rightarrow 0$, $-d[M]/dt \propto [C]^{4-5}$; if $k_i^{-1} \rightarrow 0$, $-d[M]/dt \propto [C]^{2-3}$. Since experimentally $-d[M]/dt \propto [C]^{3-5}$, none of these conditions is allowable. However, if $K_1 \rightarrow 0$, $-d[M]/dt \propto [C]^{2-5}$; if $k_p \rightarrow 0$, $-d[M]/dt \propto [C]^{3-5}$; if $k_p^{-1} \rightarrow 0$, $-d[M]/dt \propto [C]^{2-4}$. Consequently it is possible that steps 1 and 8, or alternatively step 9, may not in fact occur.

The chain length of the polymer (n) is given by

$$\frac{1}{n} = \frac{k_t + k_{tr}[MC]}{k_p[MC] + k_p^{-1}[MC_2]}$$

If $k_p^{-1} \rightarrow 0$ this becomes

$$\frac{1}{n} = \frac{k_{tr}}{k_p} + \frac{k_t}{k_pK_1[M][C]} \quad \dots \quad (a)$$

or if $K_1 \rightarrow 0$ and $k_p \rightarrow 0$

$$\frac{1}{n} = \frac{k_t}{k_p^{-1}K_2K_3[M][C]^2} + \frac{k_{tr}K_1}{k_p^{-1}K_2K_3[C]} \quad \dots \quad (b)$$

Results given in Part VII on the variation of molecular weight (M) during polymerisation without solvent show that

$$M = 680 + 6.80p \quad \dots \quad (17)$$

Since p is a function of both $[M]$ and $[C]$, this equation is of the form of equation (a) rather than of (b). This suggests that in fact $k_p^{-1} \rightarrow 0$ and that the step 9 originally postulated does not occur. Final kinetic expressions therefore are

$$\frac{-d[M]}{dt} = \frac{k_pK_1K_4}{k_t} [M]^2[C]^2[W] (k_i + k_i^{-1}K_2K_3[C]^2) \quad \dots \quad (18)$$

and

$$\frac{1}{n} = \frac{k_{tr}}{k_p} + \frac{k_t}{k_pK_1[M][C]} \quad \dots \quad (19)$$

Detailed Mechanism of Initiation and Propagation.—The interpretation already given of the variation of the dependence of the rate of polymerisation on acid concentration in different media and of the initial rapid consumption of acid, in terms of monomer-catalyst complex formation, receives support and clarification when other reactions of the chloroacetic acids are considered.

Bell *et al.*¹ studied the acid-catalysed rearrangement of *N*-bromoacetanilide in chlorobenzene solution and found that the Brønsted relation is obeyed

$$\log k_c = a \log K_a + \log G \quad \dots \quad (20)$$

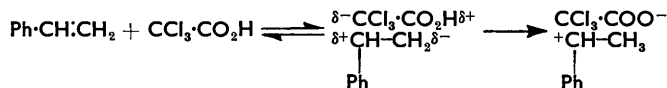
where k_c is the catalytic coefficient, K_a the acid dissociation constant, and a and G are constants. This was taken as indicating that proton transfer occurs, in this particular

¹ Bell and Brown, *J.*, 1936, 1520; Bell, *Trans. Faraday Soc.*, 1938, **34**, 229.

case at least, following the "acidity" of the catalysts as measured in aqueous solution, for acetic and the three chloroacetic acids. For the styrene polymerisation k_o (overall rate constant) increased in approximately the same proportion as K_a for di- and tri-chloroacetic acid (Part VII) which show the same trend. Whether such a relation is obeyed is however dependent on the nature of the solvent. Thus, for the depolymerisation of paraldehyde catalysed by trichloroacetic acid, Bell² gives the relative rates of the reaction in nitrobenzene, benzene, anisole, and ethyl acetate as 1000 : 30 : 1 : 0.01. The low value of the last two relative rates is interpreted in terms of complex formation between the catalyst and the basic oxygen of the solvent. The "apparent" order with respect to the acid concentration varied from 1.6 to 2.5 in different solvents. Caldin and Lidwell³ observed a similar deviation from simple kinetic behaviour in the acid-catalysed racemisation of optically active ketones in chlorobenzene. In this case extensive complex formation has been confirmed by cryoscopic and polarimetric methods.

