The Relation between Reduction Potential and Solvation Energy for some Arylmethylium Ions

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The polarographic half-wave potentials, $E_{\frac{1}{2}}$, of arylmethylium ions in $MeSO_3H$ range from −0.275 V for Ph_2HC^+ to −0.955 V for $(4\text{-}MeOC_6H_4)_3C^+$, against the $Hg/HgSO_4/98\%\ H_2SO_4$ electrode. The narrowness of this span, equivalent to *ca.* 70 kJ mol^{-1}, is explained in terms of the ionization potentials E_i of the corresponding radicals and the solvation enthalpies ΔH°_S of the ions. Since the factors which increase E_i also diminish ΔH°_S, the sum of E_i and ΔH°_S, which determines $E_{\frac{1}{2}}$, does not change much from one extreme of the array of ions to the other, although both terms may vary over a much greater range. A comparison of $E_{\frac{1}{2}}$ for the three triarylmethylium ions in $MeSO_3H$ and CH_2Cl_2 shows that (*a*) as the charge becomes more diffuse, the difference between $E_{\frac{1}{2}}$ for any one ion in the two solvents I and II, $_{\mathrm{I-II}}\Delta E_{\frac{1}{2}}(\mathrm{R}^+)$, becomes smaller; and (*b*) the difference in $E_{\frac{1}{2}}$ between two ions, $^{\mathrm{A-B}}\Delta E_{\frac{1}{2}}$ becomes smaller for a given solvent, the more polar that solvent. The value of $E_{\frac{1}{2}}$ obtained in different solvents can be correlated by a new kind of diagram in which the origin of the axes represents the $E_{\frac{1}{2}}$ of Ph_3C^+. For each of three very different ions the $E_{\frac{1}{2}}$ values are almost identical in CH_2Cl_2 and MeCN; this can be attributed to the fact that $E_{\frac{1}{2}}$ is not that of a free cation, but of a cation which is part of an ion pair or a higher aggregate, formed from the abundant supporting electrolyte.

In the course of our polarographic studies on organic cations we determined the half-wave potentials, $E_{\frac{1}{2}}$, for various arylmethylium ions.[1–11] The aim of the present work was to extract from these values some new information concerning the relative magnitude of their solvation enthalpies in three very different solvents. A comparison of our results [obtained in methanesulphonic acid (MSA) and dichloromethane (DCM)] with those of Volz and Lotsch[12] [obtained in cyanomethane (CM) solutions] yields some useful conclusions.

Table 1. $E_{\frac{1}{2}}$ values of carbenium ions in $MeSO_3H$ at *ca.* 295 K. [Ion] = 10^{-3} mol dm^{-3}. Reference electrode; $Hg/HgSO_4/98\%\ H_2SO_4$.

Ion number	Cation	$-E_{\frac{1}{2}}$/V	$n\alpha$
1	Ph_2HC^+	0.275	0.88
2	Ph_2MeC^+	0.565	0.92
3	$Ph_2(n\text{-}C_3H_7)C^+$	0.575	0.88
4	3-Methyl-1-phenylindan-1-yl	0.585	0.85
5	$(4\text{-}ClC_6H_4)_3C^+$	0.61	—
6	$(4\text{-}MeOC_6H_4)_2HC^+$	0.62	—
7	Ph_3C^+	0.635	1.0
8	$(2\text{-}EtC_6H_4)PhMeC^+$	0.66	—
9	$(2,4\text{-}Me_2C_6H_3)_3C^+$	0.70	0.69
10	$(2\text{-}MeC_6H_4)_3C^+$	0.745	0.80
11	$(4\text{-}MeC_6H_4)_3C^+$	0.745	1.0
12	$(4\text{-}MeOC_6H_4)Ph_2C^+$	0.82	—
13	$(4\text{-}MeOC_6H_4)_3C^+$	0.955	—

Results and Discussion

$E_{\frac{1}{2}}$ *in MSA.*—In MSA the ions listed in Table 1 give a single reduction signal (wave or peak, depending on the apparatus used), and as the corresponding $E_{\frac{1}{2}}$ value depends slightly on the concentration of the precursor from which the ion is generated, all potentials are given for 10^{-3} mol dm^{-3} solutions.[3] This signal corresponds to reduction of the carbenium ion to the radical:[2]

$$\mathrm{R^1R^2R^3C^+ + e \rightarrow R^1R^2R^3C^\bullet} \qquad (1)$$

The fate of the radical does not concern us here. The appropriate tests showed that the reductions are diffusion controlled, and the $n\alpha$ values in Table 1 show that most of the reductions are reversible or nearly so.

