Oxidation and Reduction Potentials of Transient Free Radicals[1]

D. D. M. Wayner,* D. J. McPhee, and D. Griller*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received July 13, 1987*

Abstract: The oxidation and reduction potentials of a variety of carbon-centered radicals have been measured by a technique that makes use of modulated photolysis for radical generation and phase-sensitive voltammetry for their detection. The measured half-wave potentials were close to the thermodynamically significant $E°$ values for the arylmethyl radicals and led to estimates of $pK_a(RH)$ and $pK_R(ROH)$ as well as data for the solvation energies of these ions and radicals.

The electron donor and acceptor properties of a molecule in the gas phase are characterized by the ionization potential, IP,[2] and electron affinity, EA.[3] However, these properties are not directly relevant to the liquid phase where solvation of ions becomes important. In fact, the solution analogues of the ionization potential and electron affinity of a molecule are the electrochemical oxidation and reduction potentials[4] which, for the vast majority of persistent molecules, are easily measured by standard techniques.

Transient species such as free radicals in solution are beyond the scope of conventional electrochemistry since they cannot be sustained, over long periods of time, at concentrations high enough for routine measurements. Nevertheless, information on the electrochemical properties of free radicals is highly desirable, since these species participate in a plethora of electron-transfer reactions.

In response to the problem, a number of attempts have been made to develop methods that can accomodate short-lived free radicals. For example, relatively high concentrations of free radicals have been generated by pulse radiolysis in the presence of electron acceptor molecules that had well-defined reduction potentials.[5,6] The success or failure of electron transfer between a radical and an acceptor gave a rough indication of the radical oxidation potential. By selecting a series of acceptor molecules with different reduction potentials, it became possible to "bracket" the oxidation potential for the radical.[5,6]

Pulse radiolysis has also been used with direct polarographic detection of the radicals formed.[7] However, the technique has been largely restricted to water as solvent which reacts rapidly with most ions formed on reduction or oxidation of free radicals.[7a] This means that the measured potentials reflect irreversible processes and may therefore be of limited thermodynamic significance.[7a]

Aprotic solvents allow an alternative approach since they provide a medium in which solutions of some organic ions can be prepared. These are then either oxidized or reduced to the corresponding free radical.[8-11] However, the method has several drawbacks. First, solutions of this kind are difficult to characterize unequivocally. Second, the ions are sometimes adsorbed onto electrode surfaces so that desorption becomes a complicating factor in the interpretation of the electrochemical data; and third, the number of organic ions, especially carbocations, that are amenable to this approach is quite limited.

We have developed a method for measuring the reduction and oxidation potentials of free radicals in aprotic solvents that uses the radical itself as the electroactive species.[12] In this approach, radicals were generated by modulated photolysis[13] and monitored electrochemically with phase-sensitive detection which enhanced instrumental sensitivity by several orders of magnitude.[13-15]

We have now used the technique to measure the half-wave potentials, $E_{1/2}$, for the oxidations and reductions of 19 organic radicals. Analysis of the data suggests that $E_{1/2}$ values for the radicals, $R^•$, are generally within 100 mV of the standard potentials, $E°$, for their oxidations and reductions. These values can therefore be used to calculate a variety of useful thermodynamic properties including $pK_a(RH)$, $pK_R(ROH)$, and solvation free energies for the corresponding carbocations and carbanions.

Experimental Section

Materials. Acetonitrile was stirred for 24 h over $KMnO_4$, filtered through Celite and distilled. The distillate was stirred over CaH_2 for 12 h and fractionally distilled under 1 atm of nitrogen. The purified acetonitrile was stored over 3A molecular sieves. Tetrabutylammonium perchlorate (TBAP, Eastman) was recrystallized three times from 10% hexane in ethyl acetate. The crystals were dried in a vacuum oven (40 °C, 10 Torr) and were stored in a desiccator. Di-*tert*-butyl peroxide (DTBP, Aldrich) was passed through a column of activated alumina before use. With the exceptions listed below, all other chemicals were commercially available and used as received.

1,1-Diphenylethane was synthesized according to the method of Olah and Prakash.[16]

N,N-Dimethylaniline was fractionally distilled from KOH and stored under an atmosphere of nitrogen.

Instrumentation. A block diagram of the instrument used in this work is shown in Figure 1. Radicals were generated in the electrochemical