The dimerisation of the carboxylic acid catalysts also in many cases appears to play a fundamental rôle in determining the kinetic order of acid-catalysed reactions. In the acid-catalysed rearrangement of *N*-bromoacetanilide⁴ the dependence of the rate on catalyst concentration varied with catalyst concentration but was eliminated at low concentrations of catalysts. Even in the absence of demonstrable complex formation considerable effects of the medium are to be expected in solvents of low dielectric constant when carboxylic acids are employed.⁵ In aprotic solvents unable to solvate the hydrogen ion the acids will not ionise and acid catalysis must be related to the un-ionised acid molecules. The reaction between ethyl diazoacetate and carboxylic acids, which liberates nitrogen, was studied by Briegleb⁶ who concluded that the reaction is kinetically of the second order with respect to the dimeric acid molecules which are supposed to be autocatalytic. Briegleb⁶ has also shown that both the monomeric and the dimeric form of the acids possess appreciable moments and can exert a polarising influence. Nernst and Hohmann⁷ found the rate of the reaction of 3-methylbut-2-ene with various carboxylic acids, including the chloroacetic acids, to be proportional to the square of the acid concentration both in 3-methylbut-2-ene itself and in benzene solution. They assume the rate to be proportional to $[C_2]$, but an equally good interpretation is that the rate is proportional to $[C_2]^2$. Goldschmidt³ found the self-esterification of di- and tri-chloroacetic acid in alcohol solution to be of the second order with respect to the acid.

The phenomena of autocatalysis and complex formation are clearly well established in simple reactions of the chloroacetic acids and it is not surprising that they appear in the polymerisations which these acids catalyse. The initiation mechanism suggested for the polymerisations $M + C \rightleftharpoons MC \longrightarrow M^+C^-$ could perhaps be applied equally to the simple reactions. The influence of the medium in promoting the rate would be to facilitate the formation of the active species M^+C^- in media of higher dielectric constant. The variations in kinetic order with different reaction media are to be ascribed to the different degrees of autocatalysis required in media of different dielectric constant. The monomer-catalyst complex could perhaps be represented as a polarisation complex with a finite probability of transition to an ion-pair



The autocatalysis then appears in the propagation step as the reaction of the carbonium

² Bell, *J.*, 1936, 1792.

³ Caldin and Lidwell, *Trans. Faraday Soc.*, 1938, **34**, 236.

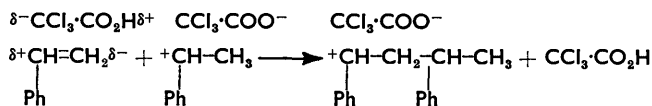
⁴ Bell and Levinge, *Proc. Roy. Soc.*, 1935, *A*, **151**, 211.

⁵ Brønsted and Bell, *J. Amer. Chem. Soc.*, 1931, **53**, 2478.

⁶ Briegleb, *Z. phys. Chem.*, 1930, *B*, **10**, 205.

⁷ Nernst and Hohmann, *Z. phys. Chem.*, 1893, **11**, 361.

ion with the polarised monomer of a monomer-catalyst complex, the catalyst facilitating this process by its polarising influence on the second monomer :



It seems probable that the dielectric constant of nitromethane is high enough to allow reaction of the carbonium ion with unpolarised monomer molecules and the autocatalytic effect is consequently not observed.

The Increase of Activation Energy with Reaction Rate.—It was observed (Part VII) that, except for the polymerisations in absence of solvent, increased dielectric constant of the medium results in increased overall energy of activation (E_0) as well as increased reaction rate. Solvation of the reactants by catalyst molecules as already envisaged could only lead to a decrease of E_0 with increased reaction rate, and so some other effect is masking the normal expected result. The increase in E_0 with dielectric constant is associated with an increase in the frequency factor A , which approaches the value predicted by simple collision theory ($\sim 2 \times 10^{11}$) as the dielectric constant is increased. The overall energies of activation can be written as $E_0 = E_i + E_p - E_t$ where E_i , E_p , and E_t are the energies of activation of initiation, propagation, and termination respectively. For ethyl bromide solutions, $E_p - E_t = -850$ cal. from the dependence of molecular weight upon temperature. Since molecular weight is little influenced by the dielectric constant of the medium, the value of $E_p - E_t$ is not likely to vary much from one solvent to another. If the approximate value -1 kcal. is assigned to it approximate values of E_i may be obtained. Values of E_0 , E_i , and A_i are shown in the Table.

