The Formation of Relatively Stable Protonated Anion-radicals in the Cathodic Hydrogenation of Quinonemethides

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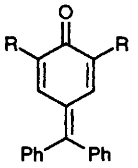
Examination of the cathodic hydrogenation of two examples of quinonemethides reveals an unusual pathway in which the anion radicals of the quinonemethides fuchsone and its dimethyl analogue are protonated reversibly at oxygen by substituted phenols in DMSO to give relatively stable triarylmethyl radicals which are not reduced at the first reduction potential of the quinonemethides; this behaviour contrasts with that usually found, *i.e.* anion-radicals are usually formed at more cathodic potentials than reduction potentials of radicals derived from them by protonation.

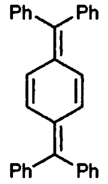
The anion-radical of fuchsone **1** is formally a relatively weakly basic phenolate yet it is an effective electrogenerated base in DMF solution.[1] In this context protonation of anion-radicals derived from **1** and from its dimethyl analogue **2** reveals the unusual formation of a relatively long-lived triarylmethyl radical **5**, the electrochemical reduction of which can be observed because it is less easily reduced than the starting quinonemethide. This behaviour is importantly different from that normally found for cathodic hydrogenation.

The anion-radicals of **1** and **2** have two sites for protonation, *i.e.* at carbon or at oxygen in contrast to the anion radical of Thiele's hydrocarbon **3** which can protonate only at carbon. We have taken **3** as a hydrocarbon analogue of the quinonemethides.

In the absence of proton donors cyclic voltammetry reveals the anion-radicals of **1** and **2** to be stable at all applied sweep rates in the range 0.1 V s^{-1} to 2000 V s^{-1} (peaks R^1 and O^1 in Fig. 1); for **3** this is the case at sweep rates >10 V s^{-1}. The dianion formation is completely chemically reversible only at high sweep rates (>500 V s^{-1}), presumably because these highly basic species react rapidly with residual water in the solvent (DMSO). This is consistent with the value at low sweep rates of $-dE^p_2/d\log v$ = 30 mV, found for **1** and **2**, *i.e.* an EC reaction first-order in dianion. The relevant reversible potentials are displayed in Table 1.



R
1 Bu^t
2 Me



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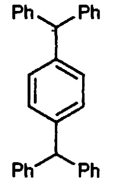

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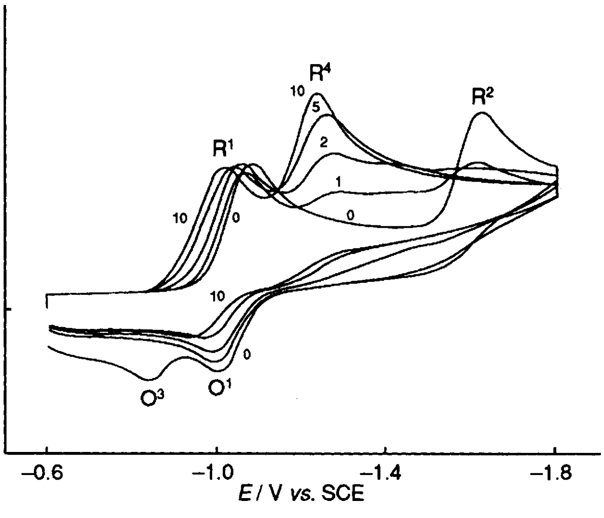


Fig. 1 Cyclic voltammetry of **2** at 10 V s^{-1} at a Hg cathode (0.6 mm diameter). Substrate 1 mmol dm^{-3} in DMSO (0.1 mol dm^{-3} Bu_4NPF_6) in the presence of: 0. 1, 2, 5 and 10 mmol dm^{-3} of 4-chlorophenol.

