Polarography of Organic Cations in Acid Solutions. Part 3.[†,‡] Three 1,1-Diarylethyl Ions in Sulphuric and Methanesulphonic Acids

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The u.v. spectra and polarography of the 1,1-bis-(2,4-dimethylphenyl)ethyl (1) and 1,1-di-*o*-tolylethyl (2) carbenium ions in 15M-H_2SO_4 and in anhydrous and aqueous $MeSO_3H$ have been investigated. The reductions are irreversible and can be interpreted by the reaction scheme proposed previously. An explanation is suggested why a spectrum but no reduction wave could be found for the 1,1-bis-(2-methyl-4-chlorophenyl)ethyl ion (3). Our present and earlier $E_{\frac{1}{2}}$ values for carbenium ions in acids are presented on a scale based on the trityl cation; this provides a convenient reference potential for media in which ferrocene breaks down.

When in the course of other studies three new 1,1-diarylethylenes became available, it was opportune to study the characteristics of the carbenium ions derivable from them by protonation. The spectroscopic and polarographic work reported here is an extension of our earlier studies [1,2] and provides further insight about how the characteristics of the ions vary with the substitution pattern in the aryl groups.

EXPERIMENTAL

Apparatus.—For the polarography we used a Beckman Electroscan 30 instrument and a Kalousek cell with mercury–mercurous sulphate–98% sulphuric acid electrode (MSE) as reference electrode. A platinum wire served as the auxiliary electrode. The dropping mercury electrode had the following characteristics: $t = 2.53$ s, $m = 4.37$ mg s^{-1} at $h = 40$ cm in 15M-H_2SO_4 at zero applied potential.

The spectra were recorded on a Perkin-Elmer 402 spectrophotometer with 2-cm silica cells.

Materials.—The olefins (Table 1), prepared by Dr. Werner Obrecht in these laboratories, were purified by standard methods. Acids used were AnalaR 98% H_2SO_4 (Hopkin & Williams) and anhydrous $MeSO_3H$ (May & Baker).

Procedure.—*Spectroscopy*. Solutions of the olefin in acid were made by Bertoli and Plesch's 'open protonation' technique [2] with methylene chloride as solvent. The spectrometer cells were filled by syringe under a nitrogen blanket; the spectra were scanned from 210 to 700 nm with the acid as reference.

The oscillator strength, *f*, of the ions was calculated as described.[3]

Polarography. Since the acids themselves conduct sufficiently, no base electrolyte was required. The acid (20 ml) in the polarographic cell was purged with White-Spot nitrogen, and then a base curve was recorded. The olefin was added as a 10^{-2}M-solution in CH_2Cl_2 and its extraction was facilitated by fast stirring with the nitrogen stream. When all CH_2Cl_2 had evaporated, the polarogram was recorded. All the experiments were performed at room temperature (*ca.* 18 °C).

Spectroscopy

Results and Discussion.—In 15M-H_2SO_4 the protonations of olefins 1(H) and 2(H) were instantaneous and complete

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[†] Part 2 is ref. 1*b*.

[‡] This is also considered as Part 4 of the series 'Spectroscopic Studies on Carbonium Ions derived from Aromatic Olefins,' the preceding part of which is ref. 2.

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[1] (*a*) P. H. Plesch and I. Sestakova, *J. Chem. Soc.* (*B*), 1970, 87; (*b*) P. H. Plesch and I. Sestakova, *J. Chem. Soc.* (*B*), 1971, 1337.

[2] V. Bertoli and P. H. Plesch, *J. Chem. Soc.* (*B*), 1968, 1500.

[3] V. Bertoli and P. H. Plesch, *Spectrochim. Acta*, 1969, **25A**, 447.

for olefin concentrations between 10^{-5} and 10^{-4}M. At 10^{-4}M (3)H was incompletely protonated so that the extinction coefficients could not be measured. In anhydrous methanesulphonic acid only (1)H was protonated completely, whereas protonation of (2)H was incomplete, and with 3(H) no absorbance was obtained even up to 10^{-4}M-concentrations.