The ranking of the ions in Table 1 is as expected, but the difference between $E_{\frac{1}{2}}$ for the most reactive ion (No. 1) and the most inert ion (No. 12), amounts to only *ca.* 70 kJ mol^{-1}. This first part of the Discussion attempts to explain why this span is so unexpectedly small. We start with the well-known approximate identification of $E_{\frac{1}{2}}$ with E° (the standard reduction potential of the ion measured against some arbitrary standard in the first instance (see the Appendix); and we relate E° to ΔG° for the reduction process (1), so that we obtain:

$$-FE_{\frac{1}{2}} \approx -FE^\circ = \Delta G^\circ \qquad (2)$$

Further,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (3)$$

and

$$\Delta H^\circ = \Delta H^\circ_S(\mathrm{R^+}) - E_i(\mathrm{R^\bullet}) - \Delta H^\circ_S(\mathrm{R^\bullet}) + Z' \qquad (4)$$

Here $\mathrm{R^+}$ is the carbenium ion from equation (1), ΔH°_S are solvation enthalpies, $E_i(\mathrm{R^\bullet})$ is the ionization potential of radical $\mathrm{R^\bullet}$, and Z' includes all electro-energetic terms which do *not* depend upon the nature of R. If, to a first approximation, $T\Delta S^\circ$ and $\Delta H^\circ_S(\mathrm{R^\bullet})$ are taken to be independent of the nature of R and are incorporated into Z, then:

$$Z = Z' - \Delta H^\circ_S(\mathrm{R^\bullet}) - T\Delta S^\circ \qquad (5)$$

and

$$-FE_{\frac{1}{2}} \approx \Delta H^\circ = \Delta H^\circ_S(\mathrm{R^+}) - E_i(\mathrm{R^\bullet}) + Z \qquad (6)$$

Table 2. $E_{\frac{1}{2}}$ values for three ions in two solvents.

Ion	CH_2Cl_2 $E_{\frac{1}{2}}$/V	CH_2Cl_2 ${}^{A-B}\Delta E_{\frac{1}{2}}$/V	${}_{I-II}\Delta E_{\frac{1}{2}}$/V	$MeSO_3H$ $E_{\frac{1}{2}}$/V	$MeSO_3H$ ${}^{A-B}\Delta E_{\frac{1}{2}}$/V
$(4\text{-}ClC_6H_4)_3C^+$	0.6	0.135	1.21	−0.61	0.025
Ph_3C^+	0.465	0.465	1.10	−0.635	0.320
$(4\text{-}MeOC_6H_4)_3C^+$	0.00		0.955	−0.955	

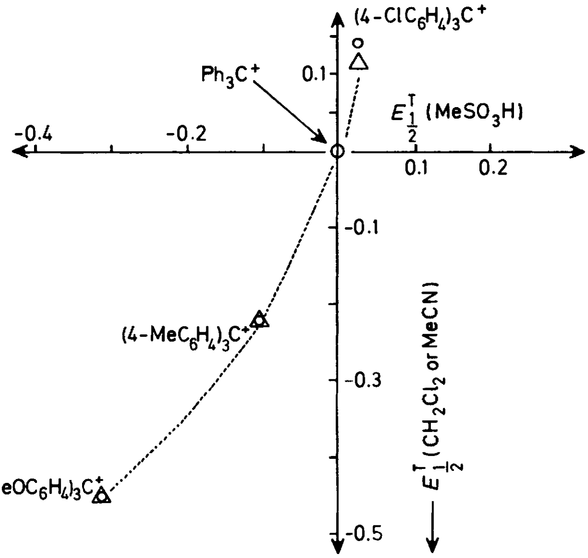

Figure. The correlation between $E^{\mathrm{T}}_{\frac{1}{2}}$ in $MeSO_3H$ and in CH_2Cl_2 (○) and MeCN (△).

