312. *The Kinetics of Acid-catalysed Cyclisation of Distyrene and Di-(α-methylstyrene).*

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The conversion of the unsaturated dimers of styrene and α-methylstyrene into the cyclic isomers has been studied, using the catalysts perchloric, sulphuric, and chlorosulphonic acids in solution in ethylene dichloride between 25 and 84°. Di-(α-methylstyrene) with perchloric acid is quantitatively converted into the cyclic form at rates which are second-order in both catalyst and dimer. Distyrene with this acid gives the same kinetics but some polymer is also formed. Distyrene with sulphuric and chlorosulphonic acids requires high temperatures (>60°) and gives complex kinetics resulting from irreversible consumption of the catalysts.

STYRENE and α-methylstyrene are well known to form dimers which exist in isomeric forms, one unsaturated (I) and one having an indane structure (II). This Paper describes a kinetic study of the acid-catalysed conversion of form (I) into form (II) in solution in ethylene dichloride and other solvents. The reactions are believed to go through the intermediate carbonium ion (III) and to be relevant therefore to the cationic polymerisation of styrene and α-methylstyrene, which produces both saturated and unsaturated chains believed to have the terminal structures analogous to (II) and (I), respectively.
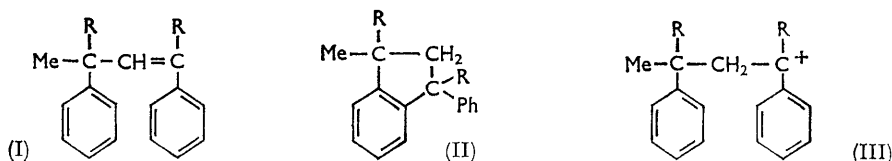
The related cyclisation of the linear dimer of 1,1-diphenylethylene (I; R = Ph) was studied by Evans and his colleagues,[1-3] using Friedel–Crafts catalysts (and co-catalysts). With antimonic chloride and with stannic chloride (and water or hydrochloric acid as co-catalyst) the cyclisation is very slow at room temperature (weeks); with titanium tetrachloride (and hydrochloric acid) it is much faster (hours).

EXPERIMENTAL

Fig. 1 shows the apparatus used. The Pyrex reaction vessel A had a working capacity of 30 ml., and could be mounted as shown in a vapour-bath, an ice-bath, or a conventional thermostat at 25°. Before use the apparatus was cleaned and dried, evacuated to 0·1 mm., and purged for 1 hr. by a slow stream of dried (H_2SO_4 and P_2O_5) nitrogen. Solvents and catalyst solution were introduced from a pipette through the ground-glass joint. A countercurrent of dry nitrogen was maintained to prevent ingress of moist air, and to mix the reagents. The unsaturated dimer (~0·5 ml.) was then injected, through the bore of tap B, from a small syringe which served also as a weight-pipette. Samples for analysis were forced up into the microburette C by nitrogen pressure. The samples were quenched by glacial acetic acid or methanol, and analysed for unsaturation by bromination in glacial acetic acid, or by Byrne and Johnson's method [4] using bromine–sodium bromide in aqueous methanol. Both methods were satisfactory for the analysis of distyrene, but with di-(α-methylstyrene) only the second proved adequately rapid.

Materials.—The two distyrenes were prepared from freshly distilled styrene by Rosen's methods.[5]

[1] Evans and Price, *J.*, 1959, 2982.
[2] Evans and Owen, *J.*, 1959, 4123.
[3] Evans, James, and Owen, *J.*, 1961, 3532.
[4] Byrne and Johnson, *Analyt. Chem.*, 1956, **28**, 126.
[5] Rosen, *J. Org. Chem.*, 1953, **18**, 1701.

Unsaturated distyrene (1,3-*diphenylbut*-1-*ene*). This could not be isolated absolutely pure, but a fraction (b. p. 144—146°/1 mm.) was obtained which was 94·2% unsaturated, the remainder being the saturated dimer, as demonstrated by gas–liquid chromatography. This fraction was a colourless viscous liquid with strong ultraviolet absorption at 253 mμ (ε 2·35 × 10^5).

Saturated distyrene (3-*methyl*-1-*phenylindane*). A pure product (b. p. 162—165°/15 mm.) was isolated (<0·5% unsaturation); it was a viscous liquid, homogeneous in gas–liquid chromatography, and with peaks in the ultraviolet at 266 mμ (ε 1·36 × 10^5) and 273 mμ (ε 1·1 × 10^5).

