oxycarbonyl)propyl)-3-(ethoxycarbonyl)-4-((benzyloxy)carbonyl)-5-(benzyloxy)pyridine (28) after flash chromatography as a mixture of 3,4 positional isomers: CI, *m/e* 506 (MH^+). This mixed ester (10.2 g) was heated for 50 min at reflux in benzene with NaOEt/EtOH to afford 7.9 g of the crude β-keto ester (**29**, but with a CO_2Et group α to the ketone): CI, *m/e* 398 (MH^+). This was heated at reflux in 2.4 N aqueous HCl with 10% ethanol for 2 h to afford a 41% yield of the ketone **3-(benzyloxy)-4-(ethoxycarbonyl)-5-oxo-5,6,7,8-tetrahydroquinoline (29)** as a waxy solid after flash chromatography: CI, *m/e* 326 (MH^+); ^1H NMR δ 1.38 (t, 3 H), 2.16 (m, 2 H), 2.68 (t, H), 3.09 (t, 2 H), 4.49 (q, 2 H), 5.23 (s, 2 H), 7.73 (m, 5 H), 8.44 (s, 1 H); IR 2950, 1735, 1695 cm^{-1}.

The ketone **29** in ethanol was reduced with 4 equiv of $NaBH_4$ in 5% aqueous NaOH for 10 min at 0 °C and then quenched with aqueous NH_4Cl. The product **3-(benzyloxy)-4-(ethoxycarbonyl)-5,6,7,8-tetrahydro-5-hydroxyquinoline (30)** was obtained as a waxy solid in 99% yield: CI, *m/e* 328 (MH^+). This was optically resolved to afford the *S* enantiomer **31** by reaction with carbonyl diimidazole to produce **32** and then reaction with (*S*)-(−)-(2-phenylethyl)amine (Aldrich) to produce the diastereomeric carbamates **33** which were separated by MPLC on a size B Lobar Li Chroprep Si60 column with EtOAc/petroleum. The fractions were monitored by HPLC, and all fractions with more than 90% of the first eluting peak were pooled and rechromatographed. Base-line separation was obtained, and the first peak (**34**) was typically obtained with less than 0.5% contamination, as judged by HPLC. This first peak was cleaved back to the resolved alcohol **31** by treatment with 1.7 equiv of $HSiCl_3$[38] and 1.2 equiv of Et_3N in benzene heated under reflux for 30 min.

Resolved alcohol **31** was converted to the mesylate ester, which was immediately allowed to react with 3-(dimethylamino)propanethiol and NaH in THF. Silica preparative plate chromatography afforded the pure thioether **35** in 82% yield as a tan oil, with correct IR and ^1H NMR. This was reduced with $LiAlH_4$ and the product **37** was isolated by preparative silica plate chromatography in 58% yield; it had the expected IR and ^1H NMR spectra. This was oxidized with CrO_3–pyridine complex in CH_2Cl_2, affording aldehyde **38** in 81% yield (IR 2950, 1725, 1710 cm^{-1}; ^1H NMR includes a 1 H singlet at δ 10.59). With hydroxylamine this gave the oxime in 87% yield, which was reduced in acetic acid with an excess of zinc dust for 30 min at room temperature. The product amine **39** was isolated by Sephadex CM25 chromatography (NH_4HCO_3 gradient) in 26% yield and converted to **5-((3-(dimethylamino)propyl)thio)-4-(aminomethyl)-3-hydroxyl-5,6,7,8-tetrahydroquinoline (36)** by 30-min heating under reflux in 6 N aqueous HCl. The product, isolated by Sephadex CM25 chromatography, was obtained in 82% yield as an off-white air-sensitive solid. Field-desorption (FD) MS, *m/e* 296 (MH^+); ^1H NMR δ 1.87 (m, 4 H), 2.1–2.9 (m, 8 H), 2.29 (s, 6 H), 4.11 (s, 2 H), 4.26 (br, 1 H), 7.84 (s, 1 H).

