884. *Spectroscopic Studies on Carbonium Ions Derived from Aromatic Olefins. Part I. Styrene and Related Olefins*

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The kinetics of protonation of styrene by perchloric acid in methylene dichloride have been studied spectroscopically at room temperature. The ultraviolet and visible spectra of the 1-phenylethyl and related carbonium ions are given and the discrepancies between our results and those of other authors are discussed and resolved.

THE polymerisation of styrene catalysed by acids and Lewis acids has been widely studied, and Mathieson [1] has reviewed this subject very thoroughly. The chemical interpretation of the reactions involved in these systems has invariably been based on the assumption that the chain carriers produced in the initiation reaction are carbonium ions, *i.e.*, 1-phenylethyl, and subsequently polystyryl, ions. The literature, however, does not provide any irrefutable proof for this interpretation, although a number of attempts at providing such proof have been made.[2] We approached the problem of testing the carbonium-ion theory by choosing a polymerisation system which was alleged to involve a relatively high concentration of 1-phenylethyl carbonium ions during the whole of the reaction,[3] namely the system perchloric acid–styrene. Our findings have been reported.[4] This Paper is concerned with the spectroscopic characterisation of the expected carbonium ions. Although alleged spectra of these ions have been published by several authors, the important discrepancies between their results, and the fact that their reaction media differed substantially from our own, induced us to re-examine the issue by a more rigorous technique than had been used by others.

EXPERIMENTAL

Technique. All the reactions to be described were carried out at room temperature (20—23°) in an all-glass high-vacuum spectroscopic device [5] fitted with a 1-cm. silica cell. The olefin solutions were made up under vacuum in the device and their concentration was computed spectroscopically. Reactions were then started by crushing a phial of perchloric acid in the

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[1] A. R. Mathieson, "The Chemistry of Cationic Polymerisation," ed. P. H. Plesch, Pergamon Press, London, 1963, ch. 6.

[2] (*a*) D. O. Jordan and F. E. Treloar, *J.*, 1961, 734; (*b*) D. J. Metz, *J. Polymer. Sci.*, 1961, **50**, 497; (*c*) A. G. Evans, P. M. S. Jones, and J. H. Thomas, *J.*, 1957, 104.

[3] D. C. Pepper and P. J. Reilly, *J. Polymer. Sci.*, 1962, **58**, 638.

[4] A. Gandini and P. H. Plesch, *Proc. Chem. Soc.*, 1964, 240; *J. Polymer Sci., Part B, Polymer Letters*, 1965, **3**, 127.

[5] A. Gandini, P. Giusti, P. H. Plesch, and P. H. Westermann, *Chem. and Ind.*, 1965, 1225.

olefin solution, and scanning could be started 20—30 sec. later. All the spectra were recorded with a Unicam S.P. 700 automatic spectrophotometer.

Materials. Methylene dichloride,[6] perchloride acid,[7] and 1-phenylethanol [7] were purified and dosed as described. Styrene was purified as published,[8] transferred to the vacuum line, dried over calcium hydride then over barium oxide, where it was stored in the dark at liquid-nitrogen temperature. Its vapour was dosed volumetrically into the device by high-vacuum distillation. α-Methylstyrene (B.D.H.) was fractionated under high vacuum; the middle fraction was kept *in vacuo* in a flask attached to the vacuum line; dosings were performed as for styrene. The dimers of styrene (1,3-diphenylbut-1-ene and 1-phenyl-2-methylindane) were prepared by Risi and Gauvin's procedure,[9] followed by fractional distillation at reduced pressure. High-temperature vapour-phase chromatography was used as purity test for these compounds: the linear dimer contained less than 0·1% by volume of cyclic impurities, the cyclic dimer (50 : 50 mixture of *cis*- and *trans*-isomers) contained about 3% by volume of 1,3-diphenylbut-1-ene. The physical properties, the ultraviolet, and the infrared spectra of these compounds agreed well with those published. 1,2-Dichloroethane was purified and dosed as described for methylene dichloride.[6]

RESULTS

Kinetics of the Protonation of Styrene.—The best working conditions were attained with an approximately hundredfold excess of acid over styrene; more acid made side reactions too important, less acid tended to slow down the protonation reaction, so that a mixture of 1-phenylethyl and polystyryl ions was obtained, because of partial oligomerisation of the styrene.

The absorption maximum in the visible spectrum due to the 1-phenylethyl ion was located in a few preliminary runs at 427 ± 1 mμ. The D_{427} increased during the first few minutes following the mixing of the reagents, so that the rate of protonation could be measured by scanning at this wavelength against time. The reaction traces of four such experiments gave good first order plots up to 90—95% conversion (Table 1). A plot of the logarithm of the slope of the first-order plot against the logarithm of the acid concentration gave a straight line with slope 0·24 ± 0·02 and intercept at log $[HClO_4] = 0$ of $-1·63 \pm 0·02$.