TABLE 1

Spectroscopic characteristics of the carbenium ions

Olefin (RRC = CH$_2$)	No.	M.p. (°C)	Ion (RRCH·CH$_2$)	No.	Solvent	$\lambda_{max.}$/nm	$10^{-3}\varepsilon_{max.}$	$\frac{f_s}{f_l}$	$\frac{f_s}{f_l}$	f_t
R = Ph			R = Ph		15M-H_2SO_4	315 427	12.5 40.25	0.104 0.531	0.196	0.635
						(314) [a] (427)	(12) (39)	(0.097) [b] (0.504)	(0.192)	(0.601)
					$MeSO_3H$	315 425	11.0 37.5	0.085 0.518	0.164	0.603
R = 2,4-$Me_2C_6H_3$	(1)H	44.5	R = 2,4-$Me_2C_6H_3$	(1)	15M-H_2SO_4	338 485	16.9 35.8	0.137 0.503	0.272	0.640
					$MeSO_3H$	338 480	12.8 30.5	0.129 0.479	0.269	0.608
R = *o*-tolyl	(2)H	42.6	R = *o*-tolyl	(2)	15M-H_2SO_4	332 444	16.3 33.5	0.148 0.556	0.261	0.714
					$MeSO_3H$	334 450				
R = 2-Me,4-Cl-C_6H_3	(3)H	33.3	R = 2-Me,4-Cl-C_6H_3	(3)	15M-H_2SO_4	348 491				

[a] Values in parentheses are from ref. 3. [b] In ref. 3 this f_s-value was misprinted; the value given here was recalculated from the original curve; f_s and f_l are, respectively, the oscillator strengths of the short and long wavelength peaks.

All spectra showed two well-shaped maxima. The spectroscopic characteristics of the ions are given in Table 1. For comparison, the values for the parent olefin are also shown. The wavelengths of both peaks increase in the order (3) > (1) > (2) > Ph_2C^+Me. This reflects the ranking of the ions with regard to diarylalkyl character [4,5] which is in the reverse direction, due to electronic and steric factors.

Polarography

Results.—Quantitative results were obtained only for ions (1) and (2) in 15M-H_2SO_4 and for ion (1) in anhydrous $MeSO_3H$. In less concentrated H_2SO_4 ($\leqslant$14M), neither (1)H nor (2)H were protonated quantitatively, and in more concentrated acid ($\geqslant$16M) no reduction wave was found, presumably because it lies beyond the breakdown potential of the acid. Olefin (3)H was so slightly soluble in H_2SO_4, even up to 17.5M, that only the spectrum, but no polarogram, could be obtained.

Ions (1) *and* (2) *in* 15M-H_2SO_4 *and* $MeSO_3H$.—For ion (1) in $MeSO_3H$ the limiting current decreased linearly with increasing water concentration, the i_d for 10 vol % of water being one half of that for the anhydrous acid. The lower basicity of (2)H compared to (1)H is shown by the fact that it is not completely protonated even in anhydrous $MeSO_3H$. For both ions in both the acids a single reduction wave was obtained (Figure 1). The limiting currents were diffusion controlled (linear i_d *vs.* $h^{\frac{1}{2}}$ plots), and were proportional to the concentration of the ions. The $E_{\frac{1}{2}}$, the log–plot slope, and $n\alpha$ values are given in Table 2, and the results show the irreversible nature of all the waves. Comparison of diffusion currents and diffusion current constants for these ions with those of known n value (triphenylmethyl [1] and 1,1-diphenylethyl ions [1] and nitrobenzene,[6] wave heights taken for the same acid concentration or corrected for viscosity [7]) indicates clearly that two electrons are involved in the reduction of ions (1) and (2) in H_2SO_4, but only one electron in the reduction of ion (1) in $MeSO_3H$.

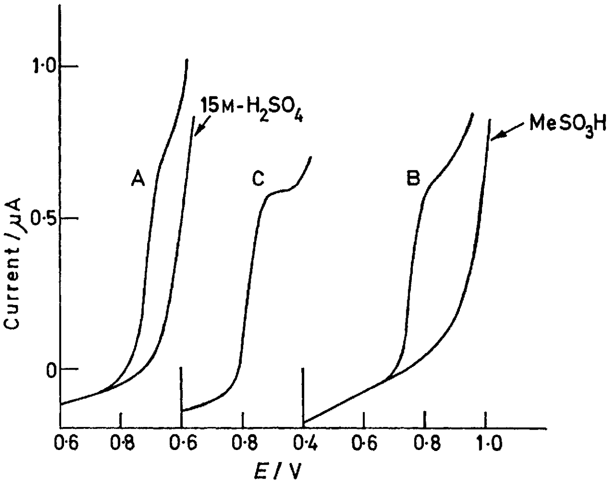

FIGURE 1 Polarograms of carbenium ions (2.5×10^{-4}M): (A) ion (1) in 15M-H_2SO_4; (B) ion (1) in $MeSO_3H$; (C) ion (2) in 15M-H_2SO_4

The dependence of $E_{\frac{1}{2}}$ on concentration was as in Figure 2: for ion (1) $E_{\frac{1}{2}}$ became less negative with increasing ion

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[4] G. A. Olah, C. U. Pittman, R. Waack, and M. Doran, *J. Amer. Chem. Soc.*, 1966, **88**, 1488.