By a similar sequence **31** was converted to **40**, FD MS, *m/e* 252 (MH^+); ^1H NMR δ 0.97 (t, 3 H), 1.2–2.9 (m, 10 H), 3.97 (center of dd, J = 12 Hz, 2 H), 4.26 (brs, 1 H), 7.82 (s, 1 H).

Transaminations by 36 and 40. Reactions with pyruvic acid, with 2-ketovaleric acid, and with indolepyruvic acid were performed in methanol at pH 4.00 and 30.0 °C with solutions 0.16 mM in the pyridoxamine derivative and in zinc acetate and 1.6 mM in keto acid. The kinetic studies were done as described above for compounds **11–20**; the stereochemical product analyses were done as described above for compound **6**. The data are listed in Table II.

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Acidity-Oxidation-Potential (AOP) Values as Estimates of Relative Bond Dissociation Energies and Radical Stabilities in Dimethyl Sulfoxide Solution

Frederick G. Bordwell* and Mark J. Bausch

Contribution from the Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60201. *Received August 30, 1985*

Abstract: Oxidation potentials (E_{ox}) for the fluorenide ion and 21 substituted fluorenide ions have been measured in Me_2SO solution. The E_{ox} values for 2-substituted fluorenide ions were found to plot linearly with the corresponding pK_{HA} values in Me_2SO for the conjugate acids of these anions. Points for 3-methoxy-, 3-methyl-, 3-(methylthio)-, 3-(phenylthio)-, 1,2-benzo- and 2,3-benzofluorenide ions deviated from this plot. A combination of pK_{HA} and E_{ox} values gave acidity-oxidation-potential (AOP) values, which, when related to the AOP for fluorene itself, indicate that these remote substituents stabilize the fluorenyl radical by 0.4–1.5 kcal/mol. The 3-F and 3-$PhSO_2$ substituents do not stabilize the radical appreciably. A similar analysis for $GC_6H_4CHCN^-$ anions revealed radical stabilization by 4-Me_2N and 4-Ph, as well as by 4-MeO, 4-Me, and 4-PhS substituents, but not by 4-F or 4-CF_3. A similar analysis for 9-substituted fluorenes revealed much larger Δ(AOP) values, indicating radical-stabilizing effects for Me_2N, MeO, Me, MeS, and Ph donor substituents and also for the acceptor substituents, H_2NCO, MeOCO, and CN. These effects for substituents attached to a carbon atom bearing a relatively high spin density were in the range of about 2–11 kcal/mol. The effects on anion and radical stabilizations deduced from ΔpK_a and Δ(AOP) values, respectively, are compared.

Electrochemical redox potentials have been correlated with a number of experimentally derived properties including pK_a values of organic acids, Hammett σ constants, NMR chemical shifts, gas-phase ionization potentials, and kinetic data. Breyer demonstrated as early as 1938 that acidity constants of para-substituted benzenearsonic acid, *p*-$GC_6H_4AsO_3H$, could be correlated with their reduction potentials.[1] Later Zuman, in his book on polarography, collected numerous examples where E_{ox} values had been correlated with Hammett-type σ constants.[2] Federlin and his colleagues have published pK_a values in Me_2SO solution for over 100 carbon acids, mostly of the type RCOCHGG′, where G is a second acidifying function such as CN, CO_2R, $CONH_2$, COR, SO_2R, or Ar and G′ is also of this type or is hydrogen. The pK_a values for several of these families were correlated with the oxidation potentials of the corresponding anions.[3] More recently, Bank and his students have reported a correlation between pK_a values in cyclohexylamine for a series of substituted diphenyl- and triphenylmethanes vs. the oxidation potentials of their lithium salts in DME solution.[4] Also, Breslow and his students have related

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[1] Breyer, B. *Ber.* **1938**, *71*, 163–171.

[2] Zuman, P. "Substituent Effects in Organic Polarography"; Plenum Press: New York, 1967.