The separation of the first and second peak potentials (corresponding to R^1 and R^2 in Fig. 1) is significant (Table 1). For the quinonemethides the E^0 values are separated by *ca.* 585 mV whereas for Thiele's hydrocarbon the separation is only 241 mV; the separations of R^1 and R^2 are less for the low-sweep rate experiments because of the anodic shift of R^2 caused by protonation of the dianion. From the $[E^0{}_2 - E^0{}_1]$ differences equilibrium constants for disproportionation of the anion-radicals can be calculated and are 8.4×10^{-5} for **3** and 1.1×10^{-10} for **1** and **2**.

Protonation of the dianions by residual water gives species of the type MH^- where M = **1**, **2** or **3**. At low sweep rates reversal of the cathodic sweep after R^2 gives a new oxidation peak, O^3, which is ascribed to oxidation of MH^-, Table 2. When M = **1** or **2**, the potential of O^3 is highly dependent on whether the electrode material is Hg or Pt, indicating the involvement of mercury in the process.

The dianions derived from **1** or **2** may be protonated either at oxygen or at carbon giving substituted triphenylmethyl anions and substituted phenolate ions, respectively. The relative thermodynamic stabilities of the two possible protonation products may be evaluated from the known pK_{DMSO} values for 2,6-dimethylphenol (18.5)[2] Ph_3CH (30.6)[3] and 2,6-di-*tert*-butylphenol (16.9)[3] showing that the dianions will protonate at carbon to give phenolate anions. Interpretation of O^3 as oxidation of anions of the phenolate type is further supported by oxidation of the corresponding phenolate ions formed by deprotonation of genuine samples of the parent

Table 1 Reversible potentials for first and second electron transfers

Compound	$-E^0{}_1$/V *vs.* SCE	$-E^0{}_2$/V *vs.* SCE	ΔE^0/V
1	1.152	1.740	0.588
2	1.074	1.661	0.587
3	1.493	1.734	0.241

Table 2 Oxidation potentials for the mono-protonated dianions[a]

M	$-E^0{}_3$ (Pt)	$-E^0{}_3$ (Hg)	$-E^p{}_3$ (Pt)	$-E^p{}_3$ (Hg)
1	0.22 (0.23)	—	0.16 (0.17)	0.81 (0.82)
2	— (0.17)	—	0.08 (0.10)	0.83 (0.81)
3	0.87	0.86	0.74	0.76

[a] Potentials *vs.* SCE. v = 10 V s^{-1}. Reversible potentials determined under steady-state conditions. Values in parenthesis refer to the analogous phenolate ions.

phenols, *cf.* Table 2. The oxidation potentials found at Pt-electrodes are in the same potential range as the potential reported for the chemically reversible oxidation of 2,4,6-tri-*tert*-butylphenolate in MeCN at Pt ($E^0 = -0.27$ V *vs.* SCE).[4]

The anion-radical of Thiele's hydrocarbon is protonated by residual water; at *ca.* 1 V s^{-1} the first peak is no longer reversible and the normalised height, $I_p/v^{1/2}$, of the first peak is increased relative to that of the second peak and to its normalised height at fast sweep rates. On a yet longer time scale, controlled potential coulometry showed that, even in the absence of added proton donor, Thiele's hydrocarbon **3** is smoothly reduced at either the first or second reduction potentials in a 2 F mol^{-1} process. Preparative-scale reduction at a mercury cathode and in only nominally dry DMF gave 2 F mol^{-1} reduction and the expected product **4**. In the presence of proton donor (4-chlorophenol) the first reduction peak doubles in height and is anodically shifted; the second reduction peak disappears. Based on the magnitude of the second-order rate constant determined from the kinetic shift of the two-electron peak in the presence of 4-chlorophenol protonation *via* disproportionation to the dianion can be ruled out; this indicates that in this case cathodic hydrogenation of Thiele's hydrocarbon **3** follows the mechanism already well established[5] for the 2e–2H$^+$ reduction of aromatic hydrocarbons, *i.e.* the protonated anion radical is more easily reduced than the starting material. Preparative electrolysis of **1** at the potential of the first peak in the presence of acid also gives clean 2 F reduction to the corresponding phenol. However, detailed examination reveals important differences in mechanism.