The dimers of α-methylstyrene were prepared by Hersberger's methods.[6]

Unsaturated di-(α-methylstyrene) (4-*methyl*-2,4-*diphenylpent*-2-*ene*). This was a colourless liquid (b. p. 136°/1 mm.) containing 5% of the saturated isomer.

Saturated di-(α-methyl styrene) (1,3,3-*trimethyl*-1-*phenylindane*). The first product was a colourless liquid (b. p. 170°/17 mm.), 97% saturated. On prolonged standing at 0° it gave waxy crystals, m. p. 52° [from light petroleum (b. p. 60—80°)], with ultraviolet absorption at 265 mμ (ε 1·21 × 10^3) and 272 mμ (ε 1·0 × 10^3).
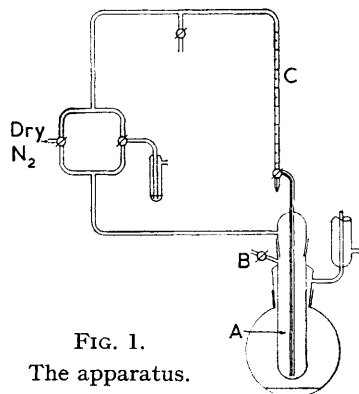
Ethylene dichloride (1,2-*dichloroethane*). The commercial solvent was shaken with successive quantities of sulphuric acid until the acid no longer became coloured, and then washed free from acid with dilute sodium hydroxide. After drying successively over calcium chloride and calcium hydride it was distilled through a column of *ca.* 20 theoretical plates (b. p. 83·2—83·3°/758 mm.) and stored over calcium hydride in a vessel fitted with an automatic burette protected from moisture by guard tubes containing phosphorus pentoxide.

Anhydrous perchloric acid. In an adaptation of the method of Redlich *et al.*,[7] 72% aqueous perchloric acid (AnalaR) was mixed with a four-fold excess of concentrated sulphuric acid, and distilled at 55—60°/<1 mm. into a receiver tube containing ethylene dichloride cooled to −183°. After the distillation the apparatus was allowed to warm to room temperature so that the anhydrous acid was diluted by the solvent before the receiver was detached. (On a few occasions localised explosions occurred, destroying the ground-glass joint to the receiver but without detonating the perchloric acid solution. The explosions appeared to be associated with condensation of the anhydrous acid on the surfaces of the joint; they did not occur when this joint was kept warm.) The solution of perchloric acid was quickly transferred to a dry-box, its concentration determined by titration with barium hydroxide, and diluted with dry ethylene dichloride to a convenient stock concentration (20—100mM). Such solutions remained colourless for about one week at room temperature, and apparently indefinitely at 0°. The acidity remained constant during these periods unless atmospheric moisture was admitted. If this happens the acidity falls, being collected into an aqueous phase which eventually becomes visible as droplets on the vessel walls.

Sulphuric acid solutions. Freshly distilled AnalaR concentrated sulphuric acid was equilibrated with ethylene dichloride at the required temperature, using the methods of Hayes and Pepper.[8]

Chlorosulphonic acid solutions. Redistilled acid (b. p. 158°) was stored in a dry-box and made up in dry ethylene dichloride as required (readily soluble).

FIG. 1.
The apparatus.

RESULTS

The systems studied were: perchloric acid–di-(α-methylstyrene) (0—61°); perchloric acid–distyrene (0—61°); sulphuric acid–distyrene (61—84°); chlorosulphonic acid–distyrene (77°). With di-(α-methylstyrene), the only product was the cyclic dimer. With

[6] Hersberger, *et al.*, U.S.P. 2,429,719/1947.
[7] Redlich, *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 13.
[8] Hayes and Pepper, *Trans. Faraday Soc.*, 1961, **57**, 432.

distyrene, appreciable proportions of low molecular weight polymer were also formed (30—50% of product insoluble in methanol).