[3] Lochert, F.; Federlin, P. *Tetrahedron Lett.* **1973**, 1109–1112. Kern, J. M.; Federlin, P. *Ibid.* **1977**, 837–840. Kern, J. M.; Federlin, P. *Tetrahedron* **1978**, *34*, 661–670. Kern, J. M.; Sauer, J. D.; Federlin, P. *Ibid.* **1982**, *38*, 3023–3033.

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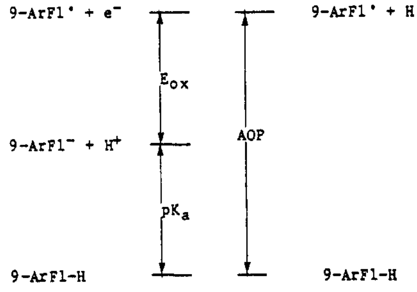

Figure 1. Hypothetical description of AOP values.

gas-phase bond dissociation energies to oxidation potentials of salts of strongly basic carbanions in a variety of media in order to estimate pK_a values.[5] Klingler and Kochi have obtained an excellent Brønsted-type correlation between anodic peak potentials for alkylmetals in acetonitrile and their ionization potentials in the gas phase.[6]

During the past 10 years, we have developed an acidity scale in dimethyl sulfoxide solution that encompasses many common classes of weak organic acids.[7] In this and subsequent papers, we will show how these acidity values can be combined with oxidation potentials of the corresponding anions to obtain estimates of relative homolytic bond dissociation energies. These, in turn, provide estimates of relative radical stabilities in Me_2SO solution.

In theory, equilibrium acidity measurements and oxidation potentials, both measured in Me_2SO solution and expressed in kilocalories per mole, can be combined to obtain relative homolytic BDEs, as brought out in eq 1-4.[8]

$$\text{H-A} \rightleftarrows \text{H}^+ + \text{A}^- \quad (pK_a) \qquad (1)$$

$$\text{A}^- \rightleftarrows \text{e}^- + \text{A}\cdot \quad (E_{ox}) \qquad (2)$$

$$\underline{\text{H}^+ + \text{e}^- \rightleftarrows \text{H}\cdot \quad (E_{red})} \qquad (3)$$

$$\text{HA} \rightleftarrows \text{H}\cdot + \text{A}\cdot \quad (\text{BDE}) \qquad (4)$$

Since E_{red} for the proton is constant, differences in the sum of the oxidation potentials of the anions and the acidity constants for their conjugate acids (pK_{HA}) can be taken as measures of relative BDEs or relative radical stabilities (eq 5).

$$pK_{HA} + E_{ox} = \text{AOP} \quad (\text{kcal/mol}) \qquad (5)$$

For example, Δ(AOP) values for two acids of similar structure, HA_1 and HA_2, will give a measure of their relative BDEs, or of the relative stabilities of the radicals, $A_1\cdot$ and $A_2\cdot$, assuming that the differences in the ground-state energies of HA_1 and HA_2 are small compared to differences in their homolytic BDEs (Figure 1). This approach is limited in practice by the irreversibility of the oxidation potentials for most anions. Nevertheless, we have observed that when families of anions wherein basicities have been changed by remote substitution are used, good correlations between E_{ox} and pK_{HA}, or between E_{ox} and log k for electron-transfer reactions, are often obtained. In these instances, the extent of irreversibility of E_{ox} throughout the family appears to be similar enough to permit estimates of relative BDEs and of relative radical stabilities by this method.

In recent years, methods have been developed that allow reasonably good estimates of homolytic BDEs in the gas phase to be made. Values from a recent review for GCH_2–H BDEs are summarized in Table I. These values provide an estimate of the ability of the substituent, G, to stabilize the $GCH_2\cdot$ radical, relative to the methyl radical.

