

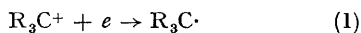
Polarography of Organic Cations

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IN the course of studies on the nature of the chain-carriers in cationic polymerisations it became important to find a method of detecting and characterising organic cations (carbonium ions, oxonium ions, and others), which would also be applicable to ions having no distinctive absorption in the u.v. and visible part of the spectrum and also to those which are not sufficiently stable to be studied by ^1H n.m.r. methods. We have developed an apparatus and method which enables us to detect and identify such ions by polarography; here we outline our method, and give the half-wave potentials for the reduction of some representative ions in two very different media: concentrated sulphuric acid and methylene dichloride. The few earlier studies in this field concern the trityl,¹ cyclopropenium,² and tropylium³ ions.

An organic cation, such as a carbonium ion, is reduced at the dropping mercury cathode to a radical



at a certain potential, which is characteristic of the ion-in-solution. The term ion-in-solution means the ion together with its solvation shell, and its

properties depend on the nature of the ion and of the solvent. For methylene dichloride solutions the reductions involve one electron, and the radicals thus formed presumably dimerise. In sulphuric acid solution, the reduction involves two electrons because the radicals react further with solvent:



The greater the potential required for the reduction, the more stable is the ion-in-solution.

Sulphuric acid solvent.—Purest commercial 98% sulphuric acid gives a very irregular polarogram. However, if water is added to give a 97 or 96% acid, and this is stirred under reduced pressure for $1\frac{1}{2}$ hr., a perfectly level base line up to the breakdown potential of the acid (*ca.* -0.9 v) is obtained. The conductivity of sulphuric acid being sufficient, no base-electrolyte is required. The ionogenic precursor (olefin or carbinol) was introduced by a syringe against a flow of dry nitrogen, as an approximately 10^{-2}M -solution in carbon tetrachloride. If the acid is well stirred it extracts the precursor rapidly from the solution, with minimal side-reactions.

TABLE

*Polarographic characteristics of some carbonium ions*Temperature $20 \pm 2^\circ$; concentrations in the range 10^{-5} to 5×10^{-3} M.All figures are the average of at least four experiments; uncertainty in $E_{\frac{1}{2}}$ values ± 0.01 v.

Precursor	Ion	HClO ₄ in CH ₂ Cl ₂		97% H ₂ SO ₄		<i>I</i> ^g (ev)
		$-E_{\frac{1}{2}}$ (v)	<i>nα</i>	$-E_{\frac{1}{2}}$ (v)	<i>nα</i>	
Ph ₃ CHOH	Ph ₃ C+H	0.00	0.8	0.59	1.7	7.35
Ph ₃ C+ClO ₄ ⁻	Ph ₃ C+	0.12—0.14 ^a	—	—	—	—
Ph ₃ CCl + HgCl ₂ ^b	Ph ₃ C+	0.14	—	—	—	—
Ph ₃ CH + Ph ₃ CH ^c	Ph ₃ C+	0.13	—	—	—	—
Ph ₃ COH	Ph ₃ C+	0.15 ^d	—	0.78	1.9	7.25
Best value	Ph ₃ C+	0.135 ± 0.01	0.9 ^e	—	—	—
Ph ₂ C:CH ₂	Ph ₂ C+CH ₃	0.06	0.8	0.76	1.7	—
Ph ₂ C:CHPh	Ph ₂ C+CH ₂ Ph	0.05	0.7	0.72	1.6	—
Ph ₂ C:CPh ₂	Ph ₂ C:CPh(C ₆ H ₆) ⁺	-0.22	0.7	— ^f	—	—
1,3,5-Cycloheptatriene	Tropylium	0.45	0.9	0.87	1.9	6.60
(C ₃ H ₅) ₂ CH-OH	(C ₃ H ₅) ₂ C+H	—	—	0.87	1.8	—

^a Range of ten experiments with the salt; no HClO₄ added.^b No HClO₄ added.^c Progressive changes in the polarogram show disappearance of the diphenylmethyl and appearance of the trityl ion, which is complete in 1 hr. at concns. of 10^{-3} M.^d Two experiments only, both giving 0.15 v.^e Mean value from all experiments with trityl ion.^f Olefin insoluble in sulphuric acid.^g *I* is the ionisation potential of the radical corresponding to the ion shown in column 2.