Cyclisations Catalysed by Perchloric Acid.—The initial concentration of unsaturated dimer was usually taken as *ca.* 0·1M, and that of catalyst 1—9mM (according to tem-
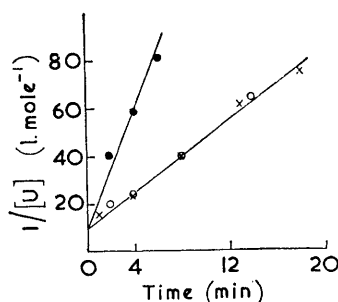

FIG. 2.   Typical second-order plots for di-(α-methylstyrene)–HClO₄–(CH₂Cl)₂.

$[HClO_4]_0$:   × $7·5 \times 10^{-5}$M (61°);   ○ $3·2 \times 10^{-4}$M (25°);   ● $1·3 \times 10^{-3}$M (0°).
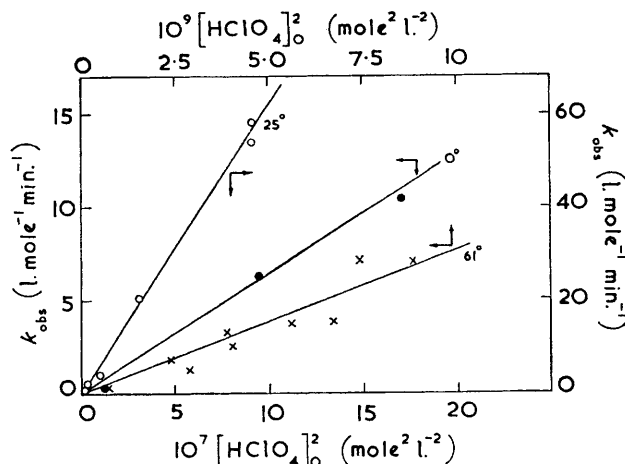

FIG. 3.   Dependence of rate on $[HClO_4]_0{}^2$ for di-(α-methylstyrene) in ethylene dichloride.
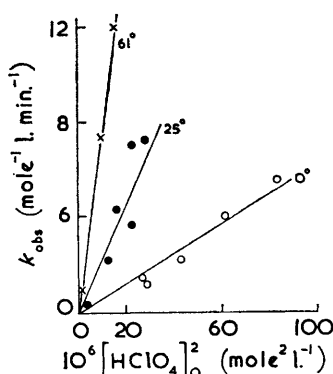

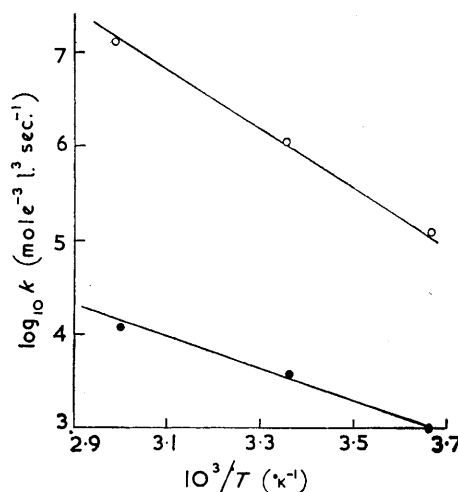FIG. 4.   Dependence of rate on $[HClO_4]_0{}^2$ for distyrene in ethylene dichloride.

FIG. 5.   Arrhenius plots for reactions initiated by perchloric acid: ○ di-(α-methylstyrene); ● distyrene.

perature) for distyrene and 0·03—0·3mM for di-(α-methylstyrene).   The disappearance of unsaturation was followed to 80—90% conversion and occasionally to >95%.   Under these conditions the reactions were quite fast (half-lives 2—10 min.) and in nearly all cases followed a second-order dependence on concentration of the unsaturated dimer over virtually the whole conversion.   [With di-(α-methylstyrene) at the lowest catalyst concentrations ($<7 \times 10^{-5}$M), deviations attributable to loss of catalyst occurred at conversions >60%.]   Typical second-order plots are shown in Fig. 2 for di-(α-methylstyrene).   The results for distyrene show a similar degree of scatter but no trend from second-order plots.