Table I. Gas-Phase Homolytic Bond Dissociation Energies for GCH_2-H Compounds[a]

G	BDE[b]	Δ(BDE)[b]	G	BDE[b]	Δ(BDE)[b]
H	105	(0.0)	Me_3Si	99	6
Me	98	7[c]	F_3C	107	-2
t-Bu	100	5[c]	MeCO	98	7
HO	94	11	CN	93	12
MeO	93	12	Ph	88	17
Me_2N	84	21			

[a] From: McMillen, D. I.; Golden, G. M. *Annu. Rev. Phys. Chem.* **1982**, 37, 493–532. [b] In kilocalories per mole. [c] See Tsang (Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872–2880) for a discussion of the heats of formation of alkyl radicals.

Table II. Oxidation Potentials (E_{ox}) and Equilibrium Acidities (pK_{HA}) for Substituted Fluorenide Ions in Me_2SO at 25 °C

subst.	E_{ox}, V[a]	ΔE_{ox}[b]	pK_{HA}[c]	ΔpK_{HA}[b]	Δ(AOP)[b]
H	−0.194	(0.0)	22.6	(0.0)	(0.0)
3-MeO	−0.316	−2.81	23.9_5[d]	+1.84	−0.97
3-Me	−0.259	−1.50	23.4[d]	+1.10	−0.40
2-Me	−0.221	−0.623	23.1	+0.68	+0.06
2,7-$(MeO)_2$	−0.195	−0.23	22.9_5	+0.48	+0.25
2-MeO	−0.189	+0.005	22.7_5	+0.205	+0.20
3-F	−0.169	+0.58	22.1[d]	−0.68	−0.10
3-MeS	−0.172	+0.51	21.4_5	−1.57	−1.1
2-F	−0.088	+2.44	21.0	−2.19	+0.25
4-aza	−0.046	+3.41	20.5_5	−2.81	+0.60
2-Br	−0.038	+3.60	20.0	−3.56	+0.04
3-PhS	−0.061	+3.07	19.9[d]	−3.70	−0.63
2-MeS(O)	+0.041	+5.42	19.7_5	−3.90	+1.5
2-PhCO	−0.017	+4.08	19.5	−4.25	−0.18
2-$MeSO_2$	+0.056	+5.76	18.5	−5.62	+0.14
2-CN	+0.062	+5.90	18.2	−6.03	−0.13
2-$PhSO_2$	+0.083	+6.39	18.1	−6.16	+0.22
2,7-Br_2	+0.112	+7.06	17.9	−6.44	+0.62
3-$PhSO_2$	+0.179	+8.60	16.2_5[d]	−8.70	−0.10
2,7-$(CN)_2$	+0.281	+10.95	14.6	−10.96	0.0
2,3-benzo	−0.289	−2.19	23.1	+0.685	−1.5
1,2-benzo	−0.082	+2.58	19.7	−4.0	−1.4

[a] Obtained by using Pt working and auxiliary electrodes and a Ag/AgI reference electrode in Me_2SO containing 0.1 M $Et_4N^+BF_4^-$ at a sweep rate of 100 mV/s. Ferrocene/ferrocinum redox was used as a standard for the reference electrode. The (irreversible) E_{ox} values were taken as equal to E_p (the voltage at the peak of the oxidation curve), reproducible to ±10 mV. [b] In kilocalories per mole. [c] Unless otherwise noted from: Bordwell, F. G.; McCollum, G. *J. Org. Chem.* **1976**, *41*, 2391–2395. [d] Branca, J. C. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1979.

