146. *The Cationic Polymerization of Styrene. Part I. The 1-Phenylethyl Cation.*

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Styrene and 1-phenylethyl alcohol dissolve in concentrated sulphuric acid–acetic acid mixtures to give yellow solutions. This coloration is attributed to the presence of the ions $PhMeHC^+$ and $Me{\cdot}CHPh{\cdot}OH_2^+$, the latter being the more stable. In solutions of 1-phenylethyl chloride and stannic chloride in 1,2-dichloroethane and of 1-phenylethyl chloride and aluminium chloride in carbon tetrachloride, the 1-phenylethyl ion also exists. This observation confirms the feasibility of many reaction mechanisms derived from kinetic data.

POLYMERIZATION of styrene by acids or Friedel–Crafts halides has been assumed generally to occur by a mechanism involving a carbonium ion as intermediate.[1] The carbonium ion is formed by addition to the olefin of a proton from the hydrogen acid or from a cocatalyst–halide complex. Theoretical calculations by Gold and Tye [2] and by Yonezawa *et al.*[3] suggest that the proton addition should bring about the formation of the 1-phenylethyl cation which would then be the initiating species of the polymerization. Until very recently there has been no direct evidence for the existence of this ion but only circumstantial evidence derived from studies of reaction mechanisms.[4]

Since it has been shown [5] that water is an essential cocatalyst for the polymerization of styrene by aluminium chloride, thus indicating that initiation must occur by proton addition, it became desirable to have more direct evidence for the existence of the 1-phenylethyl ion. We have measured the spectra of solutions of styrene in concentrated sulphuric acid (in which, from the conclusions of Gold and Tye,[6] it was to be expected that the 1-phenylethyl ion would be formed), as well as in certain organic solvents to determine whether the ion can exist under the conditions that occur during polymerization.

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[1] Pepper, *Quart. Rev.*, 1954, **8**, 100.

[2] Gold and Tye, *J.*, 1952, 2184.

[3] Yonezawa, Higashimura, Katagiri, Hayashi, Okamura, and Fukui, *J. Polymer Sci.*, 1957, **26**, 311.

[4] Ward, *J.*, 1927, 445; Bergmann and Polanyi, *Naturwiss.*, 1933, **21**, 378; Hughes, Ingold, and Scott, *J.*, 1937, 1201, 1271; Bodendorf and Böhme, *Annalen*, 1935, **516**, 1; Hart, quoted by Streitwieser, *Chem. Rev.*, 1956, **56**, 622.

[5] Jordan and Treloar, *J.*, 737.

[6] Gold and Tye, *J.*, 1952, 2172.

Since this work was completed, Inoue and Mima [7] and Grace and Symons [8] have published spectra of styrene in sulphuric acid solution. The results of these authors, however, differ in detail from ours.

EXPERIMENTAL

Materials.—Commerical styrene was dried ($CaCl_2$), distilled at reduced pressure, and redistilled *in vacuo* three times, only the middle third being taken each time. 1-Phenylethyl alcohol was prepared by Grignard reaction from methylmagnesium bromide and benzaldehyde and fractionally distilled (b. p. 110°/15 mm.). Further distillation gave a product with an identical spectrum. 1-Phenylethyl chloride was prepared by Kharasch and Kleiman's method.[9] Stannic chloride (B.D.H.) was distilled *in vacuo* three times, the first half being rejected each time, and finally sealed in breakable phials. Aluminium chloride (B.D.H.) was mixed with its own volume of pure aluminium turnings, sublimed *in vacuo* through an 18 in. column of aluminium turnings, and collected in breakable phials as a white crystalline material. 1,2-Dichloroethane and carbon tetrachloride were commercial products purified by standard methods. Concentrated sulphuric acid and glacial acetic acid were analytical reagents.