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Table I. Electrochemical Properties of Free Radicals[a,b]

radical	method[c]	$E_{1/2}^{\mathrm{ox}}$ (V vs SCE)	α[d]	$E_{1/2}^{\mathrm{red}}$ (V vs SCE)	α[d]
$\mathrm{Ph\dot{C}H_2}$	1, 2	0.73	0.36	-1.45 [-1.43,[i] -1.3[j]]	0.54
$\mathrm{Ph\dot{C}HCH_3}$	2	0.37	0.32	-1.60	0.49
$\mathrm{Ph\dot{C}(CH_3)_2}$	2	0.16	0.39	-1.73	0.54
$\mathrm{Ph_2\dot{C}H}$	1, 2	0.35 [0.33[e]]	0.60	-1.14 [-1.16,[i] -1.13[k]]	0.60
$\mathrm{Ph_2\dot{C}CH_3}$	2	0.23	0.37	-1.34 [-1.42[k]]	0.30
9-fluorenyl	2	0.76	0.33	-0.76 [-0.68,[l] -0.85[m]]	0.41
$\mathrm{(CH_3)_3\dot{C}}$	1	0.09	0.28	*n* [-2.00,[o] -2.54[p]]	*q*
$\mathrm{CH_3O\dot{C}H_2}$	2	-0.24	0.20	(-1.3)	*q*
$\mathrm{CH_3CH_2O\dot{C}HCH_3}$	2	-0.45	0.21	(-1.2)	*q*
$\mathrm{(CH_3)_2CHO\dot{C}(CH_3)_2}$	2	-0.10	0.32	-0.79	0.39
$\overline{\mathrm{CH_2CH_2CH_2\dot{C}HO}}$	2	-0.35 [-0.8[f]]	0.34	(-1.0)	*q*
$\overline{\mathrm{CH_2CH_2OCH_2\dot{C}HO}}$	2	-0.08 [-0.8,[f] -0.12[g]]	0.26	(-1.0) [-1.28[g]]	*q*
1,3-dioxolan-2-yl	2	0.31[h]	0.60	(-1.2)	*q*
1,3-dioxolan-4-yl	2	-0.34[h]	0.25	(-1.2)	*q*
1,3,5-trioxan-2-yl	2	0.20	0.27	(-1.1)	*q*
$\mathrm{(CH_3)_2N\dot{C}H_2}$	2	-1.03 [-1.2[f]]	0.54	(-2.0)	*q*
$\mathrm{(CH_3CH_2)_2N\dot{C}HCH_3}$	2	-1.12	0.60	(-2.0)	*q*
$\mathrm{(PhCH_2)_2N\dot{C}HPh}$	2	-0.92	0.42	-1.79	0.68
$\mathrm{PhN(CH_3)\dot{C}H_2}$	2	-0.85	0.30	-2.03	0.22

[a] In acetonitrile, 0.10 M TBAP, gold minigrid. [b] All values ±50 mV average of at least three determinations; literature values in square brackets. Values in parentheses are less reliable. [c] Method 1: eq 1. Method 2: eq 2 and 3. [d] Calculated from eq 4 and 6 (see text). [e] Reduction of cation, $\mathrm{CH_2Cl_2}$, 0.1 M TBAP (ref 19). [f] Pulse radiolysis/polarography oxidation of radical; $\mathrm{H_2O}$, 0.35 M $\mathrm{Na_2SO_4}$; pH 11 (ref 7a). [g] Pulse radiolysis/polarography; $\mathrm{H_2O}$, 0.35 M $\mathrm{Na_2SO_4}$; pH 3 (ref 7a). [h] Values assigned by comparison to THF derived radical and 1,3,5-trioxan-2-yl. [i] Oxidation of anion; THF/HMPA (4:1), 0.1 M TBAP, -62 °C (ref 11e). [j] Pulse radiolysis/polarography; $\mathrm{H_2O}$, 0.35 M $\mathrm{Na_2SO_4}$ (ref 7a). [k] Oxidation of anion; DME, 0.10 M TBAP (ref 9b). [l] Oxidation of anion; DMSO, 0.1 M TEAP (ref 10). [m] Oxidation of anion; DMSO, 0.1 M TBAP (ref 8a). [n] No definitive reduction wave was observed (see text). [o] Reduction of radical; DMF, 0.1 M TMAP (ref 20). [p] Reduction of radical; $\mathrm{CH_3CN}$, 1.0 M TBAP (ref 11). [q] Broad waves, $\alpha < 0.2$.

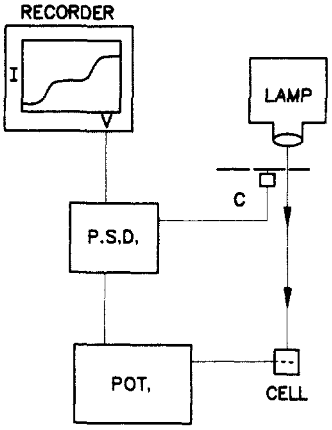

Figure 1. Block diagram of the instrument: C, light chopper; POT, potentiostat; PSD, phase sensitive detector (lock-in amplifier).

cell by photolysis of appropriate precursors (vide infra) with use of a 1000 W Hg/Xe arc lamp (Oriel Corp.). The output from the lamp was modulated with a light chopper (EG and G Model 9479) that was fitted with a specially designed iris so that the light intensity at the sample rose and fell as a sine wave.