In contrast, there is a notable lack of methods for measuring homolytic BDEs in solution. As point out by Hine,[10] there is a paucity of equilibrium data concerning substituent effects on free-radical stabilities in sharp contrast to the extensive equilibrium data describing substituent effects on anion or cation stabilities. Efforts to estimate the effects of remote substituents on radical stabilities by kinetic methods have been handicapped by the presence of polar effects in most radical reactions. In attempts to construct Hammett-type $\sigma\cdot$ constants, most authors have resorted to dual-parameter equations to correct for the presence of these polar factors. The agreement between the scales is poor.[11] Of the various $\sigma\cdot$ scales that have been developed, the $\sigma_C\cdot$ scale, wherein a benzyl-type radical is produced by a thermolysis reaction, and the $\sigma_\alpha\cdot$ scale, which is based on ESR hyperfine coupling constants for benzyl radicals, appear to be least subject to polar effects.[11] When the relative AOP values are compared, we have been able to obtain estimates of the effects of both remote and

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(4) Bank, S.; Ehrlich, C. L.; Zubieta, J. A. *J. Org. Chem.* **1979**, *44*, 1454–1458. Bank, S.; Schepartz, A.; Giammateo, P.; Zubieta, J. A. *Ibid.* **1983**, *48*, 3458–3464.

(5) Breslow, R.; Schwartz, J. *J. Am. Chem. Soc.* **1983**, *105*, 6795–6796 and references cited therein.

(6) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790–4798.

(7) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006–7114. Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295–3299.

(8) This thermodynamic cycle has been used to obtain gas-phase pK_a's and, by combining proton-transfer reactions and electron affinities, to evaluate gas-phase homolytic bond dissociation energies. The present method is the solution counterpart of Brauman's method.[9]

(9) Brauman, J. I. "Frontiers of Free Radical Chemistry"; W. A. Pryor, Ed.; Academic Press: New York, 1980.

(10) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley; New York, 1975; Chapter 10. McMillen, D. I.; Golden, G. M. *Ann. Rev. Phys. Chem.* **1982**, *37*, 493–533.

(11) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221–1227. Wagner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164–1168.

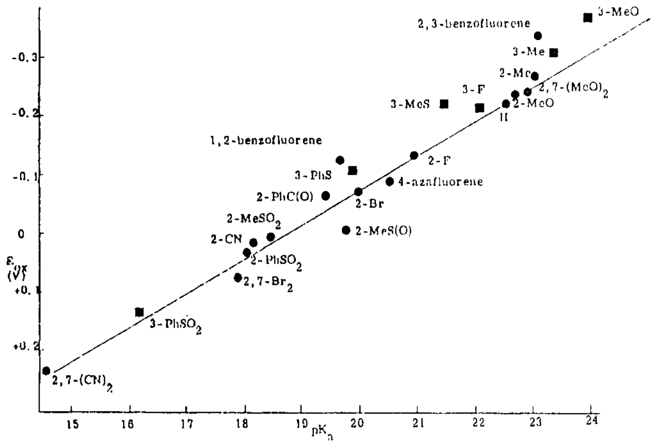


Figure 2. Plot of oxidation potentials (E_{ox}) vs. pK_{HA} values in Me$_2$SO solution for 2-substituted fluorenide ions (●); points for 3-substituted fluorenide ions are shown as squares (■).

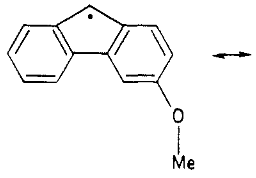
proximate substituents on radical stabilities that compare favorably with those deduced by other methods.

Results and Discussion

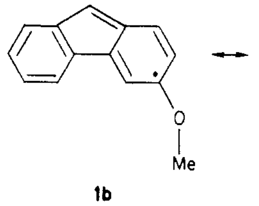
Δ(AOP) Values for Remotely Substituted Fluorenide Ions. The (irreversible) oxidation potentials for fluorenide ion and 21 of its ring-substituted derivatives are summarized in Table II, together with their pK_{HA} values. The ΔE_{ox} and ΔpK_{HA} values are then summed to obtain Δ(AOP) values, which provide an estimate of the effect of remote substituents on the stability of the fluorenyl radical.

Examination of Table II shows that substituents in the 2-, 4-, or 7-ring positions have positive values and are therefore apparently mildly radical destabilizing. The 2-PhCO and 2-CN substituents are the only exceptions, and the negative values for these are probably within the experimental error of the measurements (ca. ± 0.3 kcal/mol).

