

Review Article

# Redox Properties of Free Radicals<sup>1</sup>

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## Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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The direct electrochemical detection of free radicals by photomodulation voltammetry is reviewed. The relationship between the measured half-wave potentials and the standard potentials, applications in thermochemical cycles and the balance between delocalization and solvation in benzylic and alkyl systems are discussed. Some new data on the redox properties of the most simple alkyl radicals, i.e. methyl, ethyl, 2-propyl and *tert*-butyl are presented.

Over the years there has been growing interest in experimental approaches to distinguish organic chemical reactions that involve simple nucleophilic/electrophilic processes from those involving electron transfer. In general, this first requires a thermochemical estimate of the feasibility of electron transfer from the relevant electrode potentials. This allows, in turn, the rate of an electron transfer reaction to be estimated using Marcus theory. Comparison of the predicted rates of electron transfer with experimentally determined values often, but not always, allows a mechanistic distinction to be made. For a detailed discussion of the applications of Marcus theory to the study of electron transfer in organic chemistry we refer the reader to *Electron Transfer in Organic Chemistry* by Lennart Ebersson.<sup>2</sup>

When combined with other thermodynamic parameters, electrode potentials can be used to estimate either homolytic or heterolytic bond dissociation energies.<sup>3</sup> One of the first applications of redox potentials of organic ions in thermochemical cycles was, in fact, reported Ebersson and coworkers in 1963.<sup>4</sup> This seminal work stimulated a number of studies and developments that continue today. Breslow used thermochemical cycles to estimate the  $pK_a$  values of weak acids (including methane) as well as  $pK_{R+}$  values of alcohols.<sup>5–12</sup> Nicholas and Arnold devised three cycles in order to estimate the  $pK_a$  of toluene radical cation.<sup>13</sup> While these cycles are all equivalent, they provided slightly different values and point to the importance of understanding and evaluating the reliability of thermochemical data from the literature.

In particular, great care must be taken when combining data that pertain to the gas phase with solution values or when combining measurements made in more than one solvent. Bordwell and coworkers overcame this problem by using  $pK_a$  values and redox values that they obtained in DMSO to estimate the  $pK_a$  of a number of radical cations in that solvent.<sup>14–18</sup>

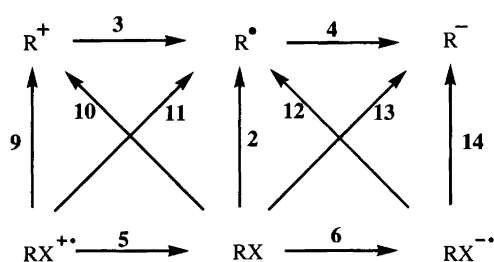
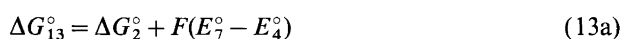
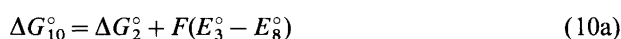
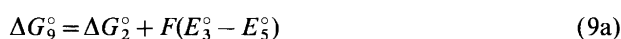
More recently, attention has been shifted towards the use of electrode potentials to estimate homolytic bond energies. The groups of Bordwell<sup>19–30</sup> and Arnett<sup>31–36</sup> have determined the homolytic bond energies of a large number of C–H, O–H, N–H, C–C, C–O, C–S and C–N bonds. The X–H bond dissociation energies (BDE) were determined using an empirical approach in which the bond dissociation enthalpy is related to the oxidation potential of the conjugate base,  $E^{ox}(X^-)$  and the  $pK_a$  of the neutral acid [eqn. (1)]. The empirical relationship has provided hundreds of bond energies that cannot be otherwise determined. However, some care must be taken as there are no corrections in the empirical relationship for systematic deviations in the electrode potentials due to monotonic changes in homogeneous kinetics<sup>3</sup> or for hydrogen bonding between the solvent and highly acidic X–H bonds.<sup>37</sup>

$$BDE = 1.37pK_a + 23.06E^{ox}(X^-) + C \quad (1)$$

The relationships between electrode potentials and the homolytic and heterolytic cleavage reactions of a molecule, RX, and its corresponding radical ions can be represented conveniently in a thermochemical mnemonic as shown in Scheme 1.<sup>3</sup> This Scheme is completely defined by only seven independent parameters which can be