This type of analysis is not new (see below) but, unlike some previous authors, we will refrain from attempting an absolute evaluation of Z and instead investigate what information can be extracted from a differential approach.

If one writes equation (6) for two ions, A and B, in the same solvent and subtracts one from the other, one obtains for ${}^{A-B}\Delta E_{\frac{1}{2}}$, the difference between the half-wave potentials of the two ions, equation (7):

$$-F\,{}^{A-B}\Delta E_{\frac{1}{2}} = \Delta H^{\circ}_{S}(A^+) - E_i(A^{\cdot}) - \Delta H^{\circ}_{S}(B^+) + E_i(B^{\cdot}) \quad (7)$$

This equation helps us to understand why $\Delta E_{\frac{1}{2}}$ of the ions at the extremes of Table 1 is so relatively small: the reason is that those factors which reduce E_i, such as increasing substitution by Me or MeO groups, do so by reducing the charge density at the central C-atom and therefore they also produce a reduction in the enthalpy of solvation, $\Delta H^{\circ}_{S}(R^+)$. Therefore, although both ΔH°_{S} and E_i for different ions can vary over a wide range, their difference changes only slightly.

It is of course evident that if one could obtain the E_i values for any two radicals $R^{\cdot}$, the corresponding $\Delta\Delta H^{\circ}_{S}$ could be calculated. It is curious that although most of the radicals of interest here could probably be generated simply by introducing the corresponding dimers into a mass spectrometer where they would dissociate into the required radicals, their ionization potentials do not appear to have been measured.

A useful practical result of our work is that $E_{\frac{1}{2}}$ of the triphenylmethylium ion was found to be a convenient reference potential for strongly acidic solutions as the ion is very stable under such conditions, for which, in fact, there is no other convenient standard.

Comparison of $E_{\frac{1}{2}}$ *in MSA and DCM.*—Polarography in pure liquid acids such as MSA is relatively simple because the ions resulting from the self-ionization of the acid provide the conductivity needed, and the main operating precautions required are the exclusion of oxygen (for electrical reasons) and of water (for chemical reasons). In solvents which do not self-ionize, (which means effectively all organic liquids which are not acids) polarography is more difficult because a supporting electrolyte is needed to provide adequate conductivity. The use of a supporting electrolyte, *e.g.* tetrabutyl ammonium perchlorate, introduces three complications: unless it is very rigorously dried, it will carry with it an important quantity of water; its nature and concentration influence the $E_{\frac{1}{2}}$ (slightly); and, because its concentration is usually in the 10^{-1} mol dm^{-3} range, the polarographic reduction is no longer that of an isolated ion, but that of an ion which is part of an ion-pair or a higher aggregate.

It should be possible to obtain $E_{\frac{1}{2}}$ for unpaired ions either by Fleischmann's technique[13] (which was published too late for the Keele Research Group, now dispersed, to make use of it), or by extrapolating $E_{\frac{1}{2}}$, obtained conventionally with varying concentrations of supporting electrolyte, to zero ionic strength.

Table 2 contains $E_{\frac{1}{2}}$ values for three ions in the two solvents MSA and dichloromethane. Two effects are evident: (*a*) the minor effect is that ${}_{I-II}\Delta E_{\frac{1}{2}}$ (difference between two solvents) becomes smaller as the charge becomes more diffuse; (*b*) a much stronger effect is that ${}^{A-B}\Delta E_{\frac{1}{2}}$ (difference between two ions) is much smaller for the more polar solvent.

As before, one can seek an explanation in terms of the energetics of the processes involved. The formulation of equation (4) for ion A^+ and the two solvents I and II yields equation (8) for the difference between the $E_{\frac{1}{2}}$ values obtained for the same ion in the two solvents:

$$-F_{I-II}\Delta E_{\frac{1}{2}}(A^+) = \Delta H^{\circ}_{S}(A^+)_{I} - \Delta H^{\circ}_{S}(A^+)_{II} + Z'_{I} - Z'_{II} - T[\Delta S^{\circ}(A^+)_{I} - \Delta S^{\circ}(A^+)_{II}] \quad (8)$$

As before, the Z' terms are independent of the nature of A^+.