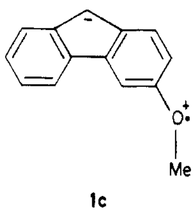
The E_{ox} values for 2-substituted fluorenide ions become progressively more positive as their basicities decrease, a pattern that has been observed several times previously.[2,3] A plot of E_{ox} vs. pK_{HA} is linear (Figure 2) with a slope near unity when the x and y axes are calibrated in kilocalories per mole. The difference in the E_{ox} values for 2,7-dimethoxy- and 2,7-dicyanofluorenide ions, which are at the termini of the line, is 11.6 kcal/mol, a number matched exactly by the difference in their pK_{HA} values in kilocalories per mole. The exact match is fortuitous, but examination of Table II shows that there is a remarkably good match between ΔE_{ox} and ΔpK_{HA} values for 2-substituents throughout the table. On the other hand, the ΔE_{ox} values for most 3-substituents are more negative than predicted by the pK_{HA} values. This causes the points for 3-MeO, 3-Me, 3-MeS, and 3-PhS substituents to fall appreciably above the line in Figure 2. The more facile loss of an electron for fluorenide ions containing these remote substituents can be explained by their ability to stabilize the radical being formed by delocalization of the odd electron, e.g., as in resonance contributors **1a**–**1c**.



1a

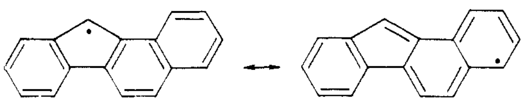


1b



1c

The largest stabilizing effects are exerted by the 1,2- and 2,3-benzo substituents (1.5 and 1.4 kcal/mol, respectively). The fused benzene rings allow additional delocalization of the odd electron, e.g., as in resonance contributors **2a** and **2b**.



2a **2b**

The 3-F and 3-PhSO$_2$ functions are unusual in that their effects on E_{ox} are nicely matched by the basicity predictions, i.e., the Δ(AOP) values are −0.1 kcal/mol in each instance (Table II), indicating no radical delocalization.

Radical-Stabilizing and -Destabilizing Effects of Remote Substituents in Fluorenes and in Phenylacetonitriles. According to the thermodynamic cycle presented earlier, the Δ(AOP) values in Table II represent the effect of 2- and 3-substituents on the BDEs of the C–H bonds at the 9-position of fluorene, relative to that of hydrogen. Examination of Table II shows that 10 of the Δ(AOP) values for substituents in the 2- and 2,7-positions are positive, whereas only 2 are negative (2-PhCO, −0.18 and 2-CN, −0.13); that for 2,7-(CN)$_2$ is zero. The positive values suggest radical destabilization, which is in agreement with the conclusion that the meta substituents are, in general, radical-destabilizing.[11] (The 2-position in fluorene is primarily meta, but has some para character.[12b]) In contrast, the Δ(AOP) values for the 6 substituents in the 3-position are all negative. The Δ(AOP) values for the 3-F and 3-PhSO$_2$ substituents (each −0.10) are too small to be significant, but the values for 3-MeO (−0.97), 3-Me (−0.40), 3-MeS (−1.1), and 3-PhS (−0.63) all appear to be large enough to indicate an appreciable lowering of the C–H BDE, suggesting stabilization of the radical by the remote substituent. This interpretation is strengthened by the observations of appreciable negative values for the 2,3- and 1,2-benzo substituents, −1.5 and −1.4, respectively. These substituents each provide an additional planar benzene ring over which the odd electron can be delocalized.