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written as the sum of a bond dissociation free energy (BDFE),  $\Delta G_2^\circ$ , and the difference between two standard potentials [ $E^\circ$ , eqns. (2)–(14)]. The explicit thermochemical relationships based on the homolytic BDFE [eqn. (2)] and six electrode potentials are given as eqns. (9a)–(14a). The mnemonic is of practical value in that it allows the parameters required to complete a thermochemical cycle to be easily visualized. The vertical arrows represent the loss of  $X^\cdot$ , the horizontal arrows the addition of an electron, and the diagonal arrows the loss of  $X^+$  (up to the right) and of  $X^-$  (up to the left). For  $X=H$ , it can be seen that eqn. (13) is transformed into eqn. (1).



Scheme 1. Thermochemical mnemonic describing the interrelationship of thermodynamic parameters.

One of the problems that has limited the use of thermochemical cycles has been the dearth of relevant redox data. In the gas phase the ease with which a radical loses or gains an electron is characterized by its ionization potential (IP) and electron affinity (EA). Many of these

data have been tabulated or are available from databases.<sup>38,39</sup> In energetic terms, these values represent the differences between the enthalpies of formation of the radical and respective ions. Conversion into electrode potentials is problematic as it requires both a correction for solvation of the ions as well as for an entropy change to convert enthalpy into free energy.

### Redox potentials of radicals

Direct determination of standard potentials of organic molecules has been the preoccupation of many organic electrochemists. For chemically reversible couples the measurements are straightforward. However, the vast majority of organic ions and radical ions are very short-lived (i.e. chemically irreversible) and not amenable to direct determination. Provided the heterogeneous kinetics are favorable, it is sometimes possible to measure voltammograms at a very high scan rate (up to  $10^6 \text{ V s}^{-1}$ ) so the timescale of the voltammetric experiment is similar to the lifetime of the radical ion.<sup>40</sup> However, there are other problems associated with making direct electrochemical measurements on radicals since both the radical and product ions are often very short-lived. To establish these data two experimental approaches have been used. Electrochemical measurements have been made on solutions of stable ions. However, there are only a limited number of organic ions that can be prepared in this way. Alternatively, electrochemical measurements have been made on solutions of transient radicals. This requires that the radicals are produced in relatively high concentrations and that the measurements are complete in a short period of time (ca.  $10^{-9}/[R^\cdot] \text{ s}$ ).

Henglein used pulse radiolysis to generate free radicals in aqueous solutions and detected their oxidation or reduction using a hanging mercury drop. Since pulse radiolysis produces a known concentration of radicals this technique also allowed the kinetics of the free radicals to be determined. Savéant and coworkers<sup>41</sup> used a laser to photoeject electrons from a metal electrode into non-aqueous solutions and devised a method to measure the reduction of radicals produced by the dissociative electron capture of the solvated electrons. One of the limitations of this approach is that the measurements must be made below the potentials of zero charge of the electrode since the yield of solvated electrons is negligible at or above this value. We refer readers to the literature for detailed descriptions of these techniques. In this paper we will review a method developed in our laboratory for the direct determination of oxidation and reduction potentials of photochemically generated free radicals.

### Photomodulation voltammetry

We have developed an electrochemical method (photomodulation voltammetry, PMV) that makes use of the modulation principle to increase the sensitivity of electrochemical detection.<sup>3,42-53</sup> The apparatus (Fig. 1) can

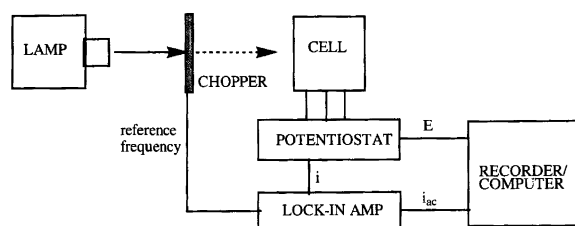


Fig. 1. Block diagram of the photomodulation instrument.

detect radicals having lifetimes of the order of 1 ms at concentrations as low as  $10^{-7}$  M. In general the timescale of detection is not a problem since most radicals disappear by a second-order self-reaction. The principle of operation is reasonably straightforward. Radicals are produced by photolysis using a high pressure Hg-Xe lamp whose output is modulated sinusoidally using a mechanical chopper.

