8.3, 13.9, 28.8, 62.2, 72.8, 162.2. IR 1750, 1540, 1340 cm^{-1}. HR-MS (M + NH_4^+) 205.1188, calcd for $C_8H_{17}N_2O_4$ 205.1182.

Ethyl *trans*,*trans*-2,3-Dimethyl-1-nitrocyclopropanecarboxylate (13e). ^{1}H NMR: δ 1.14 (m, 6 H), 1.21 (t, J = 7.2 Hz, 3 H), 1.94 (m, 2 H), 4.17 (q, J = 7.2 Hz, 2 H). ^{13}C NMR: δ 8.5, 13.9, 26.8, 62.8, 73.4, 166.7.

Ethyl *cis*-2-Acetoxy-1-nitrocyclopropanecarboxylate (13f). ^{1}H NMR: δ 1.24 (t, J = 7.0 Hz, 3 H), 1.99 (s, 3 H), 2.18 (d, J = 7.5 Hz, 2 H), 4.25 (q, J = 7.0 Hz, 2 H), 5.07 (t, J = 7.5 Hz, 1 H). ^{13}C NMR: δ 13.8, 20.2, 21.9, 56.8, 63.1, 68.4, 160.7, 169.5. IR 1750, 1550, 1360 cm^{-1}. HR-MS: (M + NH_4^+) 235.095, calcd for $C_8H_{18}N_2O_6$ 235.0931.

Ethyl *trans*-2-Acetoxy-1-nitrocyclopropanecarboxylate (13g). ^{1}H NMR: δ 1.23 (t, J = 7.3 Hz, 3 H), 1.92 (dd, J = 8.6, 7.5 Hz, 1 H), 1.99 (s, 3 H), 2.34 (dd, J = 8.6, 5.9 Hz, 1 H), 4.21 (q, J = 7.3 Hz, 2 H), 4.85 (dd, J = 7.5, 5.9 Hz, 1 H). ^{13}C NMR: δ 13.8, 20.3, 20.6, 55.2, 63.3, 68.4, 163.8, 169.5.

Ethyl *cis*-2-*n*-Butyl-1-nitrocyclopropanecarboxylate (13h). ^{1}H NMR: δ 0.82 (t, J = 7.1 Hz, 3 H), 1.2 (m, 9 H), 1.58 (dd, J = 8.9, 6.1 Hz, 1 H), 1.78 (dd, J = 10.5, 6.1 Hz, 1 H), 2.35 (m, 1 H), 4.25 (q, J = 7.1 Hz, 2 H). ^{13}C NMR: δ 13.8, 13.9, 22.1, 23.0, 27.5, 30.3, 30.6, 62.6, 70.5, 163.5. IR 1750, 1550 cm^{-1}. HR-MS: (M + NH_4^+) 233.1501, calcd for $C_{10}H_{21}N_2O_4$ 233.1508.

Ethyl *trans*-2-*n*-Butyl-1-nitrocyclopropanecarboxylate (13i). ^{1}H NMR: δ 0.82 (t, J = 7.1 Hz, 3 H), 1.2 (m, 9 H), 1.62 (dd, J = 12.8, 6.2 Hz, 1 H), 1.76 (dd, J = 8.5, 6.2 Hz, 1 H), 2.05 (m, 1 H), 4.22 (q, J = 7.1 Hz, 2 H). ^{13}C NMR: δ 13.6, 13.7, 22.0, 22.1, 27.7, 29.0, 30.2, 62.6, 71.4, 165.8.

Ethyl *syn*-7-Nitrobicyclo[4.1.0]heptane-7-carboxylate (13j). ^{1}H NMR: δ 1.05 (m, 2 H), 1.23 (m, 2 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.88 (m, 4 H), 2.30 (m, 2 H), 4.29 (q, J = 7.2 Hz, 2 H). ^{13}C NMR: δ 13.8, 19.1, 20.2, 28.4, 62.3, 72.0, 162.0. IR 1750, 1550 cm^{-1}. HR-MS: (M + H^+) 214.1075, calcd for $C_{10}H_{16}NO_4$ 214.1082.

Ethyl 2,2-Dimethyl-*cis*-3-methyl-1-nitrocyclopropanecarboxylate (13k). ^{1}H NMR: δ 1.11 (d, J = 6.6 Hz, 3 H), 1.15 (s, 3 H), 1.23 (t, J = 7.1 Hz, 3 H), 1.30 (s, 3 H), 2.17 (q, J = 6.6 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H). IR 1750, 1550 cm^{-1}. HR-MS: (M + H^+) 202.1079, calcd for $C_9H_{16}NO_4$ 202.1082.

Ethyl 1-Nitro-*trans*-3-methyl-*cis*-2-phenylcyclopropanecarboxylate (13l). ^{1}H NMR: δ 1.12 (t, J = 7.3 Hz, 3 H), 1.36 (d, J = 6.7 Hz, 3 H), 2.52 (dq, J = 11.3, 6.7 Hz, 1 H), 3.58 (d, J = 11.3 Hz, 1 H), 4.13 (q, J = 7.3 Hz, 2 H), 7.3 (m, 5 H). IR 1740, 1540 cm^{-1}. HR-MS: (M + H^+) 250.105, calcd for $C_{13}H_{16}NO_4$ 250.1082.