In Figs. 3 and 4 the observed second-order constants $[k_{obs} = d(1/[U])/dt]$ are plotted against the square of the initial concentration of perchloric acid. Despite some scatter, these plots seem essentially linear and indicate the overall kinetic equation:

$$-d[U]/dt = k_{exp}[HClO_4]_0^2[U]^2 \quad (U = \text{unsaturated dimer}),$$

and the following values for the overall rate constant (k_{exp}):

Temperature		0°	25°	61°
k_{exp} (mole^{-3} l.^{3} sec.$^{-1}$)	Di-(α-methylstyrene)	1.07×10^5	1.03×10^6	1.28×10^7
	Distyrene	1.0×10^3	3.7×10^3	12.0×10^3

Fig. 5 shows that the temperature-dependence of k_{exp} follows the Arrhenius relationship, and yields experimental activation energies (E): for di-(α-methylstyrene), $E = 14.0$ kcal. mole^{-1}; for distyrene, $E = 7.3$ kcal. mole^{-1}.

A few experiments on the effect of solvent polarity were made with di-(α-methylstyrene) at 25° in mixtures of ethylene dichloride with carbon tetrachloride, and with

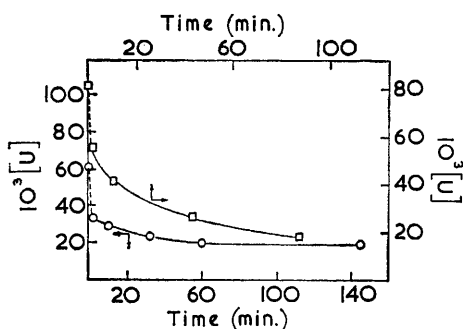Fig. 6.   Reaction curves for distyrene initiated by: □ sulphuric acid, 21mM, 77°; ○ chlorosulphonic acid, 21mM, 77°.

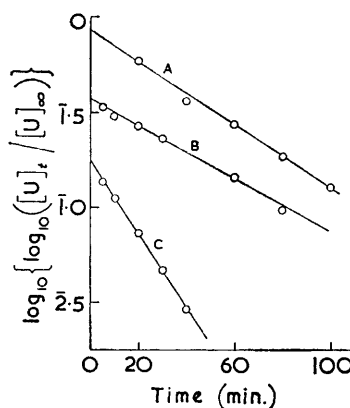Fig. 7.   Log-log plots for distyrene–sulphuric acid.

$[H_2SO_4]_0$: A, 20.7×10^{-3}M (77°); B, 15.8×10^{-3}M (84°); C, 13.4×10^{-3}M (71°).

nitrobenzene. The reactions remained second-order in dimer but were reduced in rate approximately one hundred-fold in a 1 : 1 mixture with carbon tetrachloride, and two-fold in a 3 : 1 mixture of ethylene dichloride and nitrobenzene.

Cyclisation of Distyrene by Sulphuric and Chlorosulphonic Acids.—With these systems the cyclisation was undetectable at room temperature. To obtain measurable rates the reactions were followed between 61 and 84° with sulphuric acid, and at 77° with chlorosulphonic acid. Initial dimer concentration was varied in the range 40—140mM, and acid concentration was 10—25mM in ethylene dichloride.

The general kinetic pattern was much more complex than that in the reactions catalysed by perchloric acid. In all cases there was an extremely rapid initial drop in unsaturation, followed by a period (1—2 hours) of much slower reaction which finally ceased before all unsaturation had disappeared. Typical reaction–time curves are shown in Fig. 6.

With chlorosulphonic acid the initial rapid fall in unsaturation $(\Delta[U]_i)$ was directly proportional to, and very nearly equal to, the initial concentration of chlorosulphonic acid, *i.e.*,

$$\Delta[U]_i = 0.9[ClSO_3H]_0 \quad (\text{up to } [ClSO_3H] \sim 0.08\text{M}).$$

With sulphuric acid $\Delta[U]_i$ was more irreproducible and showed no simple correlation with acid concentration.

The subsequent decrease in rate and premature cessation of reaction was shown to result from consumption of the acid and its conversion into a form where it was still partially titratable but inactive in catalysing the cyclisation, *i.e.*, most probably substituted into the aromatic rings by sulphonation. Thus the titratable acidity was found to fall at the same rate as the unsaturation, but only to 30—70% of its initial value. In a special experiment where the acid concentration was maintained constant, the unsaturation fell continuously to zero.