Two methods are used to generate the radicals. Photolysis of a suitable precursor (e.g. a ketone) produces the radical directly [eqn. (15)]. Perhaps a more general approach is the photolysis of di-*tert*-butyl peroxide to generate reactive *tert*-butoxyl radicals which then abstract a hydrogen atom from RH to produce  $R^{\cdot}$  [eqns. (16)–(17)]. The modulated photolysis causes the concentration of the radicals in solution to modulate at the same frequency as the lamp. In the vicinity of the electrode, diffusion to the electrode can compete with the second-order self-reaction, thus producing an alternating current at the lamp frequency at potentials where the radical can be oxidized or reduced. The small a.c. current can be detected using a lock-in amplifier. As the potential is scanned a voltammogram of potential versus the *alternating* current can be constructed. A voltammogram obtained for the diphenylmethyl radical is shown in Fig. 2.

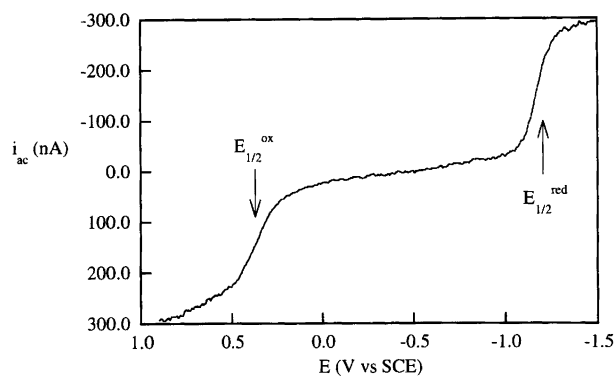
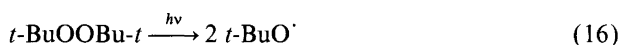
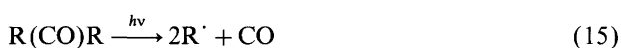


Fig. 2. Photomodulation voltammogram of the diphenylmethyl radical.

The voltammetric cell, constructed from Teflon, contains a quartz window, a gold minigrad working electrode, a platinum coil counter-electrode and a Ag/AgCl or SCE reference electrode. Solutions are allowed to flow slowly through the cell (ca.  $10 \text{ ml min}^{-1}$ ) in order to avoid depletion of the photochemical precursors. The gold minigrad is actually sandwiched between two quartz windows. The inner window contains a 5 mm diameter hole that defines the working area of the electrode. Alternating currents in the range 0–500 nA are detected using a standard potentiostat and a lock-in amplifier. The phase of signal is determined by direct detection of the modulated light source using a photodiode.

### Voltammetric analysis

The shape of a photomodulation voltammogram is typically sigmoidal with a defined diffusion limited plateau. In this regard it resembles a polarogram or rotating disk voltammogram in which a diffusion layer near the electrode surface is relatively constant. The analogy is a little deceptive in that the limiting ac current in a photomodulation voltammogram represents a time-dependent phenomenon and depends on, for example, the frequency of the modulation. As in any modulation experiment, the measured signal is expected to lag in time with respect to the modulation source. This is best thought of, in a physical sense, as a forced damped harmonic oscillator. The total signal is a vector with a component in phase with the lamp and a component out of phase. Thus one can define a phase angle,  $\phi$ , that describes the time lag [eqn. (18)] where  $I_{in}$  and  $I_{out}$  are the in-phase and out-of-phase components respectively. In the most simple system, the damping lifetime,  $\tau$  (i.e. the inverse of a first-order chemical rate constant), is simply related to the phase angle and the frequency in radians per second,  $\omega$  [eqn. (19)]. Thus by plotting the phase angle as a function of frequency it is possible to determine the lifetime of the transient species.