Ethyl 1-Nitro-*cis*-3-methyl-*trans*-2-phenylcyclopropanecarboxylate (13m). ^{1}H NMR: δ 0.88 (t, J = 7.2 Hz, 3 H), 1.28 (d, J = 6.4 Hz, 3 H), 2.68 (dq, J = 9.2, 6.4 Hz, 1 H), 3.47 (d, J = 9.2 Hz, 1 H), 3.91 (q, J = 7.2 Hz, 2 H), 7.3 (m, 5 H).

Ethyl *cis*-2-Isopropyl-1-nitrocyclopropanecarboxylate (13n). ^{1}H NMR: δ 0.97 (d, J = 2.4 Hz, 3 H), 1.00 (d, J = 2.5 Hz, 3 H), 1.16 (m, 1 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.62 (dd, J = 9.1, 5.9 Hz, 1 H), 1.75 (dd, J = 10.6, 5.9 Hz, 1 H), 2.19 (ddd, J = 10.6, 9.1, 9.4 Hz, 1 H), 4.27 (q, J = 7.2 Hz, 2 H). IR 1740, 1540 cm^{-1}. HR-MS: (M + H^+) 202.107, calcd for $C_9H_{16}NO_4$ 202.1082.

Ethyl *cis*-2-*tert*-Butyl-1-nitrocyclopropanecarboxylate (13o). ^{1}H NMR: δ 0.93 (s, 9 H), 1.32 (t, J = 7.3 Hz, 3 H), 1.70 (d, J = 10.0 Hz, 2 H), 2.42 (t, J = 10.0 Hz, 1 H), 4.28 (q, J = 7.1 Hz, 2 H). IR 1740, 1540 cm^{-1}. HR-MS: (M + H^+) 216.125, calcd for $C_{10}H_{18}NO_4$ 216.1231.

Ethyl *trans*-2-*tert*-Butyl-1-nitrocyclopropanecarboxylate (13p). ^{1}H NMR: δ 0.92 (s, 9 H), 1.26 (t, J = 7.3 Hz, 3 H), 1.55 (dd, J = 10.1, 6.1 Hz, 1 H), 2.02 (t, J = 10.1 Hz, 1 H), 4.21 (q, J = 7.3 Hz, 2 H).

Ethyl Oxo[hydroxy(1-methyl-2-propenyl)amino]acetate (14a) (1:1 mixture of rotamers). ^{1}H NMR: δ 1.13–1.34 (m, 4.5 H), 1.37–1.47 (m, 1.5 H), 4.22–4.34 (m, 2 H), 4.87–4.97 (m, 1 H), 5.14–5.24 (m, 2 H), 5.75–5.97 (m, 1 H), 7.6 (br, 1 H). ^{13}C NMR: δ 13.9, 15.6, 17.4, 53.5, 57.8, 62.5, 63.0, 117.3, 117.5, 135.1, 135.5, 154.3, 160.0, 160.7, 163.3. IR 3200, 1750, 1650 cm^{-1}. HR-MS: (M + H^+) 188.0923, calcd for $C_8H_{14}NO_4$ 188.0925.

Ethyl Oxo[hydroxy(1,2-dimethyl-2-propenyl)amino]acetate (14b) (1:1 mixture of rotamers). ^{1}H NMR: δ 1.31–1.40 (m, 4.5 H), 1.50–1.57 (m, 1.5 H), 1.74 (s, 3 H), 4.23–4.38 (m, 2 H), 4.77–4.83 (m, 0.5 H), 4.87–4.95 (m, 0.5 H), 4.99–5.03 (m, 2 H), 7.6 (br, 1 H). ^{13}C NMR: δ 13.8, 14.4, 15.9, 20.0, 20.4, 55.4, 59.9, 62.4, 63.0, 113.6, 113.8, 142.2, 154.2, 160.2, 160.9, 163.3. IR 3200, 1750, 1650 cm^{-1}. HR-MS: (M + H^+) 202.1075, calcd for $C_9H_{16}NO_4$ 202.1082.

Ethyl Oxo[hydroxy(2-cyclohexenyl)amino]acetate (14c) (1:1 mixture of rotamers). ^{1}H NMR: δ 1.22–1.31 (m, 3 H), 1.51–1.59 (m, 1 H), 1.75–2.02 (m, 5 H), 4.20–4.27 (m, 2 H), 4.62 (br, 0.5 H), 4.88 (br, 0.5 H), 5.43–5.50 (m, 1 H), 5.88–5.91 (m, 1 H), 8.2 (br, 1 H). ^{13}C NMR: δ 20.7, 20.8, 24.1, 24.3, 25.4, 26.7, 27.8, 27.9, 52.2, 56.6, 84.9, 85.2, 124.7, 124.8, 132.9, 133.1, 155.8, 159.8, 161.2, 163.0. IR 3200, 1750, 1650 cm^{-1}. HR-MS: (M + H^+) 214.1079, calcd for $C_{10}H_{16}NO_4$ 214.1082.