Four of the $\sigma\cdot$ scales reviewed by Dust and Arnold lead to the conclusion that the order of radical-stabilizing ability is p-MeO > p-Me.[11] The Creary scale, $\sigma_{C}\cdot$, gives the substituent order p-MeS (0.43) > p-MeO (0.24) > p-Me (0.11) > H (0.0) > p-F (−0.08). The order p-MeO > p-Me > H > p-F is also given by the $\sigma_{\alpha}\cdot$ scale. The order of Δ(AOP) values, 3-MeS (−1.1), 3-MeO (−1.0) > 3-Me (−0.4) > H (0.0) > 3-F, is similar.

The oxidation potentials for the conjugate base of phenylacetonitrile and 16 of its 3- and 4-substituted derivatives, along with the corresponding pK_{HA} data, are summarized in Table III. A plot of E_{ox} vs. pK_{HA} for the 3-substituents, which extends over 6.0 kcal/mol in E_{ox} and 4.7 kcal/mol in basicities, is linear with scatter (Figure 3). Examination of Table III shows that all the 3-substituents have positive Δ(AOP) values varying in size from +0.55 to +1.4. On the other hand, the 4-substituents, with the exception of 4-F, 4-Cl, and 4-CF$_3$, are all negative, indicating radical stabilization. The points for 4-substituents capable of delocalizing the odd electron deviate from the line in Figure 3. The order of stabilizing effects indicated by the Δ(AOP) values is 4-Me$_2$N (−3.9) > 4-MeO (−1.3) > 4-PhS (−0.7), 4-Ph (−0.7) > 4-Me (−0.4). This order is consistent with that found for Δ(AOP) values of 3-substituted fluorenide ions. The smaller effect for 4-Ph (−0.7 kcal/mol) than the 2,3-benzofluorenide ion (−1.5 kcal/mol) is understandable, since planarity of the fused phenyl substituent is enforced in the latter. The large effect of 4-Me$_2$N is anticipated by the BDE data (Table I). The failure of 4-F to exert a stabilizing effect in 4-FC$_6$H$_4$CHCN· is consistent with the result obtained for the 3-fluorofluorenyl radical and with the $\sigma_{C}\cdot$ and $\sigma_{\alpha}\cdot$ data, which predict radical destabilization. The failure of 4-CF$_3$ to stabilize the radical is in agreement with the BDE data (Table I), which suggest that the CF$_3$ function destabilizes the methyl radical.

The agreement between the apparent radical-stabilizing effects derived from Δ(AOP) values for 3-G-FlH and 4-GC$_6$H$_4$CH$_2$CN acids is surprisingly good considering the difference in the systems:

Table III. Oxidation Potentials, (E_{ox}), and Equilibrium Acidities (pK_{HA}) for Substituted Phenylacetonitrile Ions, $GC_6H_4CHCN^-$ in Me_2SO at 25 °C

G	E_{ox}, V[a]	ΔE_{ox}, kcal	pK_{HA}[b]	ΔpK_{HA}, kcal	Δ(AOP)[c]
H	−0.061	(0.0)	21.9	(0.0)	(0.0)
4-Me_2N	−0.393	−7.65	24.6	3.70	−3.9
4-MeO	−0.229	−3.87	23.7_5	2.53	−1.3
4-Me	−0.136	−1.73	22.9	1.37	−0.56
3-Me	−0.055	+0.138	22.2	0.411	+0.55
4-F	−0.070	−0.207	22.2	0.411	+0.20
3-MeO	−0.034	+0.623	21.6_5	−0.342	+0.28
4-Ph	−0.025	+0.830	20.8	−1.51	−0.68
4-Cl	+0.027	+2.03	20.5	−1.92	+0.11
3-F	+0.083	+3.32	19.5_5	−1.95	+1.4
4-PhS	+0.049	+2.54	19.5_5	−3.22	−0.68
3-Cl	+0.137	+4.56	19.5	−3.29	+1.3
3-CF_3	+0.167	+5.26	19.2	−3.70	+1.6
3-CN	+0.179	+5.53	18.7	−4.38	+1.2
3,4-Cl_2	+0.173	+5.40	18.6_5	−4.45	+0.95
3-$PhSO_2$	+0.200	+6.02	18.5	−4.66	+1.4
4-CF_3	+0.218	+6.43	18.1	−5.21	+1.2