$$\tan \phi = I_{in}/I_{out} \quad (18)$$

$$\tan \phi = \omega\tau \quad (19)$$

In the electrochemical experiment, we have treated the scheme given by eqns. (20)–(23) and numerically solved the differential equations given by eqns. (24)–(26) where  $v$  is the rate of radical formation and  $I_0$  is the maximum rate of radical formation.<sup>49</sup>



$$\partial[R^{\cdot}]/\partial t = D(\partial^2[R^{\cdot}]/\partial x^2) + v - 2k_{21}[R^{\cdot}]^2 \quad (24)$$

$$\partial[R^+]/\partial t = D(\partial^2[R^+]/\partial x^2) - k_{22}[R^+] \quad (25)$$

$$v = I_0(1 - \cos \omega t)/2 \quad (26)$$

The differential equations were solved by digital simulation using a finite difference approximation. While it is beyond the scope of this review to go into further details of the simulation, it is useful to summarize the results. The phase dependence of the radical concentration was calculated both at the electrode surface and in the bulk solution. The results for the bulk solution conform to eqn. (19), i.e., at low frequency (or short radical lifetime) the radical concentration is in phase with the lamp modulation while at high frequency (or long radical lifetime) the phase lag asymptotically approaches  $-90^\circ$ . We were surprised to find that the phase dependence of the radical concentration at the electrode surface approached  $-45^\circ$ , i.e.  $\tan(2\phi) = \omega\tau$  (Fig. 3). However, these calculations were carried out using a potential at which the redox process is diffusion-controlled so the lifetime of the radical is always shorter at the electrode surface compared with the bulk. The frequency/phase dependence of the current is more complex and depends on the lifetime of the radical, the ion and the heterogeneous rate constant. However some generalizations can be made: (1) the phase of the signal on the diffusion-limited plateau depends only on the lifetime of the radical; (2) the breadth of the wave is determined by the heterogeneous rate constant; (3) the half-wave potentials shift as a result of fast preceding or follow-up reactions;  $\partial E_{1/2}/\partial \log(k_{21}) = -31 \text{ mV decade}^{-1}$  (Fig. 4) and  $\partial E_{1/2}/\partial \log(k_{23}) = +35 \text{ mV decade}^{-1}$  (Fig. 5) for a first-order process.

Thus, the extent to which the measured half-wave potential is displaced from  $E^\circ$  depends on the same factors as in any voltammetric method. The effect of fast homogeneous chemical reactions is close to the expected  $29.6 \text{ mV decade}^{-1}$  (the difference is likely to be a result of inaccuracies in the finite difference method). The sigmoidal shape of the voltammogram is actually a reflection of a constantly modulated diffusion layer. This is achieved without convection, since the radicals are

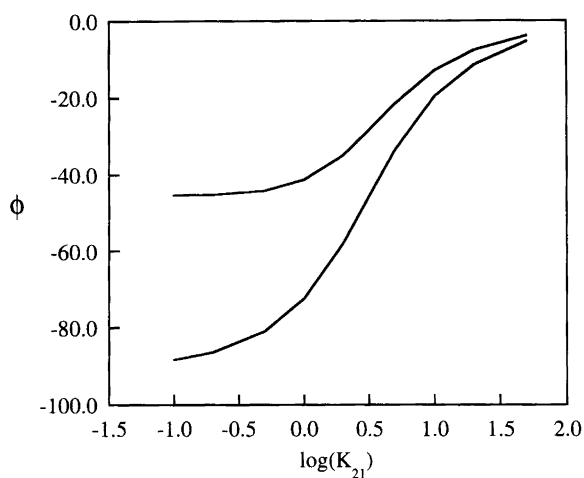


Fig. 3. Dependence of the phase lag of (a) the radical concentration in the bulk and (b) the current on the dimensionless constant  $K_{21} = 2k_{21}[R']_{\text{avg}}/2\pi\omega$ .

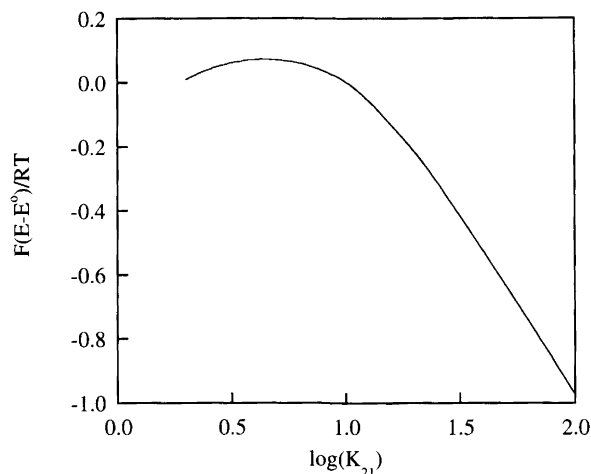


Fig. 4. Potential dependence of the rate constant,  $K_{21} = 2k_{21}[R']_{\text{avg}}/2\pi\omega$ .