The anion-radicals of the quinonemethides are not protonated in the nominally dry solvents even at low sweep speeds. In these cases more information comes from experiments which involve the deliberate addition of acids under controlled conditions. The proton donors used, and their acidities,[2,3] were phenol (pK_{DMSO}, 18.0), 4-chlorophenol (pK_{DMSO}, 16.7) and 3-cyanophenol (pK_{DMSO}, 14.8).

In contrast to the behaviour of Thiele's hydrocarbon in cyclic voltammetry, addition of proton donor to 1 mmol dm^{-3} solutions of the quinonemethides leads not to an increase in the height of the first peak but to the appearance of a new peak, at a potential intermediate between the potentials of the first and second peaks. The second reduction peak height decreases with increasing proton donor concentration and completely disappears at proton donor concentrations higher than *ca.* 5 mmol dm^{-3} while at the same time the new peak grows.

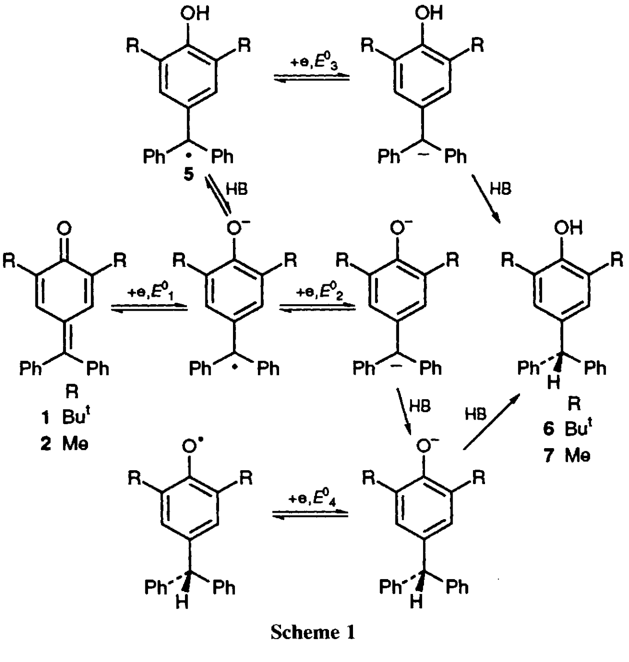
The observations are well rationalised by the mechanism outlined in Scheme 1. The peak appearing on addition of proton donor is that associated with reduction at R^4 of the oxygen-protonated anion-radical **5** which may be regarded as a substituted triphenylmethyl radical. The most convenient quinonemethide for detailed study is **2** because in this case the new peak in the presence of proton donor is well clear of the first reduction peak. The behaviour of **2** in the presence of one of the proton donors is given in Fig. 1. A key feature of the experiments with added proton donor is that the first reduction peak is shifted anodically, by an amount dependent on the concentration and acidity of the proton donor; the larger the concentration and the more acidic the proton donor, the larger the potential shift. However, if in derivative cyclic voltammetry[6] the scan is reversed prior to the potential of the new peak apparent chemical reversibility is retained for the first electron transfer process at relatively slow sweep speeds (*e.g.* 1 V s^{-1} with 4-chlorophenol in 40-fold excess). Significantly the reversibility is lost as the sweep speed is increased, *e.g.* for the above conditions the ratio of the two derivative peaks, R_I', is 0.62 at 100 V s^{-1}. This implies that reversible proton transfer is being observed, *i.e.* at the lower sweep speeds equilibrium is established whereas at the higher sweep speeds the back reaction (deprotonation) is intercepted. This interpretation is in agreement with the observation that the sweep rate necessary to intercept the back reaction decreases with increasing acidity of the proton donor (*i.e.* the larger the equilibrium constant for the proton transfer the slower is the back reaction).