TABLE 1

Protonation of styrene

Expt. No.	$[HClO_4]_0$ (10^2M)	[Styrene] (10^4M)	S * (10^2 sec.$^{-1}$)	Max. D_{427}
SGU2	3·95	3·87	1·10	1·50
SGU3	2·48	2·24	—	0·92
SGU6	1·81	1·65	0·97	0·65
SGU5	1·34	1·36	0·87	0·49
SGU4	0·780	0·723	0·80	0·21 †

* Slope of the first-order plot. † Traces of oligomers were formed during this experiment: the maximum value of D_{427} is therefore lower than expected.

These results suggest that the reaction proceeds according to the following equation:

$$(HClO_4)_4/4 + CH_2{:}CHPh \xrightarrow{k_i} CH_3{\cdot}CHPh^+ + ClO_4^-$$

$$\text{Rate} = k_i[HClO_4]^{\frac{1}{4}}\,[\text{Styrene}],\ k_i = (2·35 \pm 0·1) \times 10^2\ \text{l.}^{0·25}\ \text{mole}^{-0·25}\ \text{sec.}^{-1}$$

The $\frac{1}{4}$ power in acid indicates that this is associated in methylene dichloride solutions into molecular aggregates containing an average of 4 molecules of acid.

Characterisation of the Spectra. A plot of the final D_{427} against the styrene concentration gave a straight line passing through the origin: its slope (least-squares method) gave $\varepsilon = (3·86 \pm 0·07) \times 10^3$.

Full spectra of the solutions were frequently scanned at the end of the protonation reaction. Under the conditions described side reactions occurred, which were, however, fairly slow compared with the protonation itself. These side reactions produced a strong increase in absorption around 250 mμ, with parallel (but less strong) decrease of D_{427}. In order to obtain the full

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[6] W. R. Longworth, P. H. Plesch, and M. Rigbi, *J.*, 1958, 451.

[7] A. Gandini and P. H. Plesch, *J.*, 1965, in the press.

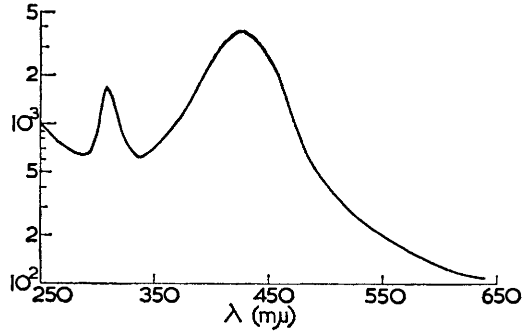
[8] R. D. Colclough and F. S. Dainton, *Trans. Faraday Soc.*, 1958, **54**, 886.

[9] J. Risi and D. Gauvin, *Canad. J. Res.*, 1936, **14**, *B*, 255.

spectrum of the 1-phenylethyl ion, the original values of D_λ at several wavelengths were derived by the extrapolation suggested by Gold and Tye.[10] Good Lambert–Beer plots were obtained by plotting the extrapolated D_λ values at a given wavelength against the styrene concentration. It was thus possible to trace the spectrum of the 1-phenylethyl ion in the region 250—800 mμ (spectrum 1); the only peak in the u.v. was at 309 ± 0·5 mμ [$\varepsilon_{309} = (1{\cdot}66 \pm 0{\cdot}05) \times 10^3$].

Three runs were carried out in the same conditions as those just described, but with 1-phenylethanol instead of styrene. The spectra exhibited two peaks, at 309·5 ± 0·5 and 429 ± 2 mμ. ε_{309} could not be obtained precisely from these experiments because of interference by a strong band at 270 mμ; $\varepsilon_{429} = (3{\cdot}8 \pm 0{\cdot}1) \times 10^3$; these results agree with those obtained with styrene.

The linear dimer of styrene was then protonated under the same conditions (three runs). Even in the presence of a large excess of acid, the protonation reaction was always accompanied by the cyclisation of 1,3-diphenylbut-1-ene to 1-phenyl-3-methylindane,[11] as indicated by the formation of peaks at 267 and 274 mμ. The computation of molar extinction coefficients for the protonated dimer and of its rate of protonation was made impossible by this complication. The spectrum of the carbonium ion had two peaks, at 308 ± 0·5 mμ and at 424 ± 1 mμ. These were certainly due to the species $CH_3{\cdot}CHPh{\cdot}CH_2{\cdot}CHPh^+$, since the pure cyclic dimer does not interact with perchloric acid under the conditions used.