The electrochemical cell was controlled with a PAR Model 174A polarographic analyzer equipped with a Model 174/50 AC interface that contained the positive feedback loop for *iR* compensation. In a typical experiment, potential was slowly scanned (10 mV/s) and the ac component of the output was measured with an Ithaco Model 391A lock-in amplifier. A plot of the ac current versus the potential gave a voltammogram of the photogenerated free radical (Figure 2).

The electrochemical cell, constructed from Teflon, had a volume of 500 μL. The working electrode (gold minigrid, 400 wires/cm, 50% transmittance, available from Buckby-Mears, Minneapolis, MN) was held in place between two quartz plates. The exterior plate served as a window for the photolyzing beam and a 0.5-cm hole cut into the center of the inner window allowed contact between the electrode and the solution. Electrical contact to the gold minigrid was made with a ring constructed from platinum foil which was designed so that the platinum was not in contact with the solution. The counterelectrode was a platinum coil located in the exit tube so that products formed at the counterelectrode did not interfere with the measurements. Contact between the reference electrode (aqueous saturated calomel electrode, SCE), and the solution was made through a luggin capillary. The cell was held together by compression with seals between the Teflon and the quartz being made with neoprene O-rings.

The electrochemical cell was *iR* compensated by using the method described by Evans.[17] Under these conditions the capacitive charging time was typically on the order of 300–500 μs. All measurements were made in acetonitrile containing 0.1 M TBAP as supporting electrolyte. Samples were allowed to flow slowly through the cell (2–3 mL/min) so as to avoid problems associated wiih sample depletion and/or product accumulation.

Results and Discussion

Our approach to the measurement of the oxidation and reduction potentials of free radicals is similar to that used in experiments where radicals were generated by modulated photolysis and were detected optically.[13] Modulated photolysis causes the radical concentration to oscillate at a fixed frequency. As a consequence the signal from the detection system, be it optical or electrochemical, contains a small oscillating component due to the free radical. This can be separated from other contributions by the use of a phase-sensitive detector which only detects signals that oscillate at the modulation frequency. Driving an experiment at a fixed frequency coupled with phase-sensitive detection can lead to enhancement in signal to noise of several orders of magnitude, and in this instance it allowed the detection of free radicals under conditions where their average concentration was ca. 10^{-7}–10^{-8} M and the average lifetime ca. 10^{-3} s. However, in practice these systems are slightly more complicated than this simple analysis would suggest.

The modulated photolysis of precursors has the effect of modulating the concentrations of the starting materials, radicals, and products, whose signals will all contribute to the ac signal obtained. The signals from the starting materials and products can be separated from those of the radicals in two ways: first, by monitoring the radicals in regions where the starting materials and products do not give strong signals, or second, by the use of phase relationships to separate the signals of interest.[13] In this work, we have relied on the former method, since in most cases the starting materials were more difficult to oxidize and reduce than the radicals. Furthermore, the phase relationships in the electrochemical experiment are further complicated by the fact that the electrode itself has a characteristic response time that

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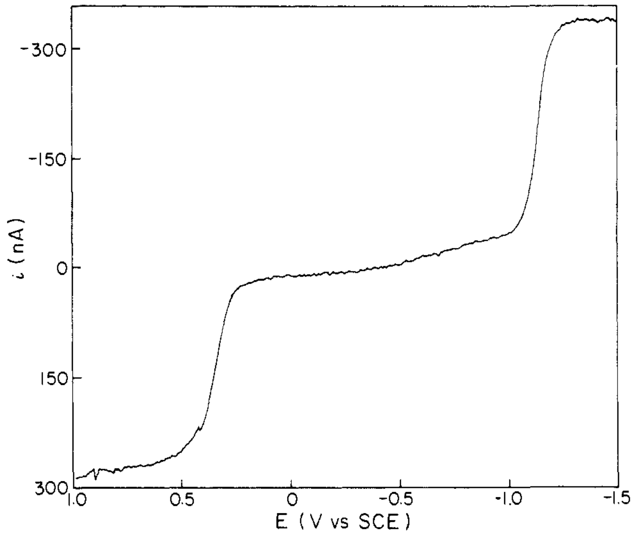

Figure 2. Voltammogram of the diphenylmethyl radical obtained from the photolysis of 1,1,3,3-tetraphenylacetone (5×10^{-3} M) in acetonitrile (0.1 M TBAP).

may cause phase shifts above and beyond those due to the simple kinetic constraints of the system.[18]

The electrochemical oxidation and reduction potentials of a variety of carbon-centered radicals were measured by using this modulation approach and are reported in Table I. In general, two methods were used to generate the radicals: photodecomposition of a ketone (method 1: eq 1) and photolysis of di-*tert*-butyl peroxide (DTBP) followed by hydrogen atom abstraction (method 2: eq 2 and 3).

$$RC(O)R \xrightarrow{h\nu} 2R^{\bullet} + CO \qquad (1)$$

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^{\bullet} \qquad (2)$$

$$t\text{-BuO}^{\bullet} + RH \rightarrow R^{\bullet} + t\text{-BuOH} \qquad (3)$$

In those cases when it was possible to generate the transient radical by both methods, the measured half-wave potentials were within 50 mV. Furthermore, the half-wave potentials were not dependent on the phase setting for the lock-in amplifier (i.e., in-phase or quadrature) nor were they dependent on the modulation frequency over the range used in the experiments (29 to 200 Hz). Consequently, most of the measurements were made under conditions that gave optimal signal-to-noise ratios in the voltammograms, i,e,, 53-Hz modulation frequency and detection of the quadrature component of the signal.