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Oxidation Potentials of Carbanions and Homolytic Bond Dissociation Energies of Their Conjugate Acids

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Oxidation potentials for carbanions derived from hydrocarbons and representative carbonyl, cyano, and nitro compounds have been measured in Me_2SO solution by cyclic voltammetry. The problem of referencing these values to the aqueous standard hydrogen electrode, SHE_{aq}, which is necessary in order to estimate homolytic bond dissociation energies (BDEs) in Me_2SO, is discussed. The $E_{ox}(A^-)$ values for the enolate ions derived from acetylacetone and diethyl malonate with $Li^+ClO_4^-$ as an electrolyte have been found to be 0.52 and 0.45 V more positive, respectively, than those using a $Et_4N^+BF_4^-$ electrolyte due to the stabilizing influence of the Li^+ ion in the lithium chelate. Oxidation potentials for the delocalized carbanions derived from nine hydrocarbons have been found to plot linearly with the equilibrium acidities of their conjugate acids. The slope is near unity but the plot exhibits considerable scatter (R^2 = 0.94), and points for 10 other hydrocarbons giving delocalized anions were found to deviate substantially from the line. The BDE estimated from the pK_{HA} and $E_{ox}(A^-)$ values for the acidic C–H bond in 6,6-dimethylfulvene (84.5 kcal/mol) is considerably above the average for the group of nine (81) and that for 9,10-dihydroanthracene is below average (78). The BDE for the latter, as well as the BDEs for toluene and propene, are within our experimental error of the corresponding gas-phase values. The BDE estimated from the acidic C–H bond in 1,1,3,3-tetraphenylpropene is 8 kcal/mol lower than that in propene.

Oxidation potentials in Me_2SO for carbanions generated from hydrocarbons or their derivatives have been (a) correlated with the acidities of their conjugate acids,[1,2] (b) related to rates of nonchain single-electron transfer (SET)

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reactions with electrophiles,[2-4] (c) combined with pK_{HA} values of their conjugate acids to estimate homolytic bond dissociation energies,[5] and (d) combined with the oxidation potentials of their conjugate acids *and* their pK_{HA} values to estimate radical cation acidities.[6]

Kern and Federlin[1] reported a linear correlation (with a slope of 1.1) between the oxidation potentials in Me_2SO for carbanions derived from the hydrocarbons cyclopentadiene (CpH_2), indene (InH_2), fluorene (FlH_2), and triphenylmethane (Ph_3CH) and the acidities of their conjugate acids. Points for some enolate ions, e.g., $PhC(CN){=}C(O^-)Ph$, were found to fit the line, but most of the 63 enolate ions of this type studied had less negative $E_{ox}(A^-)$ values than predicted by their basicities. The linearity of this plot is suspect, however, because the pK_{HA} values used were measured in varied solvents (benzene, cyclohexylamine, Me_2SO). A later correlation of this type,[2] which include anions derived from the hydrocarbons CpH_2, InH_2, FlH_2, Ph_3CH, Ph_2CH_2, $PhCH_3$, $CH_2{=}CHCH_3$, and $(CH_3)_3CH$, and had a slope of 0.53, is suspect for the same reason.

In our laboratory we have found two remotely substituted hydrocarbon families for which there is a good linear correlation between the oxidation potentials of the anions and the acidities of their conjugate acids, both measured in Me_2SO solution. These are the 2- and 2,7-substituted fluorenes,[7] and the 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes.[8] In each instance the slope of the line was near unity, which shows that the remote substituents are neither stabilizing nor destabilizing the radicals, and that for each 1 kcal/mol increase in anion basicity the oxidation potential of the anion becomes more negative by 1 kcal/mol. (Points for 3-donor substituents deviated slightly from the line defined by the 2- and 2,7-substituents in fluorenes, the $E_{ox}(A^-)$ values being more negative than predicted by the anion basicity because of small stabilizing effects of these para donors on the fluorenyl radical.[7]) The aryl groups in the 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadiene ions are constrained by steric effects to be nearly orthogonal to the *p* orbital of the carbanion. The effects of remote substituents on radicals are small, at best,[7] so it isn't surprising that their effects are essentially damped out for the aryl substituents in these pentadienyl radicals. On the other hand, it seemed likely that carbanions derived from hydrocarbons belonging to families as different as CpH_2, Ph_3CH, $PhCH_3$, and $CH_2{=}CHCH_3$ would give radicals with different degrees of delocalization, and would not give precise $E_{ox}(A^-)$ versus pK_{HA} plots. We have now measured acidities of 19 hydrocarbons and oxidation potentials of the corresponding conjugate bases, both in Me_2SO solution, in order to examine this point. It was also of interest to estimate the homolytic bond dissociation energies (BDEs) of these hydrocarbons by combining their oxidation potentials and pK_{HA} values according to the dictates of a thermodynamic cycle (eq 1).[5] This method requires that

$$\mathrm{BDE} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 55.9 \qquad (1)$$

the oxidation potentials in Me_2SO solution be referenced to the standard hydrogen electrode in aqueous solution $(SHE)_{aq}$. In the course of the present study we observed that our oxidation potentials referenced to SHE_{aq} for CpH^-, InH^-, FlH^-, and several other carbanions differed substantially from those measured by Kern and Federlin and referenced to SHE_{aq} by Eberson.[1,2,4] Part of the present study was directed, therefore, toward discovering the source of these discrepancies since the accuracy of our estimated BDEs depends on the validity of this referencing.