TABLE I. *Activation Energies and frequency factors.*

Solvent	D	Catalyst	E_0 (kcal.)	E_i (kcal.)	A_i
Styrene	2.0	Trichloroacetic acid	9.0	10.0	0.153
Ethyl bromide	4.87	"	3.0	4.0	—
Ethylene dichloride	10.5	"	8.0	9.0	1.50
Nitroethane	19.7	"	10.0	11.0	—
Nitromethane	39	"	14.0	15.0	1.9×10^5
Styrene	2.0	Dichloroacetic acid	5.5	6.5	5.61×10^{-6}
Ethyl bromide	4.87	"	3.0	4.0	—
Ethylene dichloride	10.5	"	6.0	7.0	8.09×10^{-5}
Nitromethane	39	"	8.0	9.0	1.75

Increase in energy of activation and frequency factor with the dielectric constant of the medium has also been observed in simple reactions. The reactions first kinetically investigated by Menshutkin⁹ between amines and halides have been further investigated by Cox and Hawkins¹⁰ and their results show that the value of the frequency factor approaches the collision number in solvents of high polarity, and the activation energy tends towards a maximum value.

One explanation of these phenomena, which evidently occur both in polymer and in "small-molecule" chemistry, is that the activation energies measured are depressed below their "normal" values, the depression being greater in non-polar media. A number of causes may be suggested for this, such as the endothermic formation of a complex before the reaction, the necessity for the ionisation of either of the reactants, or critical orientation conditions for reaction. The influence of the dielectric constant of the medium on

⁸ Goldschmidt, *Ber.*, 1896, **29**, 2212.

⁹ Menshutkin, *Z. phys. Chem.*, 1890, **6**, 41.

¹⁰ Cox and Hawkins, *J.*, 1921, **119**, 142; 1922, **121**, 1170.

the rates of reaction between polar molecules has been given by Laidler and Eyring¹¹ as

$$\ln k = \ln k_0 - \frac{1}{kT} \cdot \frac{D-1}{2D+1} \cdot \frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{*}^2}{r_{*}^3} + \sum_i \frac{\phi_i}{kT} \quad (21)$$

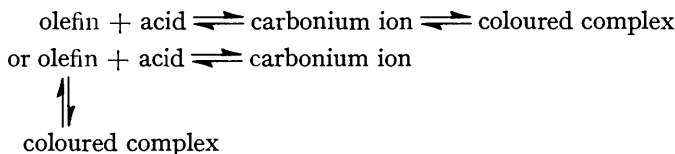
where the μ 's and r 's are respectively the moments and collision radii of the reactants (A and B) and the activated complex (*), and $\sum_i(\phi_i/kT)$ represents the non-electrostatic contribution. Where a plot of $\ln k$ against $(D-1)/(2D+1)$ is non-linear it may be inferred that the non-electrostatic term is important. This is the case for the overall rate of polymerisation (eqn. 10) but is not so for the influence of dielectric constant on molecular weight which gives a linear dependence on $(D-1)/(2D+1)$ (eqn. 11). The latter result is in agreement with a termination mechanism involving recombination of the growing polymeric cation and the catalytic anion such as has been postulated.

The suggestion that the variation of the activation energy with dielectric constant might be explained by the formation of a complex before polymerisation is worth further examination since monomer-catalyst complexes have already been postulated to explain other features of the reactions. Considering the initiation mechanism already postulated



let the energies of activation associated with the velocity constants k_1 , k_2 , and k_3 be E_1 , E_2 , and E_3 . For the overall initiation, $k_i = k_3k_2/k_1$ and $E_1 = E_2 + E_3 - E_1$. Increase in the dielectric constant of the medium appears to lead to a reduction in the extent of monomer-catalyst complex formation, perhaps through a decrease in the polarising power of the catalyst. This implies that E_2 will be increased, and E_1 decreased, by increase of D , resulting in an overall increase in the activation energy. This gives a reasonable explanation of the results in the Table. There is evidence that the energies of activation of other cationic polymerisations increase with increased dielectric constant of the media (Part VII) and so it may be that some form of endothermic monomer-complex formation occurs in these reactions also. It might be instructive to re-examine the mechanism of other cationic polymerisations in the light of these suggestions.

The initiation mechanism suggested here is essentially that of Taft, Purlee, Ritz, and Defazio,¹² Evans, Jones, Jones, and Thomas,¹³ in a study of the trichloroacetic acid-catalysed dimerisation of 1 : 1-di-*p*-tolylethylene, prefer the formulations



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¹¹ Laidler and Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303.

¹² Taft, Purlee, Ritz, and Defazio, *J. Amer. Chem. Soc.*, 1955, **77**, 1587.

¹³ Evans, Jones, Jones, and Thomas, *J.*, 1956, 2757.