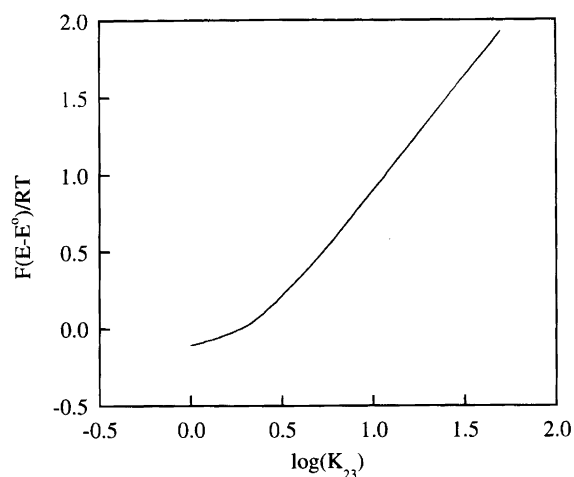


Fig. 5. Potential dependence of the rate constant,  $K_{23} = k_{23}/2\pi\omega$ .

constantly replenished near the electrode surface by the photochemical process.

The analysis of a wave is reasonably straightforward. The radical lifetime is determined by measuring the frequency dependence of the phase angle at a potential on the diffusion-limited plateau. At these potentials the redox process is diffusion controlled so follow-up reactions or heterogeneous processes do not interfere. A preliminary estimate of the heterogeneous rate constant can be made by fitting the shape of the simulated wave to the in-phase voltammogram. These estimates can be refined by fitting working curves for the potential dependence of the phase angle to the data. The phase angle approaches a limit defined by the radical lifetime at high potential and by the ion lifetime at low potentials (i.e. near the foot of the wave). The transition from one extreme to the other is in a region that is best defined as mixed homogeneous/heterogeneous kinetics (Fig. 6).

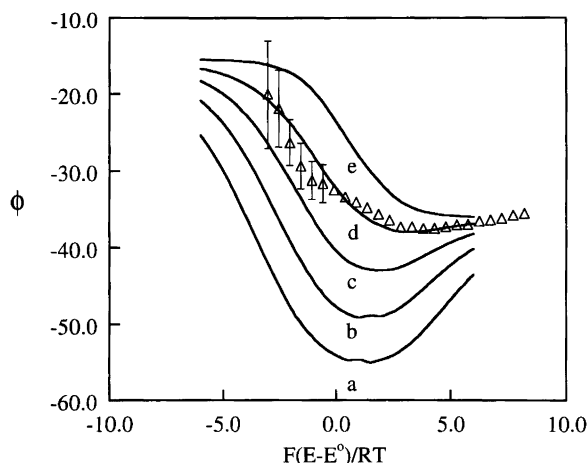


Fig. 6. Plot of the measured and computed phase angle versus potential from the oxidation of the diphenylmethyl radical (data from Ref. 49). The following parameters were used:  $k_{21} = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{22} = 1.5 \times 10^3 \text{ s}^{-1}$ . The lines represent the heterogeneous rate constant,  $k^{\circ}$  = (a) 0.01; (b) 0.02; (c) 0.04; (d) 0.1; (e)  $2000 \text{ cm s}^{-1}$ .