Providing the composition of the diffusion layer at the electrode is constant, voltammograms can be analyzed with eq 4.[21] In this equation, E is the applied potential, $E_{1/2}$ is the half-wave potential,

$$E = E_{1/2} + C \log \{(i_{\lim} - i)/i\} \qquad (4)$$

i is the current, $i_{\lim}$ is the limiting current, and C is a constant. In situations where the electrochemical process is rapidly reversible, $E_{1/2}$ is equal to E°, the standard potential for the reaction, and C is described by eq 5, where n is the number of electrons transferred. Under these conditions, C has a value of 59 mV at 298 K.

$$C = 2.303RT/nF \qquad (5)$$

Deviations from these ideal conditions are not uncommon and analyses of the voltammograms often yield values of C that are greater than 59 mV. Under these circumstances C is better defined by eq 6.[21] In this equation α is the "transfer coefficient" and has

$$C = 2.110RT/nF\alpha \qquad (6)$$

a value between 0 and 1. Small values of α are thought to be indicative of large differences in the equilibrium configurations of the oxidized and reduced forms of the electroactive species in their solvation spheres.[7a]

The voltammograms obtained in this work were analyzed by the use of eq 4 and 6 and led to values of α that were generally in the range 0.2–0.6 (Table I). This immediately indicated that the systems under investigation were not strictly reversible and therefore that the measured values of $E_{1/2}$ were not necessarily equal to standard potentials E° for the electrochemical reactions. This situation is frequently encountered in voltammetric measurements and stems from two basic causes. First, $E_{1/2}$ may be displaced due to a slow heterogeneous electron-transfer step and, second, the entire oxidation or reduction wave may be distorted because the reaction product undergoes a chemical reaction that rapidly depletes its concentration at the electrode. In our experiments, the situation was further complicated by the fact that the radicals were generated by photolysis through the gold minigrid electrode so that the radical concentration near the electrode was probably not homogeneous.[22] Despite these envisaged problems, it was possible to estimate the extent to which the measured values of $E_{1/2}$ deviated from the thermodynamically significant values of E°.

The most reliable estimates of E° are obtained when the electrochemical reaction of interest can be investigated in both directions. In the present context, this would mean carrying out one experiment with the free radical as the electroactive species and a second with the corresponding ion as the starting material. The value of E° would necessarily fall between the halfwave potentials measured for the two reactions.

In several cases such comparisons are indeed possible since data exist for the oxidation potentials of a number of organic anions that corresponded to radicals investigated in this work. The data are given in Table I and show that the measured potentials for the opposing reactions were extremely close, irrespective of the solvent used (vide infra), and that the experimental values of $E_{1/2}$ were within 100 mV of E°. We assume that this will also be true for all of the values of $E_{1/2}$ measured in these experiments.

The data in Table I for the simple arylmethyl radicals show that successive replacement of hydrogen by either methyl or phenyl groups reduces the oxidation potentials. In fact, the contribution due to a single methyl or phenyl group is about the same and is roughly −300 mV (ca. −8 kcal mol^{-1}). Presumably, both of these groups preferentially stabilize the carbocations that are the oxidation products. Interestingly, methyl and phenyl groups have opposite effects on the reduction potentials, the contributions being −150 mV (CH_3) and 300 mV (Ph). Indeed, it is possible to begin with the electrochemical data for the benzyl radical and to calculate the properties for all of the other arylmethyl radicals by treating these incremental effects as "group contributions".

The same approach can be used to calculate the oxidation and reduction potentials for the *tert*-butyl radical giving $E = 0.13$ and −2.2 V. The calculated value for the oxidation potential is in excellent agreement with that observed experimentally (Table I). However, we were not able to measure the reduction potential with any degree of confidence. A broad reduction wave was observed just below −2 V, but the voltammogram was badly affected by contributions from the reduction of di-*tert*-butyl ketone which was used as the radical precursor. Nevertheless the calculated value for the reduction is actually quite consistent with measurements or estimates obtained by other experimental techniques.[11,20]

The oxidation potentials for the α-aminoalkyl radicals are substantially lower than those of the arylmethyl radicals. For example, that for $(CH_3)_2N\dot{C}H_2$ is 1.7 eV less than the oxidation potential for the benzyl radical. This enormous reduction in the