Preparation of Solutions and Determination of Spectra.—(a) *Sulphuric acid.* Irreversible changes occur when styrene or 1-phenylethyl alcohol is added directly to sulphuric acid, for the reasons given by Grace and Symons.[8] Dilute solutions were therefore made in glacial acetic acid and then diluted ten-fold with concentrated sulphuric acid to give a final sulphuric acid concentration of 90% by volume. (Solutions in which the sulphuric acid concentration was 99% by volume gave identical results.) The spectra were measured on a Unicam S.P. 500 spectrophotometer by using matched 1 cm. silica cells with ground-glass stoppers and a sulphuric acid–acetic acid mixture of the same composition as the solvent as a reference. Since both the intensities and positions of the maxima changed with time, the complete spectrum for each solution was measured at three times after mixing and the initial spectrum determined by extrapolation, Gold and Tye's directions [6] being followed.

(b) *Organic solvents.* Stannic chloride and aluminium chloride solutions were made by cracking phials of the halide, dropping it into the solvent, and quickly stoppering the vessel. The solution was transferred in a closed system to a flask containing a measured amount of a solution of 1-phenylethyl chloride in the same solvent; it was then transferred to a dry spectrophotometer cell, again in a closed system, and the cell quickly stoppered. Water had to be excluded as completely as possible as the metal halides are readily hydrolysed. Solutions were kept at 25° until the maximum colour developed, and the spectra recorded as above.

RESULTS AND DISCUSSION

Sulphuric Acid Solutions.—Solutions of styrene in concentrated sulphuric acid are yellow and quite different in their spectral behaviour from solutions in acetic acid. This is seen from a comparison of the curves in Fig. 1. It seems clear that a new species has arisen, probably from the protonation of styrene. A comparison was made with 1-phenylethyl alcohol in sulphuric acid solution and the spectrum of these solutions is shown in Fig. 2. The positions of the maxima and their intensities are given in Table 1. In the visible region the spectra of the two compounds are virtually identical; the dependence of the optical density on molar concentration is shown for the two solutes in Fig. 3. The wavelength of the maximum absorption in the visible region is 4300 Å, differing somewhat from the values of 4400 Å and 4350 Å obtained by Inoue and Mima [7] and Grace and Symons [8] respectively. The latter authors found that the extinction coefficient for this maximum was about 10,000, much higher than the value recorded in Table 1. Grace and Symons,[10] however, observed considerable variations in the value of the extinction coefficient and for some samples obtained values of about 1000 which is in agreement with the value given in Table 1.

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[7] Inoue and Mima, *Chem. High Polymers (Japan)*, 1957, **14**, 402.

[8] Grace and Symons, *J.*, 1959, 958.

[9] Kharasch and Kleiman, *J. Amer. Chem. Soc.*, 1943, **65**, 11.

[10] Grace and Symons, personal communication.

TABLE 1. *The wavelength and extinction coefficients of the main absorption maxima of styrene and* 1-*phenylethyl alcohol in sulphuric acid.*

	Time	Peak 1		Peak 2		Peak 3	
	(hr.)	λ	ε	λ	ε	λ	ε
Styrene	0	2700	1340	3080	1310	4300	1020
	5	2700	1490	3060	1340	4300	980
	24	2700	1780	3050	1410	4300	930
	78	2700	2410	3050 *	1360	4300	710
1-Phenylethyl alcohol	0	2700	1770	3050	1930	4300	1020
	$\frac{1}{2}$	2700	2130	3050 *	1540	4300	1020
	22	2700	2250	3050 *	1500	4300	930
	42	2700	2320	3050 *	1480	4300	900

* Shoulder.

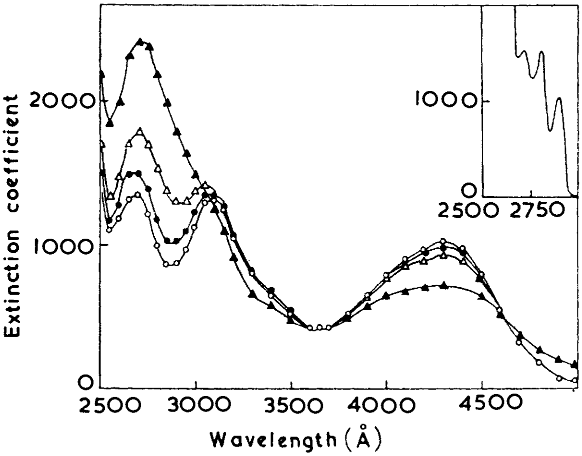


FIG. 1. *The spectrum of styrene in sulphuric acid.* ○ *initial curve obtained immediately after mixing,* ● *after* 5 *hr.,* △ *after* 24 *hr.,* ▲ *after* 78 *hr. Inset: spectrum of styrene in glacial acetic acid.*