FIG. 8. Log-log plots for distyrene–chlorosulphonic acid at 77°

$[ClSO_3H]_0$: A, $3 \cdot 75 \times 10^{-3}$M; B, $9 \cdot 2 \times 10^{-3}$M; C, $20 \cdot 5 \times 10^{-3}$M; D, $26 \cdot 0 \times 10^{-3}$M.
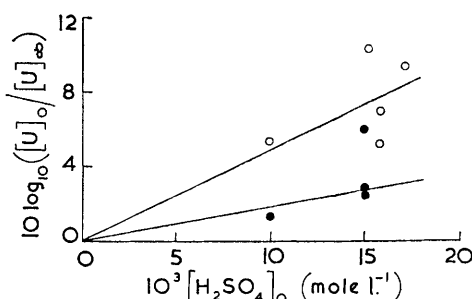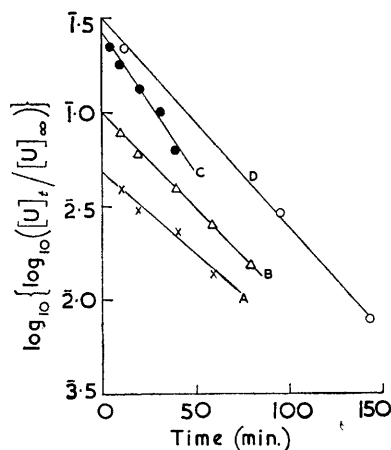

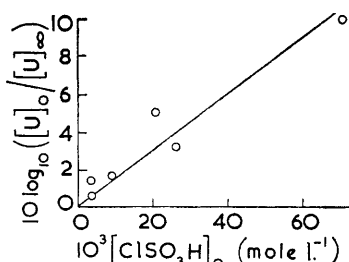FIG. 9. Dependence of final conversion on $[H_2SO_4]_0$ for distyrene at: ● 61°; ○ 84°.

FIG. 10. Dependence of final conversion on $[ClSO_3H]_0$ for distyrene at 77°.

The extent of the final conversion in normal experiments was found to be related to the initial concentration of acid, and when expressed in the form $\log([U]_0/[U]_\infty)$ it was directly proportional to it, as shown in Fig. 9 for sulphuric acid and in Fig. 10 for chlorosulphonic acid.

The rate of fall of unsaturation towards its asymptotic value $[U]_\infty$ can be described by an exponential relationship

$$(1/U)d[U]/dt = A e^{-bt}.$$

Tests of this relationship in its integrated form of plots of $\log\{\log([U]_t/[U]_\infty)\}$ against time are shown in Fig. 7 for sulphuric and in Fig. 8 for chlorosulphonic acid.

DISCUSSION

The kinetic behaviour of the reactions varies so greatly with the different acid catalysts that separate discussion is necessary.

Cyclisations Catalysed by Perchloric Acid.—For both dimers the same simple kinetic

equation is found, with rates second-order in the substrate and in initial catalyst concentration. The overall rate constants shown in the Table are not strictly comparable since the figures for styrene include a contribution, which may be as high as 30—50%, from the concurrent polymerisation reaction. However, the results demonstrate strikingly that di-(α-methylstyrene) is much more reactive than distyrene in the cyclisation reaction.

The overall kinetics differ from those found in the analogous cyclisation of the dimer of diphenylethylene (I; $R = Ph$) with stannic chloride–hydrochloric acid,[1] which gives rates of the first order in dimer, catalyst, and co-catalyst. To explain these kinetics, Evans *et. al.* postulated a relatively rapid equilibrium association to form the dimer carbonium ion (III; $R = Ph$), followed by a slow spontaneous cyclisation step. Our second-order kinetics could be explained with a similar mechanism if the cyclisation step is not spontaneous but needs the interaction of two dimer carbonium ions, *i.e.*,
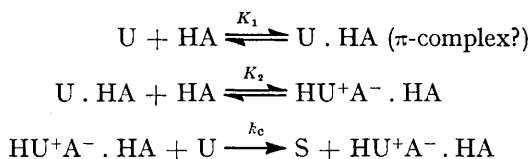
$$U + HA \underset{}{\overset{K_1}{\rightleftharpoons}} HU^+A^-$$

$$2HU^+A^+ \overset{k_c}{\longrightarrow} S + U + 2HA$$
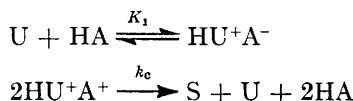
where U = unsaturated dimer, S = saturated (cyclised) dimer, and HA = perchloric acid. Hence,

$$-d[U]/dt = d[S]/dt = k_c[HU^+A^-]^2 = k_cK_1^2[HA]^2[U]^2$$
$$= k_cK_1^2[HA]_0^2[U]^2, \text{ if } K_1 \text{ is small.}$$