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oxidation potential of α-aminoalkyl radicals has been attributed[23] to the existence of a three-electron interaction in the radical in which two of the electrons lie in a bonding orbital while the third is placed in a high-energy antibonding orbital and is therefore more easily removed. The same effect is seen in the gas-phase ionization potentials of these radicals which are 1–2 eV lower than those for simple alkyl radicals.[23] These properties make α-aminoalkyl radicals excellent reducing agents as has often been observed in their solution chemistry.[24,25]

The oxidation potential of $(CH_3CH_2)_2NCHCH_3$ has been estimated by Marcus theory to be −1.6 to −1.7 V from the rate of its electron transfer to substituted benzophenones which had reduction potentials between −1.4 and −1.8 V in aqueous acetonitrile.[25] By contrast, our measured value of −1.12 V implies that the reaction is endothermic for all of the benzophenones and therefore should not have been rapid. However, the benzophenone reductions were only efficient when carried out in the presence of 0.02 M sodium hydroxide. It is therefore likely that hydroxide ion drove the reactions forward by reacting with the incipient iminium ion. A similar involvement of hydroxyl has been observed in the oxidation of 1,4-dioxan-2-yl radicals where the potential was pH dependent.[7a] Moreover, the applicability of Marcus theory under such conditions has recently been questioned.[26] We believe that these factors explain the poor agreement between our own data and those reported previously.[25]

Radicals derived from ethers, i.e., those with an α-oxygen atom, had oxidation potentials that were intermediate between those of the arylmethyl and α-aminoalkyl radicals. Indeed, the same order has also been observed for the gas-phase ionization potentials of these radicals.[23,27] The effect can again be rationalized in terms of the properties of the three-electron bond and implies that the interaction between the oxygen lone pair electrons and that in the singly occupied orbital is smaller than that found for nitrogen. As a consequence, the energy of the electron in the antibonding orbital is not as high as is found in α-aminoalkyl radicals and hence the electron is more difficult to remove.

In those alkyl radicals containing an α-nitrogen or oxygen, substitution of a single methyl group at the α-carbon led to decreases in the oxidation potentials as was observed for the arylmethyl radicals. However, the effect was attenuated for the heteroatom containing radicals and was only ca. 0.2 eV for the α-alkoxyalkyl radicals and 0.1 eV for the α-aminoalkyls.

Clearly, the group increments that were observed for the arylmethyl radicals are inapplicable in these cases. Furthermore, the oxidation potential of the radical derived from diisopropyl ether, which contains two α-methyl groups, was actually higher by 0.35 eV than that found for $CH_3CH_2O\dot{C}HCH_3$. In addition, its reduction potential was lowered by a similar amount. These observations suggest that this congested radical adopts a conformation that inhibits the overlap of the unpaired electron with the p-type lone pair on oxygen thus lowering the energy of the singly occupied antibonding orbital.

The situation was even more complex in instances where the radical center had two adjacent oxygen atoms. For example, the oxidation potential of 1,3,5-trioxan-2-yl was 0.4 eV higher than for $CH_3O\dot{C}H_2$. It has been shown in EPR experiments that the introduction of a second oxygen into α-alkoxyalkyl radicals dramatically changes their structure.[28] The electronegativity of the substituents becomes more important than the three-electron interaction and causes the radical center to become pyramidal.[28]

Table II. Acidities of Carbon Acids in Acetonitrile and DMSO[a]

RH	$pK_a(RH)_{CH_3CN}$[b]	$pK_a(RH)_{DMSO}$	ΔpK_a
$PhCH_3$	51.2	41,[c] 42[c]	9.2
$PhCH_2CH_3$	51.5		
$PhCH(CH_3)_2$	52.9		
Ph_2CH_2	43.1	32.2[d]	10.9
Ph_2CHCH_3	44.2		
Fluorene	33.8	22.6	11.2

[a] $pK_a(RH) = 0.728\ \Delta G^\circ_{-H^+}(RH)$ at 298 K. [b] Calculated from eq 7–12; the uncertainty is estimated to be ± 4 pK_a units. All bond energies from ref 31. [c] Extrapolated value (ref 36). [d] Reference 37.

Thermochemistry. The oxidation and reduction potentials of free radicals can be used in thermochemical cycles to calculate thermodynamic properties of ions and molecules.[11] For example, a simple cycle can be defined to evaluate the free energy for deprotonation of an acid RH, $\Delta G^\circ_{-H^+}(RH)$ (eq 7–12), where

$$RH(sol) \rightarrow R^\bullet(sol) + H^\bullet(sol) \qquad \Delta G^\circ_{BDE}(RH) \tag{7}$$

$$R^\bullet(sol) \rightarrow R^-(sol) \qquad -FE^\circ \tag{8}$$

$$H^\bullet(sol) \rightarrow \tfrac{1}{2}H_2(g) \qquad -\Delta G_f^\circ(H^\bullet) \tag{9}$$

$$\tfrac{1}{2}H_2(g) \rightarrow H^+(aq) \qquad \text{NHE} \tag{10}$$

$$H^+(aq) \rightarrow H^+(sol) \qquad \Delta G^\circ_{tr}(H^+) \tag{11}$$

$$\overline{RH(sol) \rightarrow R^-(sol) + H^+(sol) \qquad \Delta G^\circ_{-H^+}(RH)} \tag{12}$$

$\Delta G^\circ_{tr}(H^+)$ is the free energy associated with the transfer of a proton from water to the solvent of interest (in this case acetonitrile) and sol, aq, and g correspond to a species in the solvent, water, and the gas phase, respectively.