The ultraviolet and visible spectrum of the 1-phenylethyl carbonium ion in methylenedichloride (see also Table 2)

The spectrum of the 1-phenylethyl ion was also studied in 1,2-dichloroethane (2 runs), by the procedure described above. The protonation of styrene yielded at first the 1-phenylethyl ion; the spectrum initially had two peaks, at 309 ± 1 mμ and at 427 ± 1 mμ ($\varepsilon_{427} \simeq 4 \times 10^3$), but within a few minutes gave an additional peak in the visible region at 396 ± 1 mμ ($\varepsilon_{396} \simeq 4 \times 10^3$). The subsequent degradation reactions reduced the absorption in the visible region and increased correspondingly the absorption around 250 mμ, as in the reactions carried out in methylene dichloride.

Discussion

The first report on the spectrum of the 1-phenylethyl ion was published by Inoue and Mima;[12] only the absorption maxima were given by these authors, who dissolved liquid or gaseous styrene or 1-phenylethanol in 95% sulphuric acid in order to produce the carbonium ion. A spectrum of the protonated linear dimer of styrene in the same medium was also published. From the published curves (not all the data are given in the text), we obtained the values for $\lambda_{\text{max.}}$ shown in Table 2. Inoue and Mima assigned the peak at 450 mμ to the 1-phenylethyl ion and that at 416 mμ to the distyryl ion. This conclusion seems rather surprising since, on general considerations, only a very small hypsochromic shift would be expected to result from substitution of a hydrogen atom in the methyl group next to the chromophore by a second monomer unit. Grace and Symons[13] reported more recently on the spectrum of the 1-phenylethyl ion obtained under conditions similar to Inoue and Mima's (Table 2). A more thorough investigation of the same system was made by

[10] V. Gold and F. L. Tye, *J.*, 1952, 2148.

[11] J. M. Burton and D. C. Pepper, *J.*, 1964, 1573.

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

[13] J. A. Grace and M. C. R. Symons, *J.*, 1959, 958.

TABLE 2

Spectroscopic data on 1-phenylethyl and polystyryl ions

Compound	Solvent	Ionising agent	Alleged carbonium ion	$\lambda_{max.}$ (mμ), ($\varepsilon_{max.}$)	Ref.
Styrene (gas)	H_2SO_4	H_2SO_4	$CH_3{\cdot}CHPh^+$	316, (—); 450, (—)	12
Styrene	,,	,,	,,	435, (~10^4)	13
,,	,,	,,	,,	270, (1340); 308, (1310); 430, (1020)	2*a*
,,	CH_2Cl_2	$HClO_4$	,,	309, (1660); 427, (3860)	Present work
,,	$(CH_2Cl)_2$	,,	,,	309, (—); 427, (—)	,,
1-Phenylethanol	H_2SO_4	H_2SO_4	,,	450, (—)	12
,,	,,	,,	,,	435 (~10^4)	13
,,	,,	,,	,,	270 (1770); 305 (1930) 430, (1020)	2*a*
,,	CH_2Cl_2	$HClO_4$	,,	309·5, (—); 429, (3800)	Present work
1-Phenylethyl-chloride	$(CH_2Cl)_2$	$SnCl_4$	,,	440, (—)	2*a*
,,	CCl_4	$AlCl_3$	,,	445, (—)	,,
1,3-Diphenylbut-1-ene	H_2SO_4	H_2SO_4	$CH_3{\cdot}CHPh{\cdot}CH_2{\cdot}CHPh^+$	306, (—); 416, (—)	12
,,	CH_2Cl_2	$HClO_4$	,,	308, (—); 424, (—)	Present work
Styrene	$(CH_2Cl)_2$	$SnCl_4$	$CH_3{\cdot}CHPh{\cdot}(CH_2{\cdot}CHPh)_n{\cdot}CH_2{\cdot}CHPh^+$	410, (—)	2*a*
,,	CCl_4	$AlCl_3 + H_2O$	,,	420, (—)	,,
,,	$(CH_2Cl)_2$	$HClO_4$	,,	416, (160)	14

Jordan and Treloar,[2a] who studied the changes in the spectra with time when styrene or 1-phenylethanol was dissolved in concentrated sulphuric acid. By the usual extrapolation technique,[10] they obtained the full spectrum at the time of mixing (Table 2). The secondary reactions tended to destroy the carbonium ions and to produce species absorbing strongly around 270 mμ. These authors also studied the spectra of polymerising (or polymerised?) solutions and gave figures for the absorption maxima of the polystyryl ion in different solvents (Table 2); again a shift of 25—30 mμ was reported to take place when passing from the monomer to the polymer ion. Most recently, Reilly [14] has reported the visible spectrum of the polystyryl ion in 1,2-dichloroethane (Table 2).

A comparison of our results (also shown in Table 2) with those previously published suggests the following:

(*a*) The spectrum of the styryl ion obtained by us has no absorption maximum between 250 and 300 mμ, in contrast to the peak at 270 mμ found by Jordan and Treloar; [2a] on the other hand, we agree with these authors that there is a strong increase in absorption with time at 250—270 mμ. Jordan and Treloar probably mistook a peak due to species originating from side reactions for one belonging to the carbonium ion, because of the relatively slow scanning characteristic of their instrument (Unicam manual S.P. 500), and the peculiarly fast increase in absorption at 270 mμ after mixing.