Table I. Oxidation Potential of Anions Derived from Some Hydrocarbon, Carbonyl, Cyano, and Nitro Compounds

anion	pK_{HA}[a]	$E_{ox}(A^-)$[c]	$E_{ox}(A^-)$[e]	ΔE_{ox},[f] mV
fluorenide (HFl^-)	22.6	−0.63	−0.32	−310
indenide (HIn^-)	20.1	−0.49	−0.20	−290
cyclopentadienide (HCp^-)	18.0	−0.28	−0.028	−252
$(CN)_2CH^-$	11.1	+0.59	+0.81	−220
$PhCO(Ph)CH^-$	17.7	+0.18	+0.105	−75
$CH_3CO(Ph)CH^-$	19.9	−0.19, +0.04[d]	0.00	−190, +40[d]
$(EtO_2C)_2CH^-$	16.4[b]	+0.94	+0.73	+210
$(EtO_2C)_2(Me)C^-$	18.7[b]	+0.58	+0.40	+180
$(CH_3CO)_2CH^-$	13.3[b]	+1.04	+0.73	+310
$CH_3CO(CO_2Et)CH^-$	14.2[b]	+0.93	+0.755	+175
$(CH_3)_2(NO_2)C^-$	16.9	+0.83	+0.34	+490

[a] Values reported in earlier publications from this laboratory. [b] Corrected for ion pairing (ref 17). [c] Values chosen in ref 2 and 4 as the best available and referenced to the standard hydrogen electrode (SHE_{aq}). [d] House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59–67 reported −0.20 versus SCE. [e] Values from our laboratory referenced to SHE_{aq}. [f] The difference between columns 3 and 4; see the text for a discussion.

Results and Discussion

Referencing $E_{ox}(A^-)$ Values to the Standard Hydrogen Electrode. Unfortunately, there is no direct thermodynamic method of referencing $E_{ox}(A^-)$ values measured in solutions of Me_2SO, or other dipolar nonhydroxylic solvents, to SHE_{aq}. Our $E_{ox}(A^-)$ values for carbanions and other strongly basic anions were measured in Me_2SO by cyclic voltammetry using platinium working and auxiliary electrodes and a Ag/AgI reference electrode using a 0.1 M $Et_4N^+BF_4^-$ electrolyte. We related these values to the SHE_{aq} electrode by using the ferrocene/ferrocenium redox couple as a standard. Our $E_{1/2}$ value, determined from an average of anodic and cathodic peak potentials, for this couple is +0.875 V in Me_2SO. The value for the ferrocene couple determined in THF/HMPA has been assigned a value of 510 mV versus SCE_{aq},[9] and the accepted conversion factor from SCE_{aq} to SHE_{aq} is 240 mV.[11] Our observed values for Ag/AgI, relative to the ferrocene couple, were therefore related to SHE_{aq} by adding −125 mV algebraically (875–750). The $E_{ox}(A^-)$

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[1] Kern, J. M.; Federlin, P. *Tetrahedron* **1978**, *34*, 661–670.

[2] Eberson, L. *Acta Chem. Scand.* **1984**, *B38*, 439–459.

[3] (a) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1037. (b) *Ibid.* **1982**, *47*, 2510–2516. (c) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1985–1988. (d) Lund, T.; Lund, H. *Acta Chem. Scand.* **1986**, *B40*, 470–485.

[4] Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987; Chapter IV.

[5] Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *100*, 1229–1231.

[6] (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473–2474. (b) Bordwell, F. G.; Cheng, J.-P. Bausch, M. J.; Bares, J. E. *J. Phys. Org. Chem.* **1988**, *1*, 209–223. (c) Bordwell, F. G.; Bausch, M. J.; Branca, J. C.; Harrelson, J. A., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 225–241. (d) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867–2872.

[7] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

[8] Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2872–2877.

[9] Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748. This value was estimated from measurements in THF–HMPA, 9:1, 0.2 M $LiClO_4$ for 0.1 NCE versus the ferrocene couple of 420 mV by adding 90 mV to obtain the value versus SCE_{aq} of 510 mV.[10]

[10] Private communication from R. Breslow and B. Jaun.

[11] The conversion factor of +0.24 V for SCE_{aq} to SHE_{aq} is commonly accepted, e.g., see: Yoshida, K. *Electrooxidation in Organic Chemistry*; Interscience: New York, 1984, p xii.

values for anions derived from six hydrocarbons, including fluorene, indene, and cyclopentadiene, as well as those derived from thiophenol, phenol, aniline, and acetone, were found to give homolytic bond dissociation energies (BDEs) in good agreement with literature values when used in eq 1.[12] It later came to our attention, however, that for anions derived from five carbon acids (fluorene, indene, cyclopentadiene, malononitrile, and phenylacetone) our $E_{ox}(A^-)$ values versus SHE_{aq} were 190–300 mV more positive than those measured in Me_2SO by Kern and Federlin,[1] and referenced to SHE_{aq} by Eberson (Table I).