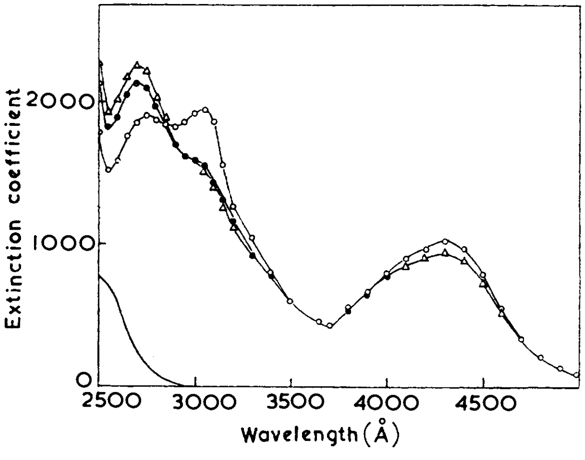


FIG. 2. *The spectrum of* 1-*phenylethyl alcohol in sulphuric acid.* ○ *initial curve obtained immediately after mixing,* ● *after* 0·5 *hr.,* △ *after* 22 *hr.:* --- *spectrum in glacial acetic acid.*

The species formed was unstable and the peak at 4300 Å decreased with time, while the intensity of the peaks in the ultraviolet region increased. Reference to Table 1 shows that, at the same time, the position of peak 2 in the styrene spectrum changes and finally assumes the same value as for peak 2 in the spectrum of 1-phenylethyl alcohol. It is clear then that the identity of the visible spectra does not necessarily imply identity of the absorbing species as previous workers have assumed.

It is suggested that 1-phenylethyl alcohol ionizes initially as follows:

$$\text{Me·CHPh·OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{Me·CHPh·OH}_2{}^+ + \text{HSO}_4{}^-$$

yielding an ion analogous to that formed by tertiary aliphatic alcohols in sulphuric acid rather than the free carbonium ion PhMeHC$^+$. This behaviour is identical with that of t-butyl alcohol in sulphuric acid,[11] and, since the bond energies of the corresponding chlorides and the kinetic evidence indicate that the t-butyl and the 1-phenylethyl ions have similar stabilities, it is to be expected that the behaviour of the corresponding alcohols would also be similar. Styrene, however, can only ionize in one way, *viz.*:

$$\text{CH}_2\text{=CHPh} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{PhMeHC}^+ + \text{HSO}_4{}^-$$

FIG. 3. *The dependence of the optical density* (D_λ) *on the concentration of solution in sulphuric acid:* ○ *styrene,* △ *1-phenylethyl alcohol.*

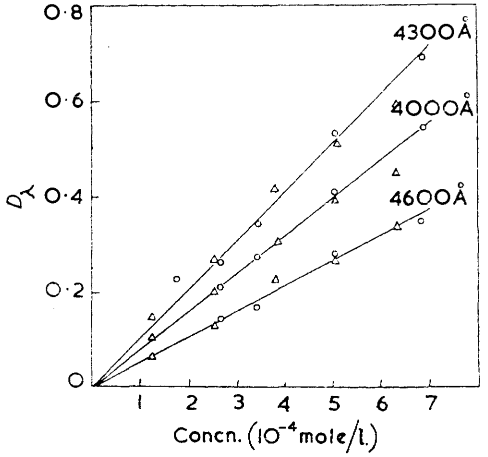
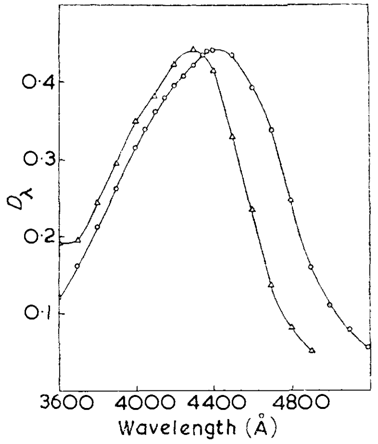


FIG. 4. *Comparison of the spectrum of styrene in sulphuric acid* ($4·35 \times 10^{-4}$M) (△), *with that of 1-phenylethyl chloride* ($1·22 \times 10^{-3}$M) *with* SnCl$_4$ ($2·14 \times 10^{-1}$M) *in 1,2-dichloroethane* (○).