### Oxidation and reduction potentials of benzylic radicals

The oxidation and reduction potentials of benzylic and substituted benzylic radicals are of fundamental importance in physical organic chemistry. Hammett used acidities of substituted benzoic acids to define the well known  $\sigma$  scale.<sup>54</sup> Later, Brown used the solvolysis of substituted cumyl chlorides to define  $\sigma^+$ .<sup>55</sup> Since then a plethora of substituent parameters have been devised, many of which provide some measure of charge development at a transition state.<sup>56</sup> In order to provide a more quantitative measure of the extent of charge development at a transition state a measure of the maximum  $\rho^+$  and  $\rho^-$  values for each system under study is needed. In principle the maximum value is achieved when the charge development is under thermodynamic control. The oxidation and reduction potentials of benzyl, cumyl, diphenylmethyl and 1-naphthylmethyl along with the corresponding  $\rho^+$  and  $\rho^-$  values are given in Table 1. The  $\rho$  values were obtained from a plot of  $E_{1/2}$  versus  $\sigma^{+/-}$ . The slope of

Table 1. Substituent effects on the oxidation and reduction potentials of some benzylic radicals.<sup>a</sup>

Radical	Process	$E_{1/2}/\text{V}$ vs. SCE	$n^b$	$\rho^c$
Benzyl	Oxidation	0.73	10	-9.3
	Reduction	-1.43	10	13.5
Cumyl	Oxidation	0.16	8	-6.8
	Reduction	-1.73	8	11
Diphenylmethyl	Oxidation	0.35	8	-5.6
	Reduction	-1.14	8	7.4
1-Naphthylmethyl	Oxidation	0.47	8	-8.4
	Reduction	-1.27	7	13.0

<sup>a</sup>Data from Ref. 48. <sup>b</sup>Number of data points. <sup>c</sup> $\rho^+$  and  $\rho^-$  for oxidations and reductions, respectively.

this line (in eV) was converted into the  $\rho^{+/-}$  values by multiplying by  $F/2.303RT$ .

It is interesting that the magnitudes of  $\rho^+$  and  $\rho^-$  for oxidation and reduction of substituted 1-methylnaphthalenes (-7.1 and 10.1, respectively) are actually smaller than the  $\rho$  values for the oxidation and reduction of the corresponding 1-naphthylmethyl radicals (-8.4 and 13.0, respectively, Table 1).<sup>51</sup> This leads to the interesting conclusion that, even though a full charge is placed in the  $\pi$ -system of the 1-methylnaphthalenes, the fraction of charge that is available for interaction with the substituent is actually less than in the 1-naphthylmethyl systems where only 50–70% of the charge is delocalized into the ring. In fact, a correlation was shown to exist between  $\rho$  for a redox reaction and the calculated (AM1) charge density at the  $C_4$  position of the radicals in Table 1. The difference between the substituent effects on radicals and on the hydrocarbons is related to the configuration of the singly occupied MO in an even alternate ion, which allows a more even distribution of charge density at all carbons in the rings, and odd alternate ions, which have a number of nodes with low charge density.

### Delocalization and solvation in carbenium ions and carbanions

Solution standard potentials are the solution equivalent of gas phase ionization potentials (IP) and electron affinities (EA).<sup>38</sup> They are connected by the solvation free energies of the neutral and ionic species [eqn. (27), where the constant,  $C$ , converts the standard potential,  $E^{\circ}$ , into an absolute potential]. If it is assumed that the neutral species have a negligible contribution to the overall change in solvation energy a simple relationship between the solvation energies, IPs and standard potentials can be established [eqns. (28) and (29)].

$$E^{\circ} = \text{IP} + \{\Delta G_{\text{sol}}^{\circ}(\text{R}^+) - \Delta G_{\text{sol}}^{\circ}(\text{R}^{\cdot})\}/F + C \quad (27)$$

$$\Delta E^{\circ} = m\Delta \text{IP} \quad (28)$$

$$\Delta \Delta G_{\text{sol}}^{\circ}(\text{R}^+) \approx (1 - m)\Delta \text{IP} \quad (29)$$