Since our relative, $\Delta E_{ox}(A^-)$ values for HFl^-, HIn^-, and HC_p^- agreed to within 60 mV with those of Kern and Federlin that were used by Eberson (Table I), it was clear that the discrepancy in the values for these anions must lie in the method of referencing. Eberson used the value for the ferrocene couple versus SHE_{aq} of 539 mV in $PrOH/H_2O$[13] to relate the values of Kern and Federlin in Me_2SO[1] to SHE_{aq}.[14] The 211-mV difference between this value and that of Breslow accounts for most of the discrepancy.[15] The $E_{1/2}$ values for the ferrocene couple are usually independent of solvent.[9] For example, in our hands the values in MeCN and Me_2SO using a Ag/AgI reference electrode are identical (875 mV). We have also found an $E_{1/2} = +0.222$ for the ferrocene couple versus the Ag/Ag^+ electrode (a silver wire immersed in a 0.01 M $AgNO_3$, 0.1 M $LiClO_4$ in MeCN solution); this electrode has been assigned a potential of +0.267 V versus SCE_{aq}.[16] When this potential is related to SHE_{aq} ($0.222 + 0.267 + 0.24 = 0.729$ V) the value obtained is within experimental error of the value of 0.750 V assigned by Breslow. We note that the $E_{1/2}$ for the ferrocene couple in water is reported to be 0.12 V less positive than that in $PrOH/H_2O$.[13] It is possible, then, that the lower $E_{1/2}$ in $PrOH/H_2O$ than in THF/HMPA, Me_2SO, or MeCN may be due in part to the hydroxylic nature of the solvent used. Difference in liquid junction potential may also play a role here.

As a further check, the $E_{1/2}$ potential for SCE_{aq} versus the ferrocene couple in Me_2SO with $Et_4N^+BF_4^-$ electrolyte was measured and found to be 438 mV, i.e., 678 mV versus SHE_{aq}. The latter value is to be compared to the 729-mV value we obtained using the Ag/Ag^+ electrode and the 750 mV value of Jaun, Schwarz, and Breslow.[9] The average of these three values is 719 mV. If this value is accepted, the estimated BDEs that we have published earlier would need to be decreased by about 1 kcal/mol. The use of Eberson's SHE_{aq} values for FlH^-, InH^-, CpH^-, $(CN)_2CH^-$, $CH_3CO(Ph)CH^-$, etc. in eq 1 would give BDE values lower by about 4 kcal/mol. The lack of a truly thermodynamic method of relating $E_{ox}(A^-)$ values in Me_2SO to SHE_{aq} therefore introduces considerable uncertainty into our estimates of BDEs. There are also uncertainties in the values chosen for the $\Delta G^\circ_{tr}(H^+)$, $\Delta G^\circ_{sol}(H^\bullet)$, and $T\Delta S^\circ$ terms used in arriving at the constant 55.9 in eq 1.[5] In addition, most of the $E_{ox}(A^-)$ values reported are for irreversible potentials, which appear to be generally about 50–100 mV more positive than the $E_{1/2}$ values for the reversible potentials in corresponding anions.[17] Therefore, it now seems likely that the value of 55.9 for the constant in eq 1 and the agreement observed with gas-phase BDEs[5] is the result of a fortuitous cancellation of errors. Nevertheless, the good agreement with gas-phase BDEs, for whatever reason, is real, and our estimated values appear to be good to ±3 kcal/mol.[5] The value of the method for determining relative BDEs within a family with greater accuracy remains unquestioned.

Table II. Comparison of $E_{ox}(A^-)$ Values for β-Dicarbonyl Enolate Ions Using Different Electrolytes

	electrolyte		
anion from	$(Et_4N^+-BF_4^-)^a$	$(Li^+-ClO_4^-)^a$	$(Li^+-ClO_4^-)^b$
acetylacetone	+0.730	+1.25	+1.24
5,5-dimethylcyclohexane-1,3-dione	+0.875	+0.94	+0.89
diethyl malonate	+0.728	+1.18	+1.14

[a] Measured by cyclic voltammetry using Pt working and auxiliary electrodes and Ag/AgI reference electrode in Me_2SO solution (0.1 M electrolyte) using a ferrocene/ferrocenium standard. Referenced to SHE_{aq} by subtracting 0.125 V (see text). [b] Kern and Federlin's values (reported relative to ferrocene)[1] were referenced to SHE_{aq} by applying $E_{1/2}$ of ferrocene = 0.750 V.

The Effect of Li^+ Ion on $E_{ox}(A^-)$ Values of Anions Capable of Chelation. The experiments of Kern and Federlin[1] differed from ours in that they used a different reference electrode ($Ag/AgCl_2^-$ rather than Ag/AgI), a different base (*t*-BuOK in Me_2SO rather than $MeSOCH_2K$), and a different electrolyte ($Li^+ClO_4^-$, rather than $Et_4N^+BF_4^-$). In exploring reasons for the discrepancies in Table I where our values were more negative than those of Kern and Federlin, we tested the effect of changing the base and the electrolyte on the oxidation potentials. An experiment with the fluorenide ion showed that, using our electrode system, a change to the *t*-BuOK base and $Li^+ClO_4^-$ electrolyte gave an $E_{ox}(A^-)$ value within 30 mV of our earlier value, indicating that these changes were not important for carbanions of this type. This is not true for anions capable of chelation, however. Since it is known that β-dicarbonyl anions chelate strongly with lithium cations,[18] it seemed likely that the discrepancies between our values and those of Kern and Federlin versus SHE_{aq} (Table I) were caused by the difference in the cation in the electrolyte (Et_4N^+, rather than Li^+). This was confirmed by experiment (Table II).