(*b*) The ε_{427} for our results in CH_2Cl_2 is roughly four times that of the ε_{430} in sulphuric acid; [2a] this can hardly be attributed to a solvent effect. It seems more likely that because of the side reaction giving the anomalous behaviour discussed under (*a*), less styrene was in fact available for protonation in Jordan and Treloar's experiments. This side reaction seems to be either sulphonation of the styrene, despite the special precautions taken by the authors,[2a] or partial polymerisation of the olefin, with consequent decrease in the number of double bonds available. This second hypothesis is corroborated by the fact that polystyrenes absorb at 260 mμ.

(*c*) Our spectrum of the 1-phenylethyl ion agrees in its pattern with the spectra of homologous carbonium ions such as 1,1-diphenylethyl and 1,1,2-triphenylethyl [10] insofar

[14] P. J. Reilly, Ph.D. Thesis, Dublin, 1962.

as they all exhibit two peaks, one in the u.v. near 300 mμ and the other in the visible at 430—440 mμ, with ε_{300} *ca.* 0·5 $\varepsilon_{430-440}$.

(*d*) The spectra of the styryl ion in methylene dichloride and in 1,2-dichloroethane are virtually the same; we have not been able to ascertain definitely the origin of the peak at 396 mμ appearing in the latter solvent after protonation. Since this peak was the only one exhibited in this region by polymerised solutions in 1,2-dichloroethane, it seems likely that its origin is related to some rearrangement of long-chain secondary carbonium ions to tertiary cations. It is possible that, owing to formation of oligomers during the protonation, the ions could isomerise:

$$CH_3{\cdot}CHPh{\cdot}CH_2{\cdot}\overset{+}{C}HPh \longrightarrow CH_3{\cdot}\overset{+}{C}Ph{\cdot}CH_2{\cdot}CH_2Ph$$

It is known that the dimethylphenylcarbonium ion absorbs at 390 mμ in sulphuric acid[13] or at 395 mμ according to another author.[15] This supports our interpretation, since the tertiary carbonium ion depicted above would have virtually the same chromophore as the dimethylphenylcarbonium ion. We cannot yet explain why this rearrangement should take place in one solvent and not in the other (methylene dichloride), but it seems likely that the protonation was faster in methylene dichloride and thus oligomerisation was avoided. The protonation of α-methylstyrene by a large excess of perchloric acid in an open system in methylene dichloride gave a solution with a peak at 394 ± 2 mμ (two runs).

(*e*) As expected, the spectrum of the distyryl ion closely resembles that of the monomer ion: only a minor hypsochromic shift of about 3 mμ for the longer-wavelength peak is produced by the substitution of one hydrogen of the methyl group by a monomer unit, in disagreement with the observations of the cited authors. However, it seems very likely that the spectra they attributed to secondary dimer (or polymer) ions were in fact due to tertiary ions of the kind illustrated under (*d*), or to some other isomeric structure. The peaks reported for these spectra were always very broad, in contrast to the sharpness of the peaks obtained in the present work. This again suggests that a mixture of different ionic species was present in the solutions studied by these authors.

(*f*) Addition of small quantities of water, alcohols, or amines to the yellow solutions destroyed the colour instantaneously. The poisonous effect of these basic substances upon the carbonium ions studied is an important feature of these systems and its quantitative aspects will be discussed when we report on the spectroscopic behaviour of the polymerising system styrene–perchloric acid–methylene dichloride.

(*g*) Following our recent discovery of the catalytic dehydration of aromatic carbinols by acids,[7] it is now evident that the spectrum obtained when 1-phenylethanol was treated with an excess of perchloric acid must be the same as that obtained when styrene is protonated under the same conditions, since in the former system the first reaction is the dehydration of the carbinol to styrene.

Although we were unable to obtain reliable values for the peak molar extinction coefficients of the distyryl ion, it seems reasonable to assume that these do not differ much from the corresponding values for the 1-phenylethyl carbonium ion. The chromophore is in fact the same in both ions, namely $\cdot CH_2{\cdot}\overset{+}{C}HPh$, and we have shown that the position of the maxima is very similar for these two ions.

The information collected was therefore considered sufficient for the specific purposes of this work, namely a knowledge of the spectroscopic characteristics of the carbonium ions which might be present during the polymerisation of styrene catalysed by perchloric acid. At the beginning of our study of the polymerising solutions we assumed that the polymer ion would have a spectrum virtually identical to that of the dimer ion; this was later proved to be true as will be shown in a future Paper dealing with that study.

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[15] H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, 1962, **66**, 1457.