Since the solvent will contain some water, the carbonium ion formed from styrene may react with it to give the more stable ion Me·CHPh·OH$_2{}^+$ which is identical with that formed by the ionization of 1-phenylethyl alcohol. This process could explain the similarity of the two spectra after the lapse of a long time.

Ionization must be complete in each case since the absorption intensities were identical over a range of solvent composition from 60% to 99% of sulphuric acid by volume.

Solutions in Organic Solvents.—It is known that Friedel–Crafts halides will enhance the ionization of aralkyl halides.[12] Solutions of 1-phenylethyl chloride and stannic chloride in 1,2-dichloroethane develop a yellow colour which reaches a maximum intensity only after 25 hours at 25°. The absorption maximum occurs at 4400 Å; comparison with the spectrum of styrene in concentrated sulphuric acid (Fig. 4) suggests that, although there is a peak shift of 100 Å, the 1-phenylethyl ion is present in this solution. A similar peak shift occurs in the spectra of the triarylmethyl cations [14] in the same two solvents, where the shift is 40 Å. The optical density of the 4400 Å peak depends linearly on the concentrations of 1-phenylethyl chloride and stannic chloride, as shown in Fig. 5. If Beer's

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[11] Hantzsch, *Z. phys. Chem.*, 1908, **65**, 41; Newman, Craig, and Garrett, *J. Amer. Chem. Soc.*, 1949, **71**, 869.

[12] Fairbrother and Wright, *J.*, 1949, 1058; Bayles, Evans, and Jones, *J.*, 1957, 1020.

[13] Evans, Price, and Thomas, *Trans. Faraday Soc.*, **1956**, **52**, 332.

[14] Evans, McEwan, Price, and Thomas, *J.*, 1955, 3098.

law holds for this peak in 1,2-dichloroethane, as in sulphuric acid, this means that the total ionic concentration is equal to K[Me·CHPhCl][$SnCl_4$] and the equilibrium

$$\text{Me·CHPhCl} + \text{SnCl}_4 \rightleftharpoons (\text{PhMeHC}^+)(\text{SnCl}_5^-) \quad \ldots\ldots\ldots \quad (1)$$

is operating. The lack of any marked curvature indicates that any separation of the ion-pair must be slight.

The ionic concentrations have been calculated by assuming that the molar extinction coefficient of the ion is the same for 1,2-dichloroethane solutions as for sulphuric acid solutions. A similar assumption has been proved true for solutions of triarylmethyl ions in the solvents *m*-cresol,[14] formic acid,[15] and nitromethane.[16] The ionic concentration has been plotted against the product of the equilibrium concentrations of Me·CHPhCl and $SnCl_4$ in Fig. 6, and the slope of the line obtained gives a value of 2·68 l. mole^{-1} for the equilibrium constant of reaction (1). It has been assumed that the activity coefficients of the reacting species are unity, since 1-phenylethyl chloride and the ion-pair are present in concentrations of 10^{-3}M and 10^{-4}M, respectively, and solutions of stannic chloride in 1,2-dichloroethane should approach ideality because of structural similarities. The value

FIG. 5. *Dependence of the optical density* ($D\lambda_{max.}$) *on concentration of reagents:* ● *1-phenylethyl chloride* ($SnCl_4$ *concn.* 5·01 × 10^{-2}M); ▲ $SnCl_4$ (*1-phenylethyl chloride concn.* 5·26 × 10^{-3}M).