[5] G. A. Olah and C. U. Pittman, *Adv. in Phys. Org. Chem.*, 1966, vol. 4.

[6] S. Wawzonek, R. Berkey, and D. Thomson, *J. Electrochem. Soc.*, 1956, 513.

[7] L. Meites, ' Polarographic Techniques,' 2nd edn., Interscience, New York, 1965, p. 141.

concentration in both acids; for ion (2) $E_{\frac{1}{2}}$ became more negative in 15M-H_2SO_4, but less negative in $MeSO_3H$, with increasing [(2)H].

TABLE 2

Half-wave potentials, $n\alpha$, and log-plot slopes for carbenium ions (1) and (2)

Ion [a]	Solvent	$-E_{\frac{1}{2}}$/V	$n\alpha$	log-plot slope/V
(1)	15M-H_2SO_4	0.89	0.78	0.045
(2)	15M-H_2SO_4	0.82	0.64	0.037
(1)	$MeSO_3H$	0.76	0.69	0.040
(2)	$MeSO_3H$	0.7	0.80	0.047

[a] [Ion] was 2.5×10^{-4}M except for (2) in $MeSO_3H$ for which the added olefin conc. was 10×10^{-4}M but the [ion] was not known accurately (see text).

Discussion.—The polarographic results described in the previous section are consistent with the mechanism proposed previously for the reduction of various aralkyl ions [1] and can be represented as:

$$\mathrm{MeAr_2\overset{+}{C}} + e \underset{}{\overset{E_1}{\rightleftharpoons}} \mathrm{MeAr_2C^{\bullet}} \qquad (1)$$

$$\mathrm{MeAr_2C^{\bullet}} \longrightarrow \text{dimer} \qquad (2)$$

$$\mathrm{MeAr_2C^{\bullet}} + \mathrm{H^+} \rightleftharpoons \mathrm{(MeAr_2C^{\bullet})H^+} \qquad (3)$$

$$\mathrm{(MeAr_2C^{\bullet})H^+} + e \xrightarrow{E_2} \mathrm{MeAr_2CH} \qquad (4)$$

1,1-*Bis*-(2,4-*dimethylphenyl*)*ethyl Ion* (1).—In sulphuric acid the number of electrons transferred was two. The first reduction occurs according to equation (1). As the proton activity is sufficiently high the radical is protonated (equation 3), and since $\mathrm{(MeAr_2C^{\bullet})H^+}$ has a greater electron affinity than $\mathrm{MeAr_2C^+}$, the second electron is transferred to it at the same potential [equation (4)]. Thus $E_1 = E_2$ and the total wave height corresponds to that of a two-electron wave.

Whether some of the radicals also dimerise [reaction (2)] can be tested as follows. The exact solution of the depolarisation scheme for such a second-order reaction accompanied by a one-electron reduction [8] gives $\Delta E_{\frac{1}{2}}/\Delta\log c = 19.7$ mV. In H_2SO_4 the value found was 45 mV which, being greater, is said to indicate that the dimerisation and protonation occur at the surface of the electrode.[9]

In methanesulphonic acid the ion gave a wave due to reaction (1) only. However, the dependence of the $E_{\frac{1}{2}}$ on the ion concentration was similar to that for a reversible wave and $\Delta E_{\frac{1}{2}}/\Delta\log c =$ *ca*. 20 mV; this value is compatible with the proposed scheme. That only one electron is involved indicates that in $MeSO_3H$ the ratio of protonation rate to dimerisation rate is so much less than in 15M-H_2SO_4, that in the less acid medium few radicals survive long enough to be available for protonation.

1,1-*Di*-o-*tolylethyl Ion* (2).—The behaviour of ion (2) in 15M-H_2SO_4 was different from that of ion (1). Its $E_{\frac{1}{2}}$ does not become less negative but more negative with increasing depolariser concentration, and $\Delta E_{\frac{1}{2}}/\Delta\log c = -55$ mV. This may indicate that the protonation of the 1,1-di-*o*-tolylethyl radical is much faster than its dimerisation.[10] It appears that some radicals do dimerise (or are lost somehow) as the diffusion currents were somewhat less than those expected for a two-electron reduction.