Methylene dichloride.—Polarographic measurements on organic cations in this solvent require that the conductivity of the system be adequate, and that the ion be either added as a salt or generated from a precursor (olefin or carbinol) and an acid, preferably anhydrous perchloric acid. Therefore the apparatus must permit introduction of reagents, by breaking phials and/or by syringe and the choice of base-electrolytes is limited to perchlorates; we used methyltriethylammonium perchlorate because it is very soluble in methylene dichloride. Since the presence of water and oxygen produces unwanted polarographic waves, it is advantageous to evacuate the observation vessel, and to distil the solvent into it from a reservoir in which the solvent is kept over a drying agent under its own vapour pressure.

Apparatus.—The apparatus with its ancillary solvent reservoir and dosing burette was developed from and resembles closely, Biddulph and Plesch's adiabatic reaction calorimeter.⁴ The observation vessel is a round-ended, flanged tube, 5 cm. diameter, and 7—10 cm. long, fitting a flanged head whose five B.14 sockets carry the following fittings: capillary (dropping mercury electrode) connected to mercury reservoir; connection to mercury pool anode; phial breaker,⁴ providing also connection to vacuum manifold and solvent reservoir; access port for syringe needle, with inlet for nitrogen; thermocouple.

Once the apparatus and solvent had been evacuated, both solvent systems could be used *in vacuo* or under dry nitrogen and both procedures

give the same results. Operation under nitrogen has the great advantage of permitting the introduction of several consecutive portions of reagents. For recording the polarograms a Tinsley Mk 19 and a Cambridge recording polarograph were used.

Results and discussion.—The results are summarised in the Table. In each case the presence of the ion was confirmed spectroscopically on samples taken from the reaction mixture. Under optimum conditions 10^{-5} M-ions could be identified with certainty.

In both solvents the polarograms had maxima when the concentration of ions exceeded ca. 10^{-3} M. The number of electrons involved in the reactions was found from the conventional plots of $\log i/(i_d - i)$ against V (i = current, i_d = diffusion current or "step height", V = applied potential) to be not integral (*nα* in Table), which shows the reductions to be irreversible, in the polarographic sense; the *nα* values indicate that in methylene dichloride one, and in sulphuric acid, two electrons take part in the reduction.

For the trityl ion in methylene dichloride the diffusion current varied linearly with concentration (2.5 to 5.5×10^{-3} M) and with temperature (17° to 24°). The half-wave potential $E_{\frac{1}{2}}$ was independent of these variables and of the reaction by which the ion was generated (the variations shown in the Table are random, due to instrument errors).

The $E_{\frac{1}{2}}$ values show a (non-linear) correlation with the ionisation potential *I* of the corresponding radicals. They generally follow the expected

order of stability, with one exception. One would expect the 1,1,2-triphenylethyl ion to be more stable than the diphenylmethylmethyl ion; that this is not so in these solutions is presumably due to the greater solvation energy of the smaller ion. The most unstable ion in our list is that derived from tetraphenylethylene, which shows that it must have a structure fundamentally different from those derived from triphenylethylene or 1,1-diphenylethylene and confirms the suggestion that protonation takes place at one of the phenyl rings.⁵

The ion derived from dicyclopropylmethanol had λ_{\max} 279 m μ and we attribute this to the dicyclopropylmethyl ion, since this ion has been reported⁶ to have λ_{\max} 273 m μ in a mixture of sulphur dioxide and antimony pentafluoride.

This work has shown that polarography can become a useful, general method for identifying and estimating organic cations, and grading them according to their stability in solution, under the very conditions in which their reactions are studied.

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