In applying this cycle, we have made three assumptions. First, we have assumed that the bond dissociation free energy can be represented by the bond dissociation enthalpy plus a contribution of −8 kcal mol^{-1} that derives from the entropy of formation of the hydrogen atom at 300 K.[29] This assumption is based on the general observation that hydrocarbons (RH) and their corresponding radicals, $R^\bullet$, differ in entropy by ca. 2 eu, which makes a negligible contribution in the present context. The second assumption is that BDE(R–H) are the same in solution as in the gas phase. This has been discussed in detail elsewhere[30] and is thoroughly supported by the excellent agreement between bond dissociation enthalpies that have been determined in solution and their gas-phase counterparts.[30] The third assumption is that the measured values of $E_{1/2}$ are essentially equal to the thermodynamically significant E° values. For the purposes of this cycle both $E_{1/2}$ and E° are defined with respect to the normal hydrogen electrode (NHE) which has a potential of −0.24 V versus SCE.

We have calculated values of pK_a for the arylmethyl radicals investigated in this work (Table II). For these radicals, the reduction waves were well defined, as was indicated by the values of α which were ≥ 0.3. Moreover, in the majority of these cases we were able to establish (vide supra) that our third assumption was valid, i.e., that $E_{1/2}$ was within 100 mV of E° (Table I). Literature values were used for BDE(R–H),[31] and the value of $\Delta G^\circ_{tr}(H^+)$ from water to acetonitrile was taken to be 11 kcal mol^{-1}.[32] The data in Table II show that the arylmethanes have very large pK_a values. Indeed, they are so large that they no longer represent any pragmatic measure of acidity. For example, a sample of ca. 10^{10} moles of fluorene in acetonitrile as solvent would only contain one molecule that was ionized. The values should therefore simply be regarded as thermodynamic properties rather than as measures of acidity per se.

A number of pK_a values for the substrates of interest have been measured by other workers in dimethyl sulfoxide as solvent by chemical equilibration techniques,[33–37] and the data are reported

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Table III. Calculated $pK_R(ROH)$ Values[a]

R	pK_R (ROH)	lit.
$PhCH_2$	-22.6	<-15[c]
$PhCHCH_3$	-14.4	<-15[c]
$PhC(CH_3)_2$	-10.1	<-15[c]
Ph_2CH	-13.3[b]	
Ph_2CCH_3	-9.1	-10.4[c]
9-fluorenyl	-17.3	<-16.6[d]
$(CH_3)_3C$	-15.5	-14.7[d]

[a] Calculated from eq 20. [b] Reference compound used in all calculations (ref 39). [c] Reference 40. [d] References 39 and 41.

in Table II for comparison. These values are 9–11 pK_a units (i.e., 13–15 kcal mol^{-1}) less than the values obtained in acetonitrile. These differences are within experimental error of the change in free energy associated with the transfer of a proton from dimethyl sulfoxide to acetonitrile (15.6 kcal mol^{-1}; 11.4 pK_a units[32]). The implication of this result is that the solvation energies of the organic anions are not appreciably solvent dependent, a suggestion that has been made elsewhere.[38]

A corollary of this result is that *relative* pK_a values will tend to be solvent independent. However, this will clearly not be the case for the *absolute* values which are likely to vary by large amounts from solvent to solvent in a way that reflects the solvation free energy of the proton in the various media. This factor has not always been considered when thermodynamic data have been derived from measurements made in different solvents.[11]

By using a similar approach, the pK_R values for the equilibrium between an alcohol and its corresponding carbocation can be determined (eq 13–19).[11]

$$ROH(sol) + H_2(sol) \rightarrow RH(sol) + H_2O(sol) \qquad \Delta\Delta G_f^\circ \qquad (13)$$

$$RH(sol) \rightarrow R^\bullet(sol) + H^\bullet(sol) \qquad \Delta G^\circ_{BDE}(RH) \qquad (14)$$

$$R^\bullet(sol) \rightarrow R^+(sol) \qquad FE^\circ \qquad (15)$$

$$H^+(aq) \rightarrow \tfrac{1}{2}H_2(g) \qquad NHE \qquad (16)$$

$$H^\bullet(sol) \rightarrow \tfrac{1}{2}H_2(g) \qquad -\Delta G_f^\circ(H^\bullet) \qquad (17)$$

$$H^+(sol) \rightarrow H^+(aq) \qquad -\Delta G^\circ_{tr}(H^+) \qquad (18)$$

$$ROH(sol) + H^+(sol) \rightarrow R^+(sol) + H_2O \qquad \Delta G^\circ_{K_R}(ROH) \qquad (19)$$

In general, pK_R values have been obtained by spectrophotometric determination of the equilibrium concentrations of the organic cations in concentrated sulfuric acid.[39] It is therefore impossible to make a direct comparison with the pK_R values obtained from our electrochemical data since these measurements were carried out with acetonitrile as solvent. Notwithstanding, we made a crude comparison, by assuming that differences between the oxidation potentials of the various radicals were solvent independent (even though one of the solvents of interest was sulfuric acid). We also assumed that the free energy difference between an alcohol and its corresponding hydrocarbon was independent of structure. These assumptions would seem to be justified for the arylmethyl moieties.