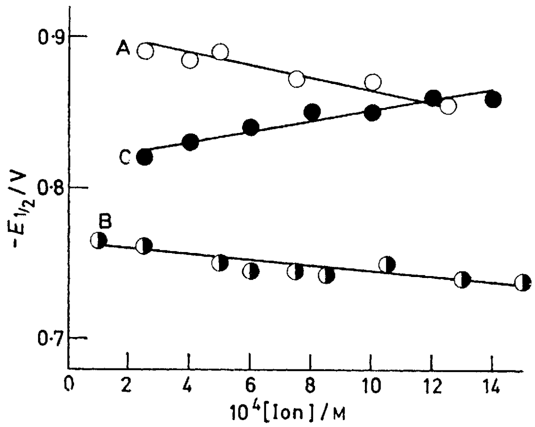

FIGURE 2 The dependence of $E_{\frac{1}{2}}$ on [Ion]: (A) Ion (1) in 15M-H_2SO_4; (B) ion (1) in $MeSO_3H$; (C) ion (2) in 15M-H_2SO_4

TABLE 3

Limiting currents and $E_{\frac{1}{2}}$ values at varying olefin concentrations in $MeSO_3H$

	10^4[Ion]/M			Limiting current/μA		$-E_{\frac{1}{2}}$/V	
10^4[Olefin]/M	Ion (1)	Ion (2) [a]	[(2)]/[(2)H]	Ion (1)	Ion (2)	Ion (1)	Ion (2)
1	1	*b*		0.28	0.04	0.765	
2.5	2.5	*b*		0.59	0.10	0.76	0.72
5	5	0.33	0.07	1.11	0.21	0.75	0.71
10	10	1.3	0.13	1.92	0.38	0.745	0.70

[a] Estimated from i_d/c of ion (1). [b] Too small to be estimated.

In anhydrous methanesulphonic acid, the ion (2) was not formed quantitatively. Although the limiting current depended rectilinearly on the concentration of the olefin, the currents were very small (Table 3). The variation of $E_{\frac{1}{2}}$ with concentration, shown in Table 3, is important. It is different from what was found with 15M-H_2SO_4, showing an anodic shift with increasing concentration; therefore, the mechanism must be as for ion (1) [reactions (1)—(4)]. We thus find that in methanesulphonic acid the dimerisation of the 1,1-di-*o*-tolylethyl radical competes effectively with its protonation. This can be explained by the relatively low acidity of methanesulphonic acid as compared to 15M-H_2SO_4, as a result of which the protonation of the radical is slower.

1,1-*Bis*-(2-*methyl*-4-*chlorophenyl*)*ethyl Ion* (3).—The olefin (3)H was not completely protonated in 17.5—15M-H_2SO_4, and no polarographic wave was obtained. A possible reason for this is that the $E_{\frac{1}{2}}$ of ion (3) [like that of ion (1)] becomes more negative with decreasing concentration and

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[8] J. Koutecky and V. Hanus, *Coll. Czech. Chem. Comm.*, 1955, **20**, 124.

[9] S. G. Mairanovskii, 'Catalytic and Kinetic Waves in Polarography,' Plenum Press, New York, 1968, p. 239.

[10] Ref. 9, p. 236.

that at the prevailing very low concentration [*ca.* 10^{-5}M estimated from the absorbances and the ε values of ions (1) and (2)] the $E_{\frac{1}{2}}$ is beyond the decomposition potential of the solvent (*ca.* −1 V).

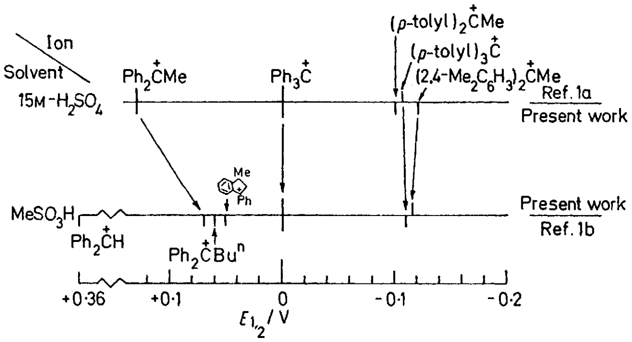

FIGURE 3 Scale of half-wave potentials for various carbenium ions with respect to that of the trityl ion. [Ion] = 1 × 10^{-3}M. The $E_{\frac{1}{2}}$ is that of the wave corresponding to reaction (1). The $E_{\frac{1}{2}}$ plotted against ref. 1*a* were derived from the original results, obtained at other acid concentrations, by extrapolating them to 15M-H_2SO_4

A Potential Scale for Solvents of High Acidity.—In Figure 3 a potential scale is shown for 1 mM concentrations of different carbenium ions with the $E_{\frac{1}{2}}$ of the trityl ion as the reference zero. As expected, the inductive effect of the substituents controls the reducibility sequence: 1,1-bis-(2,4-dimethylphenyl) > 1,1-di-*o*-tolyl > 1,1-diphenyl and tri-*p*-tolyl > triphenyl. Unfortunately, quantitative comparisons are frustrated by the fact that only some of these ions are reduced reversibly. However, it appears from our results that the trityl cation can provide a convenient reference potential in solvents of high acidity, in which ferrocene, the most widely used ' marker ', is degraded.

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