However, such a reaction seems rather unlikely, and it is more probable that the two acid molecules are required in the ionisation stage, and that the cyclisation results from an encounter between the dimer carbonium ion and a dimer molecule. Similar " solvation " by a second molecule of catalyst has been postulated in the dimerisation of diphenylethylene by stannic chloride [9] and in the polymerisation of styrene by chloroacetic acids.[10] There is also evidence that the cyclisation reaction is bimolecular in the perchloric acid-initiated polymerisation of styrene, where it is found that saturated (and believed cyclised) end-groups result from the monomer transfer process.[11]

These ideas could be formulated in the following kinetic equations

$$U + HA \underset{}{\overset{K_1}{\rightleftharpoons}} U . HA \text{ (π-complex?)}$$

$$U . HA + HA \underset{}{\overset{K_2}{\rightleftharpoons}} HU^+A^- . HA$$

$$HU^+A^- . HA + U \overset{k_c}{\longrightarrow} S + HU^+A^- . HA$$

If both equilibria are rapidly established, the cyclisation step will be rate-determining and

$$-d[U]/dt = k_c[U][HU^+A^- . HA] = K_1K_2k_c[HA]^2[U]^2.$$

Here again [HA] is strictly the equilibrium concentration of initiator and will not be exactly equal to $[HA]_0$ but to $[HA]_0/(1 + K_1[U])$ (assuming $K_2 \ll K_1$). There is some reason to expect (from the rapid initiation of polymerisation of styrene by perchloric acid) that K_1 may not be very small, but since in these experiments $[U]_0$ is only ~0·1, the product $K_1[U]$ may not be large enough to cause considerable deviations of [HA] from $[HA]_0$.

On this interpretation the observed overall rate constant $k_{exp} = K_1K_2k_c$, and the experimental activation energy is the sum of the enthalpy changes in the two equilibria plus the cyclisation activation energy; $E_{exp} = \Delta H_1 + \Delta H_2 + E_c$.

The observed rate constants are some 10^2—10^3 times greater for di-(α-methylstyrene) than for styrene. This might seem readily explicable in terms of an enhanced value of

[9] Evans and Lewis, *J.*, 1957, 2975.
[10] Brown and Mathieson, *J.*, 1957, 3608; 1958, 228, 3507.
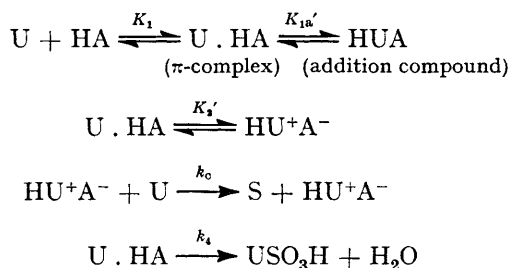[11] Pepper and Reilly, *Proc. Chem. Soc.*, 1961, 460.

K_2, since the inductive effect of the 3-methyl substituent should tend to stabilise the carbonium ion. Yet this substitution should also increase the steric hindrance to orientation into the cyclic transition state and hence increase E_c. The latter (steric) effect would of course tend to diminish the overall rate, and cannot therefore be the predominating factor. This interpretation should, however, be applied with caution, since it is not clear at present how far it can explain the large difference between the overall activation energies.

Cyclisations of Distyrene by Sulphuric and Chlorosulphonic Acids.—These acids are about equally active in catalysing the cyclisation, but much less so than perchloric acid, and give measurable rates only above 60°. At these temperatures two extra kinetic features are shown which require explanation; they are (a) the initial rapid drop in unsaturation, and (b) the consumption of acid, and limited conversion.

Qualitatively, it is probable that these features follow from the ability of these acids, unlike perchloric acid, to form stable addition compounds to the double bond and substitution products with the aromatic rings.