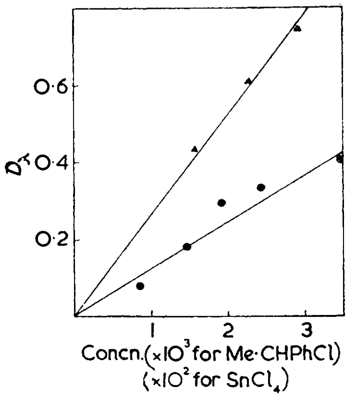


FIG. 6. *Variation of the concentration product,* [Me·CHPhCl][$SnCl_4$], *with total ionic concentration.*

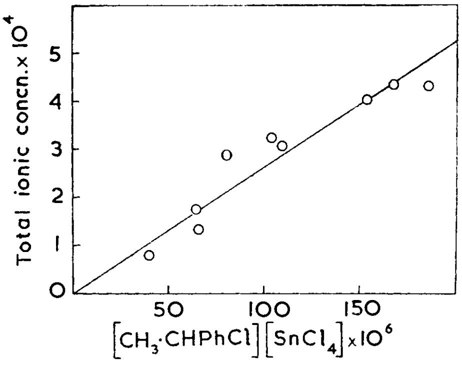


FIG. 7. *Variation of optical density and* log K *with* $1/T$ *for the equilibrium between 1-phenylethyl chloride and* $SnCl_4$ *in 1,2-dichloroethane.*

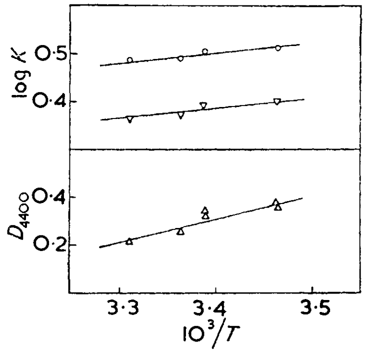
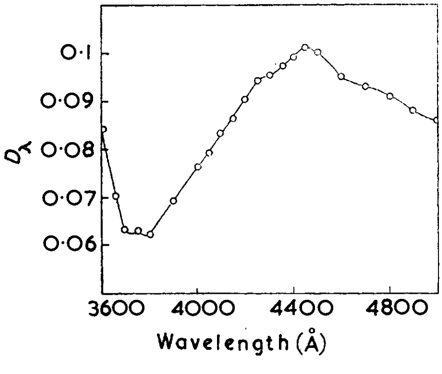


FIG. 8. *The spectrum of 1-phenylethyl chloride with* $AlCl_3$ *in carbon tetrachloride solution.*



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[15] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 568.
[16] Bayles, Cotter, and Evans, *J.*, 1955, 3104.

of ΔG° for this reaction is then $-0{\cdot}59$ kcal./mole. Fig. 7 shows the variation of log D_{4400} against $1/T$ corrected for the expansion of the solvent, and also the variation of log K with $1/T$. The slope of the straight line gives a value for ΔH° of $-0{\cdot}006$ kcal./mole, whence $\Delta S^\circ = -2$ cal. degree^{-1} mole^{-1}. The ionization of the triarylmethyl halides is always accompanied by a decrease in entropy [12–16] and hence the value obtained here is added evidence that ions are formed.

Solutions of 1-phenylethyl chloride and stannic chloride in carbon tetrachloride, however, showed no measurable absorption in the region of 4400 Å even after several days. This is to be expected, since it has been shown [17] that carbon tetrachloride is too weakly polar to permit the formation of the more stable triphenylmethyl ion arising from triphenylmethyl chloride and stannic chloride. However, when aluminium chloride was used in place of stannic chloride, a yellow colour developed in the solution, giving the visible absorption spectrum shown in Fig. 8 with the maximum at 4450 Å. The similarity of shape to that of styrene in sulphuric acid and 1-phenylethyl chloride in 1,2-dichloroethane suggests that it is due to the 1-phenylethyl ion also. Aluminium chloride would be expected to be more effective in promoting ionization than stannic chloride in view of its greater acid strength. However, the possibility of aluminium chloride molecules' helping to solvate the ion-pair must not be ignored, since it is known that mercuric chloride behaves in this manner towards triarylmethyl halides in benzene and chlorobenzene solution.[12]

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[17] Bonner, Clayton, and Gwyn Williams, *J.*, 1958, 1705.