The first, minor, effect, interpreted by equation (8), means that as the charge on the ions becomes more diffuse, the differences between the ΔH°_{S} terms, *i.e.* between $\Delta H^{\circ}_{S}(A^+)_{I} - \Delta H^{\circ}_{S}(B^+)_{I}$ and $\Delta H^{\circ}_{S}(A^+)_{II} - \Delta H^{\circ}_{S}(B^+)_{II}$, becomes smaller, and so does the difference in the ΔS° terms, which seems very plausible.

The second, and major, effect means that in the more polar solvent, in which the ΔS° values are relatively large, the change in ΔH°_{S} accompanying the change of charge-density from one ion to another is a relatively small change in a large quantity. By contrast, in the less polar solvent we are dealing with a relatively large change in a much smaller quantity.

Normalization of $E_{\frac{1}{2}}$ *Values.*—In view of the useful interpretations which can be given to the differences in $E_{\frac{1}{2}}$ values, an obvious step is to select the $E_{\frac{1}{2}}$ of one convenient ion as a zero or reference point. We follow Taft[14] and Breslow[15] in selecting $E_{\frac{1}{2}}$ for the triphenylmethylium (trityl) cation, as this ion is easy to procure and is stable under acidic conditions. It seems useful to define a quantity $E^{\mathrm{T}}_{\frac{1}{2}}$ which is $E_{\frac{1}{2}}$ of the species in question minus $E_{\frac{1}{2}}$ of the triphenylmethylium ion measured under the same conditions of concentration, temperature, solvent, and nature and concentration of base electrolyte, and against the same reference electrode:

Table 3. $E_{\frac{1}{2}}$ Values for three triarylmethyl ions in two solvents.

	I (CH_2Cl_2)		II(MeCN)		
	$E_{\frac{1}{2}}$	$E^T_{\frac{1}{2}}$	$E_{\frac{1}{2}}$	$E^T_{\frac{1}{2}}$	$_{I-II}\Delta E^T_{\frac{1}{2}}$
$(4\text{-}ClC_6H_4)_3C^+$	+0.60		+0.38		
		+0.14		+0.11	+0.03
Ph_3C^+	+0.46		+0.27		
		−0.46		−0.47	−0.01
$(4\text{-}MeOC_6H_4)_3C^+$	0.00		−0.20		

$$E^T_{\frac{1}{2}} \equiv E_{\frac{1}{2}}(R^+) - E_{\frac{1}{2}}(Ph_3C^+) \qquad (9)$$

The advantage of this procedure is that one can make useful comparisons between sets of measurements obtained under a variety of conditions. An informative example of the method is presented in the next section. In practice, it is often convenient to add trityl cations to a solution of an 'unknown' as a marker; one must, however, beware of offering to the trityl cation a substrate from which it can abstract a hydride or other ion, with formation of a more stable cation.[8]

Correlation of $E_{\frac{1}{2}}$ *Obtained in Different Solvents.*—Results obtained by ourselves on the ions 5, 7, 11, and 13 (Table 1) in MSA and DCM, and by Volz and Lotsch[12] in CM, are listed in Table 3 and plotted in the Figure, normalized against $E_{\frac{1}{2}}$ of the trityl ion, as suggested in the previous section. A remarkable feature which emerges from this representation of the results is that $E^T_{\frac{1}{2}}$ in DCM and CM seems to be independent of the solvent, despite the great difference in the dielectric constants, ε, of these solvents (DCM, $\varepsilon = 9$; CM, $\varepsilon = 37$), from which differences in ΔH°_{S}, and hence $E_{\frac{1}{2}}$, would be expected. The reason is that the measured $E_{\frac{1}{2}}$ value is not that of an isolated ion, but of one which is at least paired because of the high concentration of supporting electrolyte. If the free energy of the cation in solution is reduced by the Coulombic interaction resulting from ion-pairing, any further reduction by solvation of the resulting ion-pair is a relatively minor effect in which the dielectric constant of the solvent is not a dominant factor. Nonetheless, the very fact that there is a correlation between the reduction potentials of the paired and unpaired ions indicates clearly that the near-neutralization of the cation by pairing does not obliterate, let alone reverse, the energetic differences between the cations.