Examination of Table II shows that we were able to check the Kern and Federlin $E_{ox}(A^-)$ values for the anions derived from acetylacetone and diethyl malonate to within 50 mV for measurements with $Li^+ClO_4^-$ as the electrolyte, but that changing to the $Et_4N^+BF_4^-$ electrolyte caused a shift to less positive potentials by 520 and 450 mV, respectively (12 and 10 kcal/mol). Since $(CH_3CO)_2CH^-$ and $(EtO_2C)_2CH^-$ ions are known to ion pair strongly with Li^+ ($\log K_{as} = 4.77$ and 4.56, respectively[18]), the large shifts show that $E_{ox}(A^-)$ values in the presence of $Li^+ClO_4^-$ are providing measures of the oxidation potentials of the lithium chelates, rather than the free anions. (Potassium ions also form complexes with these anions,[18] but the K_{as} values are low enough to assure an appreciable concentration of the free anions in solution). The shifts are larger than those shown in Table I by over 200 mV because of

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[12] It now seems likely, for reasons to be discussed later, that this good agreement is the result of fortuitous cancellation of errors.

[13] Carlson, B. W.; Miller, L. L.; Neta, P.; Gradkowski, J. *J. Am. Chem. Soc.* **1984**, *106*, 7233–7239.

[14] Eberson, L., private communication.

[15] The origin of this discrepancy is not known. It is not uncommon for CV measurements made by different investigators to differ by 50 mV, or more, even when seemingly the same experimental conditions have been used, but 211 mV is well outside of experimental error.

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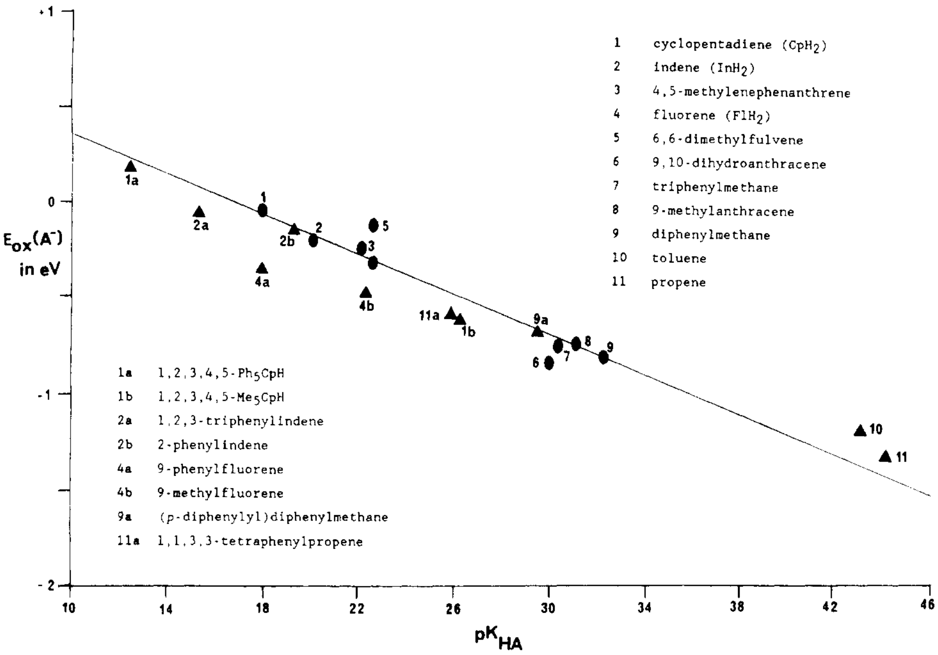

Figure 1. Plot of oxidation potentials, $E_{ox}(A^-)$, for nine highly delocalized anions derived from hydrocarbons vs the pK_{HA} values of their conjugate acids in Me_2SO solution ($R^2 = 0.94$). Points for the hydrocarbons shown as triangles were not included in the correlation.

differences in the method used for referencing the $E_{ox}(A^-)$ values to SHE_{aq}, as discussed in the previous section. For the anion derived from 5,5-dimethylcyclohexane-1,3-dione the change from Li^+ to Et_4N^+ caused only a 65-mV shift because ion pairing with Li^+ is much weaker ($\log K_{as} = 1.58$).

Correlation of Oxidation Potentials with Equilibrium Acidities in Dimethyl Sulfoxide for Hydrocarbons. The oxidation potentials of 19 hydrocarbons that form highly delocalized anions on deprotonation, together with their equilibrium acidities in Me_2SO and the homolytic bond dissociation energies of their acidic C–H bonds, are summarized in Table III.

The first 11 hydrocarbons in Table III are listed in order of increasing pK_{HA} values. Comparison of these with the $E_{ox}(A^-)$ values of their conjugate bases shows that the oxidation potentials tend to become more negative as the pK_{HA} values increase, as expected from earlier work.[1-3] The linear regression line for the first nine hydrocarbons, for which measured pK_{HA} values are in hand, has a slope of -0.0579 ($R^2 = 0.94$; sd = 0.0057). The rough linear correlation reported by Kern and Federlin is thus confirmed. This is equivalent to a slope of 0.97 when the axes are both expressed in kilocalories/mole. The plot is shown in Figure 1 with points added for phenyl and methyl derivatives of some of the nine hydrocarbons and for toluene (**10**) and propene (**11**).