A semiquantitative explanation is possible on the assumption that an early stage in the overall reaction must be the rapid addition to (and saturation of) the double bond; that the covalent compound so formed can ionise to an ion-pair capable of cyclisation, but also capable of deactivation by (internal) sulphonation. Formally these stages can be written in the equations:

$$U + HA \underset{K_1}{\rightleftharpoons} \underset{\text{(π-complex)}}{U \cdot HA} \underset{K_{1a}'}{\rightleftharpoons} \underset{\text{(addition compound)}}{HUA}$$

$$U \cdot HA \underset{K_2'}{\rightleftharpoons} HU^+A^-$$

$$HU^+A^- + U \xrightarrow{k_c} S + HU^+A^-$$

$$U \cdot HA \xrightarrow{k_4} USO_3H + H_2O$$

The observation that with chlorosulphonic acid $\Delta[U]_i \sim [ClSO_3H]_0$ would imply that K_1' and K_{1a}' are large and that $K_2' \ll K_{1a}'$. With sulphuric acid, the smaller values of $\Delta[U]_i$ would then be associated with a higher value of K_2', in keeping with the evidence from the polymerisation of styrene by sulphuric acid [12] that the initiation process (analogous here to the overall effects of K_1' and K_2') is very fast.

On these assumptions, the rate of fall of unsaturation, after the initial equilibria are established, would be determined by the rate of cyclisation of a population of ion-pairs which was continuously decreasing according to the irreversible deactivation reaction (k_4), *i.e.*,

$$[U \cdot HA] = [U \cdot HA]_0 \exp(-k_4 t) = [HA]_0 \exp(-k_4 t)$$

$$[HU^+A^-] = K_2'[U \cdot HA] = K_2'[HA]_0 \exp(-k_4 t)$$

and $\quad -d[U]/dt = d[S]/dt = k_c[HU^+A^-][U] = k_c K_2'[HA]_0 \exp(-k_4 t)[U]$

Integrating: $\quad \ln([U]_0/[U]_t) = (k_c K_2'/k_4)[HA]_0\{1 - \exp(-k_4 t)\}$

and $\quad \ln([U]_0/[U]_\infty) = (k_c K_2'/k_4)[HA]_0$ ⟶ (1)

Alternatively: $\quad \ln([U]_0/[U]_t) = \ln([U]_0/[U]_\infty)\{1 - \exp(-k_4 t)\}$

$$\ln \ln([U]_t/[U]_\infty) - \ln \ln([U]_0/[U]_\infty) = -k_4 t \quad (2)$$

From Figs. 7 and 8 it can be seen that, both for sulphuric and for chlorosulphonic acids, equation (2) describes the time-course of the reactions very well (though some of the

¹² Hayes and Pepper, *Proc. Roy. Soc.*, 1961, *A*, **263**, 63.

apparent precision of fit may come from the insensitivity of the double logarithmic plot). Different experiments with different acid concentrations are, however, very irreproducible, as shown by the scatter of points in Figs. 9 and 10, which are tests of equation (1). This irreproducibility is reflected also in the values of k_4 derived from the slopes of lines in Figs. 9 and 10. For distyrene at 77°, a more than two-fold variation is found in experiments with sulphuric acid ($k_4 = 1.4$—3.5×10^{-2} min.$^{-1}$) and a slightly smaller variation using chlorosulphonic acid ($k_4 = 1.8$—3.0×10^{-2} min.$^{-1}$). The magnitude of uncertainty in k_4 unfortunately exceeds its variation with temperature over the range studied ($10^2 k_4 = 2.5$ at 61° and 1.4—2.5 at 84°). No activation energy can be derived, therefore, though it may be concluded to be small.

If the slopes in Figs. 7 and 8 may be taken to measure $k_c K_2'/k_4$, and a mean value for k_4 taken at 2.5×10^{-2} min.$^{-1}$, the derived values of $k_c K_2'$ for sulphuric acid vary between 1.05 at 61° and 1.9 at 84° (mole^{-1} l. min.), suggesting an overall activation energy of *ca.* 10 ± 2 kcal./mole (to be compared with 7.3 kcal. with perchloric acid at lower temperatures).

Plainly the results are not sufficiently reproducible for firm quantitative conclusions to be drawn, especially as the measured rates include a contribution from the usually unknown rate of polymerisation. This latter effect can be allowed for without changing the form of the kinetic equations, but it has been judged not worthwhile to add this complication in considering these results of low precision. Prospects of improved results using sulphuric acid seem unlikely because of the difficulties of obtaining reproducible solutions of this acid, but the more controllable systems using chlorosulphonic acid should repay further study.

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