Under these conditions and with diphenylmethanol as a reference material ($pK_R = -13.3$ in sulfuric acid) many of the terms in eq 13–19 cancel and ΔpK_R is given by eq 20. The results of the calculations are given in Table III. Despite the many assumptions involved, there was excellent agreement between the data based on electrochemical measurements and those obtained by other techniques.

$$\Delta pK_a = 0.728(F\Delta E^\circ + \Delta BDE) \qquad (20)$$

Finally, comparison of the oxidation and reduction potentials of the radicals in solution with their gas-phase IPs and EAs leads to information on the total solvation energy for the system, eq 21–25. For example, in the case of the benzyl system ΔG_{21} and ΔG_{23} are 6.3 and 2.2 eV, respectively, leading to $\Delta G_{25} = -4.1$ eV (−95 kcal mol^{-1}).[42-44]

$$2R^\bullet(sol) \rightarrow R^+(sol) + R^-(sol) \qquad (21)$$

$$\Delta G^\circ_{21} = E_{ox}(R^\bullet) - E_{red}(R^\bullet) \qquad (22)$$

$$2R^\bullet(g) \rightarrow R^+(g) + R^-(g) \qquad (23)$$

$$\Delta G^\circ_{23} = IP(R^\bullet) - EA(R^\bullet) \qquad (24)$$

$$\Delta G^\circ_{21} - \Delta G^\circ_{23} = \Delta G^\circ_{sol}(R^+) + \Delta G^\circ_{sol}(R^-) - 2\Delta G^\circ_{sol}(R^\bullet) \qquad (25)$$

When the absolute potential of the electrode is known, the contributions to the total solvation energy can be partially separated. The absolute potential of the normal hydrogen electrode, NHE, has been estimated to be 4.5 eV.[45] We have used this value to convert our measurements from relative to absolute potentials, E', and were thus able to calculate the differences in solvation energies between the ions and their corresponding radicals, eq 26 and 27. The data are reported in Table IV for the systems where the ionization potentials and electron affinities have been reported.

$$\Delta G^\circ_{sol}(R^+) - \Delta G^\circ_{sol}(R^\bullet) = E'_{ox}(R^\bullet) - IP(R^\bullet) \qquad (26)$$

$$\Delta G^\circ_{sol}(R^-) - \Delta G^\circ_{sol}(R^\bullet) = E'_{red}(R^\bullet) - EA(R^\bullet) \qquad (27)$$

The ionization potentials for the radicals described in Table IV are generally considered to be reasonably reliable and interestingly lead to values of ΔG_{26} that are the same within experimental error. This implies that the solvation energies for these delocalized cations are essentially constant.

The electron affinities of the diphenylmethyl and fluorenyl radicals have been determined by an indirect method involving the equilibrium of ions in the gas phase,[46] These numbers do not appear to be reliable since the EA of benzyl in the same work was found to be 1.2 eV higher than the more recently determined values.[3,44] However, on the assumption that the values of ΔG°_{27} for these radicals will be independent of structure, as was the case for the cations, the EA's can be estimated from our solution reduction potentials and the value of ΔG°_{27} for the benzyl radical. Using this approach, we have calculated EA values of 1.15 and 1.53 eV for the diphenylmethyl and fluorenyl radicals, respectively.

Summary

The electrochemical oxidation and reduction potentials of 19 carbon-centered free radicals have been measured by modulated photolytic generation of the radicals with phase-sensitive voltammetric detection. It was found that the effect of substitution of phenyl or methyl groups on the oxidation potentials of the arylmethyl radicals was about the same. In fact, the electrochemical properties of all the arylmethyl radicals can be calculated

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Table IV. Solvation in Acetonitrile

radical	EA(R$^\bullet$) (eV)	E'_{red}(R$^\bullet$) (eV)	IP(R$^\bullet$) (eV)	E'_{ox}(R$'$) (eV)	$\Delta G°_{27}{}^{g}$ (kcal/mol)	$\Delta G°_{26}{}^{g}$ (kcal/mol)
$PhCH_2$	0.86[a]	3.31[c]	7.20[d]	5.47[c]	−56.5 (−57)[h]	−39.8
Ph_2CH	1.15[b]	3.60[c]	6.8[e]	5.09[c]	*i*	−39.3
9-fluorenyl	1.53[b]	3.98[c]	7.1[f]	5.50[c]	*i*	−36.2

[a] Reference 44. [b] Calculated from this work assuming $\Delta G°_{27}$ = −56 kcal mol. [c] Calculated assuming E'(SCE) = 4.74 eV (ref 45). [d] Reference 43. [e] Reference 47. Corrected for the difference between benzyl and diphenylmethyl measured in the same laboratory. [f] Reference 48. [g] Estimated uncertainty ±4 kcal mol^{-1}. [h] Reference 45. [i] Assumed to be −56 kcal mol^{-1}.

by treating the effect of substitution by phenyl or methyl as group contributions.