Further support for the assignment of R^4 to reduction of the protonated anion-radical comes from a consideration of the published value of the reduction potential of the triphenylmethyl radical. For $Ph_3C\cdot$ in DMSO an E^0 value of -1.05 V (Pt cathode, *vs.* SCE) has been measured;[7] this may be compared with the $E^0{}_1$ values for the starting materials **1** and **2**—Table 1. The qualitative effect of hydroxyl and alkyl substitution on the triarylmethyl radicals formed by reduction and protonation of **1** and **2** will be to shift the E^0 values lower than -1.05 V. It is likely, based on the measured[8] effects on E^0 in dimethoxyethane solution of substitution into the phenyl groups, that such a shift from -1.05 V will be significant. This is consistent with the observation of the new reduction peaks which are to the negative side of -1.152 (for **1**) and -1.074 (for **2**).

The cathodic reduction of benzaldehyde in ethanolic buffers provides another example of such behaviour although in that case the neutral radical PhCH$\cdot$(OH) is not long-lived because it undergoes rapid dimerisation.[9] The reduction of the protonated anion-radicals in the quinonemethide systems are chemically irreversible at all sweep rates and -d$E^0{}_3$/dlogv = 30 mV. This is consistent with the initial formation of an unstable carbanion, *cf.* Scheme 1, which is rapidly protonated under the conditions necessary for protonation of the anion-radicals.

An understanding of the chemistry of these systems is important for the development of their use as probases for the cathodic production of electrogenerated bases. Fuchsone **1** has been shown to be an effective probase on a preparative time-scale for the cathodic generation of ylids from phosphonium salts and phosphonate esters.[1] The quinonemethides are attractive as probases, they are relatively simple to prepare, are easy to reduce and so may be used in the presence of other, less easily reduced, reactants. In the fuchsone case the product phenol is smoothly reoxidised to the quinonemethide and the radical-anions are also of low nucleophilicity.

By a happy combination of circumstances the anion-radical of fuchsone **1** deprotonates carbon acids such as phosphonium salts slowly but effectively on the preparative time-scale.[1]



Scheme 1

Despite the stability of the protonated anion-radical thus formed the reaction drives to completion (to the corresponding phenol and phosphorus ylide) because R^4 is in this case so close to the first reduction potential. Further work will determine missing, quantitative, details of the reaction scheme including the thermodynamic basicity of the anion-radicals as well as their kinetic basicities towards carbon and oxygen acids.

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References

1 M. O. F. Goulart, S. K. Ling-Chung and J. H. P. Utley, *Tetrahedron Lett.*, 1987, **28**, 6081.
2 F. G. Bordwell, *Summary of pK$_a$'s in DMSO*, personal communication.
3 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.
4 J. A. Richards, P. E. Whitson and D. E. Evans, *J. Electronal. Chem., Interfacial Electrochem.*, 1975, **63**, 311.
5 M. F. Nielsen and O. Hammerich, *Acta Chem. Scand.* 1989, **43**, 269 and references cited therein.
6 V. D. Parker, in *Topics in Organic Electrochemistry*, ed. A. J. Fry and W. E. Britton, Plenum, New York 1986, ch. 2.
7 R. Breslow and W. Chu, *J. Am. Chem. Soc.*, 1975, **95**, 411.
8 S. Bank, C. L. Ehrlich and J. A. Zubieta, *J. Org. Chem.*, 1979, **44**, 1454; S. Bank, C. L. Ehrlich, M. Mazur and J. A. Zubieta, *J. Org. Chem.*, 1981, **46**, 1243.
9 E. Laviron and J.-C. Lucy, *Bull. Soc. Chim. Fr.*, 1966, 2202; C. P. Andrieux, M. Grzeszczuk and J.-M. Saveant, *J. Am. Chem. Soc.*, 1991, **113**, 8811.