It can be seen from eqn. (29) that a correlation between solution  $E^{\circ}$  and gas phase IP values with a slope of 1 implies that the solvation energies for a series of ions are constant. However, this is seldom the case. Plots of this kind invariably have slopes that are less than one; i.e. changes in the stabilities of ions are much less pronounced in solution. The leveling effect of the solvent can be understood, in part, in terms of a balance between solvation and delocalization. In the gas phase, ions are stabilized by delocalization (we will use this term in a broad sense and include not only  $\pi$ -conjugation but also hyperconjugation to adjacent C–X bonds). In solution, charge is also stabilized by solvation. However, since solvation is more favorable at a highly localized charge center, delocalization tends to decrease the relative contribution of this effect. Solvation energies estimated for

some carbenium ions are given in Table 2. It is interesting that all but one of the aromatic systems have solvation energies that are ca.  $38 \pm 2 \text{ kcal mol}^{-1}$  and that as the ion decreases in size, the solvation energy increases. The  $\alpha$ -methoxybenzyl radical has a solvation energy significantly higher than the other benzylic ions. We have suggested that the  $\alpha$ -methoxy group tends to localize the charge density leading to a greater solvent contribution.<sup>50</sup>

The importance of hyperconjugation is seen from changes in oxidation potentials upon replacing phenyl groups by methyl (Table 3). Both solution oxidation potentials and gas phase IP measurements suggest that a methyl group has the same effect on the stability of a carbocation as a phenyl. That is, stabilization by delocalization into a phenyl ring is almost as effective as stabilization by delocalization through hyperconjugation. For the tertiary systems the diphenylethyl, cumyl and *tert*-butyl radicals have about the same oxidation potentials and IPs (within 150 mV). For the secondary systems the increasing importance of solvation of the more localized cations is clearly evident in solution. Thus for diphenylmethyl, phenethyl and 2-propyl radicals, the oxidation potentials are within 100 mV even though the IPs in the gas phase vary by more than 500 mV. Here,

Table 2. Oxidation potentials and estimated solvation energies of some carbenium ions<sup>a</sup>

R <sup>+</sup>	$E_{1/2}/\text{V vs. SCE}$	$\Delta G_{\text{sol}}^{\circ}(\text{R}^+)/\text{kcal mol}^{-1}$
9-Fluorenyl	0.76	-36.2
Diphenylmethyl	0.35	-39.4
Benzyl	0.73	-39.9
Phenethyl	0.37	-41.3
<i>tert</i> -Butyl	0.09	-43.1
<i>N,N</i> -Dimethylaminomethyl	-1.03	-45.9
$\alpha$ -Methoxybenzyl	-0.33	-47.3
Methoxymethyl	-0.24	-56.3

<sup>a</sup>Data from Refs. 45 and 50.

Table 3. Oxidation potentials and ionization potentials of arylmethyl radicals.

Radical <sup>a</sup>	$E_{1/2}^{\text{ox}}/\text{V vs. SCE}$	IP <sup>b</sup> /eV	$\Delta G_{\text{sol}}^{\circ}(\text{R}^+)/\text{kcal mol}^{-1}$	$E_{1/2}^{\text{red}}/\text{V vs. SCE}$
Ph <sub>2</sub> CMe	0.23	$\approx 6.7^{\text{d}}$	$\approx -40$	-1.34
PhCMe <sub>2</sub>	0.16	6.6	-39.2	-1.73
Me <sub>3</sub> C	0.09	6.7	-43.1	-1.55 <sup>g</sup>
Ph <sub>2</sub> CH	0.35	6.8	-39.4	-1.14
PhCHMe	0.37	6.9	-41.3	-1.60
Me <sub>2</sub> CH	0.47 <sup>e</sup>	7.37	-49.8	-1.44 <sup>g</sup>
PhCH <sub>2</sub>	0.73	7.20	-39.9	-1.45
MeCH <sub>2</sub>	<0.99 <sup>f</sup>	8.12	<-55	-1.36, <sup>g</sup> -1.10 <sup>h</sup>
CH <sub>3</sub>	<2.49	9.84	<-60	-0.92 <sup>h</sup>

<sup>a</sup>Data from Ref. 45 unless otherwise indicated. <sup>b</sup>Data from Ref. 38. <sup>c</sup>Estimated assuming an absolute potential of SCE of 4.74 eV and  $\Delta G_{\text{sol}}^{\circ} \approx E_{1/2} + 4.74 - \text{IP}$ . <sup>d</sup>Estimated IP assuming a solvation free energy of ca.  $-40 \text{ kcal mol}^{-1}$ . <sup>e</sup>Measured in acetonitrile-0.1 M TBAP using 2,4-dimethyl-3-pentanone as the source of the radical. <sup>f</sup>Estimated upper limit assuming the solvation energy of the ethyl cation is more exergonic than that for the methoxymethyl cation (Table 2). <sup>g</sup>Ref. 57. <sup>h</sup>In acetonitrile (0.1 M TBAP) by PMV (see the text for experimental details).