Relation to Earlier Work.—The direct access to the electrical-energetic properties of an ion-in-solution which polarography and related electro-analytical techniques seem to offer, has invited many attempts to interpret the results in terms of fundamental energetic quantities, such as ionization potentials and solvation enthalpies. An early and seminal analysis by Case *et al.*[16] was followed up by an extension of the theory to various aromatic cations by Kothe *et al.*[17] They attempted the absolute calculation of the solvation enthalpies of cations, molecules, and anions of the triphenylmethyl series, and our equations (4) and (6) are derived by implicit arguments closely related to theirs, but we have preferred not to follow their attempts at absolute calculations. Such calculations are inevitably beset by a lack of data (in this instance especially the ionization energies of the radicals) and by the need for approximations of various kinds. For example, Kothe *et al.* attempted to calculate the electrical contribution to the solvation enthalpy by Born's equation, applicable to an isolated spherical ion, uninhibited by the fact that they then combined it with half-wave potentials obtained for planar ions at high ionic strength.

The relative stabilities of various carbenium ions in sulphuric acid were studied by Feldman and Flythe and discussed in terms of the energetics of ion formation.[18] However, their arguments are obscure, because they do not appear to define adequately the various energetic terms and seem to ignore solvation energies; moreover, they appear to be unaware of the near-contemporary British[16] and German[17] work. These studies are also ignored by Wasielewski and Breslow[19] who used thermodynamic arguments to derive the basicity of various cyclopropenyl anions and the bond-dissociation energies of cyclopropenols from electrochemical measurements; they also included measurements on the trityl and tropylium cations.

It therefore appears that although the fundamental basis of our considerations is not new, the use which we have made of the energetic analysis provides a better insight into the factors determining the electrochemical properties of organic cations; in other words it is heuristically more useful.

Experimental

The polarographic apparatus, reference electrodes, supporting electrolytes, solvent preparation, and preparation of the carbenium-ion solutions have been described in refs. 1–11 and 20. It is noteworthy that the reference electrode[9] described in 1978 maintained its emf of −0.130 *vs.* SCE until accidentally broken in 1983.

Appendix

In view of the range of conclusions which will be derived from the 'approximate identification of $E_{\frac{1}{2}}$ with $E^{\ominus}$' it is appropriate to clarify what is involved. We mean here that $E_{\frac{1}{2}} = E^{\ominus} + x$; the term x is omitted in the subsequent treatment because, as we will show below, it is both small and approximately constant under the relevant conditions. From the theory of polarography it follows that for reversible, one-electron systems

$$E_{\frac{1}{2}} = E^{\ominus\prime} + (RT/2F)\ln(D_R/D_O) \qquad (10)$$

where D_R and D_O are the diffusion coefficients of the reduced and oxidized forms of the electroactive species, and

$$E^{\ominus\prime} = E^{\ominus} + (RT/F)\ln(\gamma_O/\gamma_R) \qquad (11)$$

where γ_O and γ_R are the mean ionic activity coefficients of the reduced and oxidized electroactive species, respectively.[21] The shape and size of the tetrahedral triarylmethyl radical and of the propeller-shaped corresponding cation, even assuming that it carries one firmly attached solvent molecule, are very similar. For the present purposes, it is not necessary to assume that they are equal; we need only make the plausible assumption that their ratio is fairly constant, both when comparing a range of ions in one solvent and for one ion in several solvents. If we denote D_R/D_O by Q and combine equations (10) and (11), we obtain:

$$E_{\frac{1}{2}} - E^{\ominus} = (RT/F)\ln Q^{1/2}\gamma_O/\gamma_R = x \qquad (12)$$

Since Q is independent of the nature of the solvent and of the ion, $\ln Q^{1/2}$ is a constant, and probably very small, term for the reasons given above.

The reduced species is the radical $R^{\bullet}$ the activity coefficient of which, γ_{Ox}, is close to unity. The oxidized species, at any rate in the organic solvents, is not the lone carbenium ion R^+, but one that is part of an ion-pair because of the relatively high ionic strength and the low polarity of the solvents. Therefore γ_R is also close to unity and probably does not vary much from one solvent to another. Therefore our initial assumption, that x is both small and constant, is seen to be justified.

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