The decrease in the radical oxidation potentials caused by the presence of α-oxygen or nitrogen atoms was atributed to a three-electron-bonding interaction.

Analysis of the data as a whole suggested that the measured $E_{1/2}$ values were within 100 mV of the standard potential, $E°$. The values obtained were used to calculate other thermodynamic properties such as pK_a(RH), pK_R(ROH), and solvation free energies.

Steric versus Electronic Effects on the "Tilt" of the Cyclopentadienyl Rings in Adducts of Manganese Dicyclopentadienide. Molecular and Electronic Structure of Dicyclopentadienide Manganese Tetrahydrofuran

Frank Bottomley,* Petra N. Keizer, and Peter S. White

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3. *Received February 25, 1987*

Abstract: The crystal and molecular structure of the tetrahydrofuran adduct of manganese dicyclopentadienide has been determined. The C_5H_5 rings are planar, and the total "tilt" of both rings is only 3.9°. Comparison with the tilt in phosphine adducts of $(C_5H_5)_2Mn$ leads to the conclusion that the tilting of the rings in such high-spin $(C_5H_5)_2Mn(L)_n$ adducts is due to steric rather than electronic effects. Crystal data for $(C_5H_5)_2Mn(OC_4H_8)$: monoclinic, $C2/c$; a = 12.541 (1), b = 9.927 (1), c = 12.650 (1) Å; β = 125.58 (1)°; Z = 4; R = 0.025 for 111 parameters and 987 observed reflections.

The unusual properties of manganese dicyclopentadienide, $(C_5H_5)_2Mn$, and its adducts have been the subject of many investigations[1,2] since the first discovery of these compounds.[3,4] Recently Wilkinson, Hursthouse, and their co-workers discussed a series of phosphine and diphosphine adducts of $(C_5H_5)_2Mn$.[5] In these adducts the C_5H_5 rings are planar but "tilted" to a small but significant extent. Tilting occurs when the manganese–ring (centroid) vector and the normal to the plane of the ring through the manganese are not collinear but make a small angle with each other. There are two possible reasons for this tilting. The first is electronic. If $(C_5H_5)_2Mn$ is regarded as containing Mn^{2+} and two η^5-$C_5H_5^-$ ligands and η^5-$C_5H_5^-$ donates six electrons, then monoadducts of $(C_5H_5)_2Mn$ have 19 valence electrons and bisadducts have 21. Lauher and Hoffmann have analyzed the consequences of the presence of more than 18 valence electrons in $(\eta^5$-$C_5H_5)_2M(L)_n$ derivatives.[6] They attributed the tilted, slipped, or bent C_5H_5 rings in such complexes as $(C_5H_5)_2$Mo(R)(NO) (R = I, CH_3, η^1-C_5H_5[7]) and $(C_5H_5)_2W(CO)_2$[8] to the population of orbitals having π-antibonding character. These orbitals are significantly and unsymmetrically localized on the C_5H_5 rings. However, as Wilkinson, Hursthouse, and co-workers pointed out,[5] a too rigid application of the model derived by Lauher and Hoffmann to the adducts of $(C_5H_5)_2Mn$ is unwise, because both $(C_5H_5)_2Mn$ and the adducts are essentially high spin at the temperature of the X-ray diffraction experiments that determined the structures. The bonding between C_5H_5 and Mn is very ionic,[1,3,9,10] and thus the covalent model of Lauher and Hoffmann may not be valid.

Wilkinson, Hursthouse, and co-workers suggested that the second possibility, steric repulsion, was more likely to be responsible for the observed tilting of the C_5H_5 rings.[5] The evidence was not clear-cut, as is often the case with steric arguments. The balance of various steric and electronic effects was obviously very close. It occurred to us that a detailed analysis of the structure of an adduct between $(C_5H_5)_2Mn$ and a donor that had fewer steric requirements than phosphines would be a useful way to resolve the problem of whether steric or electronic effects are the cause of the tilt. A donor in which the ligating atom was from group 16 would be particularly useful, and tetrahydrofuran, C_4H_8O (THF), appeared to be an ideal candidate. An unstable adduct between THF and $(C_5H_5)_2Mn$ was described by Wilkinson and co-workers in their first report on $(C_5H_5)_2Mn$, though it appeared

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