The deviations of the individual points from the line along the Y axis are given in Table III as ΔY. These values can be considered as furnishing a rough measure of the degree to which the individual hydrocarbon skeletons provide radical versus anion stabilization, compared to the average for the group. Examination of the ΔY values shows that hydrocarbons **1**, **2**, **3**, **4**, **7**, **8**, and **9** are very similar in this respect, all having ΔY values of less than 1 kcal/mol. The point for 9,10-dihydroanthracene (**6**) falls below the line by 2 kcal/mol, suggesting relatively more radical stabilization, and that for 6,6-dimethylfulvene (**5**) falls above the line by 2.9 kcal/mol, suggesting relatively less radical stabilization. The points for toluene (**10**) and propene (**11**) fall above the line by 4.6 and 3.1 kcal/mol. The deviations for these points is not surprising since these two hydrocarbons are over 10 pK_{HA} units less acidic than the least acidic of the other hydrocarbons in Table III, and the pK_{HA} and $E_{ox}(A^-)$ values are much less reliable.[20]

Table III. Equilibrium Acidities and Bond Dissociation Energies of Hydrocarbons and Oxidation Potentials of Their Conjugate Bases

no.	hydrocarbon	pK_{HA}[a]	$E_{ox}(A^-)$[e]	ΔY[f]	BDE[g]
1	cyclopentadiene (CpH_2)	18.0	-0.028	-0.31	81
2	indene (InH_2)	20.1	-0.200	-1.2	79
3	4,5-methylenephenanthrene	22.2	-0.240	+0.20	81
4	fluorene (FlH_2)	22.6	-0.320	-0.75	79.5
5	6,6-dimethylfulvene	22.7[b]	-0.107	+2.9	84.5
6	9,10-dihydroanthracene	30.1	-0.825	-2.0	78
7	triphenylmethane	30.6	-0.740	-0.039	81
8	9-methylanthracene	31.1	-0.740	+0.45	81
9	diphenylmethane	32.25	-0.790	+0.72	82
10	toluene	(43)[c]	-1.185	+4.6	87.5
11	propene	(44)[c]	-1.330	+3.1	85.5
1a	1,2,3,4,5-Ph_5CpH	12.5	+0.208	-1.7	78
1b	1,2,3,4,5-Me_5CpH	26.1	-0.629	-2.5	77
2a	1,2,3-triphenylindene	15.2	-0.035	-3.2	76
2b	2-phenylindene	19.35	-0.115	-0.45	80
4a	9-phenylfluorene	17.9	-0.278	-4.6	74
4b	9-methylfluorene	22.3	-0.480	-3.7	75
9a	(p-diphenylyl)diphenylmethane	29.4	-0.689	-0.20	80
11a	1,1,3,3-tetraphenylpropene	25.8[d]	-0.610	-2.5	77

[a] Unless otherwise noted these values in Me_2SO have been reported earlier from this laboratory. [b] Reference 19. [c] Reference 20. [d] Hughes, D. L. Ph.D. Dissertation, Northwestern University, 1981. [e] Referenced to SHE_{aq}; this work and ref 5 and 6. [f] Calculated in kilocalories/mole from the correlation equation for Figure 1, $Y = 1.061 + (-0.0578)X$. [g] Calculated by using eq 1; ±3 kcal/mol.[5]

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(20) The pK_{HA} for $PhCH_3$ was extrapolated from that for $PhCH_2CN$ in Me_2SO.[21] The pK_{HA} of propene is judged to be somewhat higher in view of the more negative oxidation potential of its anion.[9] An estimate of pK_{HA} values using Breslow's method,[9] but with a BDE of 81 for Ph_3CH[5] and a pK_{HA} of 30.6 for Ph_3CH in Me_2SO, gives values of 44–45 for both toluene and propene. The $E_{ox}(A^-)$ values were measured using the lithium derivatives in THF with HMPA added to dissociate the lithium aggregates.[9] The presence of the Li^+ cation could lead to positive shifts of the potential (Table II), but the good agreement between the $E_{ox}(PhCH_2^-)$ value with a recently published $E_{rd}(PhCH_2^{\bullet})$ value[22] indicates that this is not a serious problem.

However, the points are near enough to the line to indicate that the values used are at least of the right order or magnitude.

α-Methyl substituents in these hydrocarbons make oxidation potentials more negative but have relatively little effect on pK_{HA} values. (For example, compare FlH_2 and 9-MeFlH in Table III; larger deviations would be expected for 9-MeO- and 9-Me_2N-FlH.[5,23] The ΔY values for 9-methylfluorene (−3.7) and pentamethylcyclopentadiene (−2.5) indicate enhanced radical stabilizing vs anion stabilizing ability, as expected. Since α-phenyl substituents stabilize both radicals and anions, it is more difficult to predict the ΔY values for these, particularly since the orientation of the Ph group will be important. The results suggest a greater radical than anion stabilizing effect for **1a**, **2a**, **4a**, and **11a**. The 2-Ph group in **2b** is at a site of low electron density, and its effect is small, as is the effect of the remote *p*-Ph group in **9a**.