the differential solvation masks the intrinsic stabilities of the ions. Using IP data and a lower limit for a solvation energy, we have estimated an upper limit for the solution oxidation potentials of the ethyl radical (<0.99 V vs. SCE) and the methyl radical (<2.49). Unfortunately, both of these values were experimentally inaccessible in a PMV experiment since the background DC currents (from oxidation of precursors) tend to overwhelm the small a.c. currents near 1 V vs. SCE. It is interesting that the oxidation of the ethyl radical is still expected to be within 200 mV of the oxidation of benzyl. As in the 2-propyl case, differential solvation leads to a relative stabilization of the smaller ion in solution.

For comparison, reduction potentials of the radicals also are included in Table 3. The reduction potential of *n*-, *sec*- and *tert*-butyl radicals have been estimated by Savéant and his coworkers.<sup>57</sup> We studied the electrochemical reduction of methyl radicals produced from the photolysis of an appropriate peroxide followed by the  $\beta$ -cleavage of *tert*-butoxyl and cumyloxyl radicals [eqn. (30)] and from the direct photolysis of methyl iodide [eqn. (31)]. All gave the same reduction wave in acetonitrile (0.1 M TBAP). The ethyl radical was produced from photolysis of 3-ethylpentyl peroxide followed by the  $\beta$ -cleavage of the alkoxy radical [eqn. (30)].



The most striking difference between the reduction and the oxidation of the radicals is the small change in potential as a function of the degree of substitution (only 0.6 eV compared with >2 eV for the oxidation). It is difficult to discuss these changes with respect to solvation energy differences because gas phase electron affinities of the radicals are not generally available. For example, the EA of methyl is only 0.08 eV,<sup>58</sup> leading to an estimated solvation energy of the carbanion of  $86 \text{ kcal mol}^{-1}$  in this acetonitrile. If we assume that the solvation energies

for ethyl, 2-propyl and *tert*-butyl are about the same, electron affinities of  $-0.17$ ,  $-0.27$  and  $-0.37$  eV, respectively, are obtained. The negative electron affinities imply that the carbanion is unstable with respect to the bound electron. Here solvation provides the only stabilizing influence in solution.

### Concluding remarks

The PMV technique allows direct electrochemical detection of a wide range of chemical intermediates with lifetimes on the millisecond or sub-millisecond timescale. One of limitations of the PMV approach lies in the fact that the radical precursors must be significantly more difficult to oxidize and reduce than the radicals themselves. As a result some of the more obvious precursors such as alkyl halides or diacyl peroxides are not always practical to use. In addition, the formation of highly electron deficient radicals is inherently difficult by hydrogen atom abstraction using the *tert*-butoxyl radical. This is not related to thermodynamic factors but to polar effects in the transition state. Consequently, the reduction potentials of simple radicals derived from methyl ketones or esters are not easily accessed by this technique.

While this review has been directed towards the characterization of free radicals, it is possible to study the electrochemistry of other transient species including excited states.<sup>59</sup> Besides being important for completing thermochemical cycles, redox potentials of free radicals have been important for the elucidation of reaction mechanisms and the design of new chemical processes based on electron transfer driven chain reactions.<sup>60</sup> In general, the potentials of radicals can be classified according to the degree of substitution and the types of substituents. The largest energetic contributions are generally observed in systems in which lone pairs interact with the incipient ion. For carbocation formation these are stabilizing interactions while for carbanion formation these interactions are destabilizing. Thus  $\alpha$ -alkoxyalkyl<sup>45</sup> and  $\alpha$ -aminoalkyl radicals<sup>44</sup> have oxidation potentials that are ca.  $-0.4$  and  $-1.0$  V vs. SCE, respectively, and tend to be reasonable chemical reducing agents. Radicals derived from dioxolanes also oxidize at very negative potentials (ca.  $-1$  V).<sup>61</sup> Rather than tabulate a large number of potentials, we have attempted to give a flavor of how this non-traditional technique fits into the world of organic electrochemistry.

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