A consideration of the BDE values (Table III) for the acidic C–H bonds in these hydrocarbons provides further insight into structural effects on radical and anion stabilities. The BDEs for **1**, **2**, **4**, **8**, **9** have been reported earlier and have been shown to be within our experimental error of the best gas-phase values.[5] The BDE for the acidic C–H bond in 6,6-dimethylfulvene (84.5 kcal–mol) is appreciably above the average for the nine hydrocarbons used for the correlation (80.7); that for 9,10-dihydroanthracene (78) is below average. The latter is within our experimental error of the gas-phase value (75.3 ± 1.5).[24] The BDE values for toluene and propene reported in Table III agree to within 1 kcal/mol with the gas-phase literature values of 88.0 ± 1 and 86.3 ± 1.5, respectively,[24] which lends further support to the validity of the pK_{HA} and $E_{ox}(A^-)$ values assigned in Table III. The BDE for 4,5-methylenephenanthrene, which can be considered to be a derivative of fluorene wherein a benzene ring has been fused across the 4, 4a, 4b, and 5 positions, is comparable to that of fluorene (81 vs 79.5 kcal/mol). The BDE 1,1,3,3-tetraphenylpropene (**11a**) (77) is 8 kcal/mol lower than that of propene, pointing to the strong delocalizing effect of the phenyl groups on the incipient radical formed on breaking the C-H bond.

Summary and Conclusions

The $E_{ox}(A^-)$ values using the Ag/AgI electrode in Me_2SO have been referenced to the aqueous standard hydrogen electrode, SHE_{aq}, by relating them to potentials of the ferrocene redox coupling, following literature methods. Evidence for the validity of the referencing method chosen comes from the good agreement between the BDEs calculated by using eq 1 and literature values. Comparison of our $E_{ox}(A^-)$ values with literature values has revealed that a change from a $Et_4N^+BF_4^-$ electrolyte to a $Li^+ClO_4^-$ electrolyte causes a positive shift of over 300 mV for β-dicarbonyl anions due to chelation with the Li^+ cation. A good linear correlation ($R^2 = 0.94$) of nearly unit slope has been observed for a plot of $E_{ox}(A^-)$ values in Me_2SO for nine delocalized hydrocarbon ions versus the pK_{HA} values of their conjugate acids in Me_2SO. The appreciable scatter in this plot and the substantial deviations observed for points for 10 additional delocalized carbanions indicates, however, that *precise* linear correlations cannot be expected for hydrocarbons with this degree of structural variation. Better precision can be expected, however, when families of anions are used wherein the basicity is changed by remote substitution because the radical-stabilizing effects of remote substituents are small.

Experimental Section

The materials were either commercially available or their sources have been described earlier.[6] They were purified by distillation or recrystallization prior to use. The purification of Me_2SO, the preparation of $CH_3SOCH_2^-K^+$, and the method for pK_{HA} determination have been described elsewhere.[25]

Cyclic voltammetric data were obtained with a three-electrode Bioanalytical Systems Inc. (BAS) apparatus and a Bausch & Lomb X-Y recorder at a scan rate of 100 mV/s. A platinum disk (BAS, polished with 0.05 micron alumina suspension between runs) and a platinum wire were used as the working and auxilliary electrodes, respectively. The reference electrode was Ag/AgI, a silver wire plated with silver iodide and immersed in a saturated Me_2SO or CH_3CN solution of tetraalkylammonium iodide. Tetraethylammonium tetrafluoroborate (0.1 M) was used as electrolyte, and all electrochemical experiments were carried out under an argon atmosphere. Other details were described previously.[6] By using an equation reported by Nicholson[26] for calculating the shift in potential due to irreversibility, we calculate that if radicals produced by anion oxidation dimerize at diffusion controlled rates (3.3×10^9), a maximum of a 90-mV shift from the true potential would occur. This is within the estimated uncertainty for our BDE calculations (±3 kcal/mol).

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Registry No. 1, 542-92-7; **1a**, 2519-10-0; **2**, 95-13-6; **2a**, 38274-35-0; **2b**, 4505-48-0; **3**, 203-64-5; **4**, 86-73-7; **4a**, 789-24-2; **4b**, 2523-37-7; **5**, 2175-91-9; **6**, 613-31-0; **7**, 519-73-3; **8**, 779-02-2; **9**, 101-81-5; **9a**, 745-36-8; **10**, 108-88-3; **11**, 115-07-1; **11a**, 4960-55-8; HFl^-, 12257-35-1; HIn^-, 12128-54-0; HCp^-, 12127-83-2; Me_2SO, 67-68-5; $LiClO_4$, 7791-03-9; $Et_4N^+BF_4^-$, 429-06-1; $(CN)_2CH^-$, 41470-37-5; $PhCO(Ph)CH^-$, 54282-53-0; $CH_3CO(Ph)CH^-$, 34438-76-1; $(EtO_2C)_2CH^-$, 14851-10-6; $(EtO_2C)_2(Me)C^-$, 71269-09-5; $(CH_3CO)_2CH^-$, 17272-66-1; $CH_3CO(CO_2Et)CH^-$, 29328-42-5; $(CH_3)_2(NO_2)C^-$, 20846-00-8; $(MeO_2C)_2CH^-$, 14851-10-6; 5,5-dimethylcyclohexane-1,3-dione, 12275-63-7.

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