[a] Obtained by using a Pt working and auxiliary electrodes and a Ag/AgI reference electrode in Me_2SO containing 0.1 M $Et_4N^+BF_4^-$ at a sweep rate of 100 mV/s. Ferrocene/ferrocinum redox was used as a standard for the reference electrode. The (irreversible) E_{ox} values were taken as equal to E_p (the voltage at the peak of the oxidation curve), reproducible to ±10 mV. [b] Bares, J. E. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1976. [c] In kilocalories per mole.

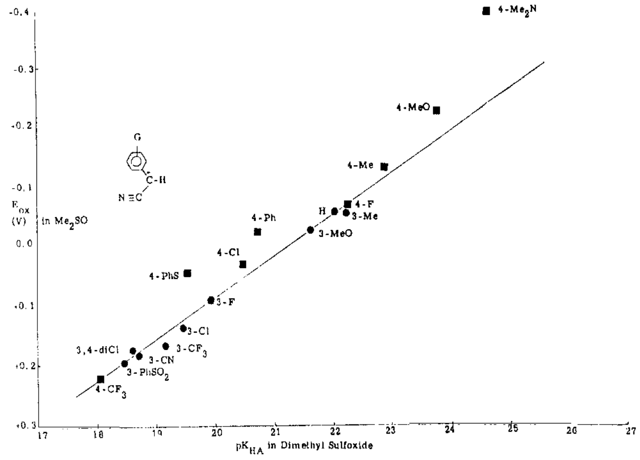


Figure 3. Plot of oxidation potentials (E_{ox}) vs. pK_{HA} in Me_2SO solution for arylcyanomethide ions, $GC_6H_4CHCN^-$.

Table IV. Equilibrium Acidities for 9-Substituted Fluorenes (9-G–Fl–H), Irreversible Oxidation Potentials for 9-Substituted Fluorenide Ions, and ΔAOP Values in Me_2SO at 25 °C

G	pK_{HA}[b]	ΔpK_a, kcal[e]	E_{ox}, V[f]	ΔE_{ox}, kcal	Δ(AOP)
H	22.6	(0.0)	−0.194	(0.0)	(0.0)
Me_2N	22.5[c]	−0.55	−0.56[g]	−8.4	−9.0
Me_2N	22.5[c]	−0.55	−0.66[h]	−10.2	−10.7
MeO	22.1	−1.1	−0.449	−5.89	−7.0
PhO	19.9	−4.1	−0.256	−1.43	−5.5
Me	22.3	−0.82	−0.355	−3.72	−4.5
Ph	17.9	−6.85	−0.153	+0.945	−5.9
Ph[a]	10.5[d]	−17.0	+0.120[i]	+7.24	−9.7
MeS	18.0	−6.7	−0.136	+1.34	−5.4
PhS	15.4	−10.3	+0.026	+5.07	−5.2
H_2NCO	11.9	−15.1	+0.363	+12.8	−2.3
MeOCO	10.35	−17.2	+0.383	+13.3	−3.9
CN	8.3	−20.0	+0.427	+14.3	−5.7
$PhSO_2$	11.5	−15.6	+0.566	+17.5	+2.1

[a] In fluoradene: see Figure 5. [b] Taken from earlier publications from this laboratory. [c] Mueller, M. E., unpublished results. [d] Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 2821–2824. [e] Statistically corrected. [f] Obtained by using Pt working and auxiliary electrodes and a Ag/AgI reference electrode in Me_2SO containing 0.1 M $Et_4N^+BF_4^-$ at a sweep rate of 100 mV/s. Ferrocene/ferrocinum redox was used as a standard for the reference electrode. The (irreversible) E_{ox} values were taken as equal to E_p (the voltage at the peak of the oxidation curve), reproducible to ±10 mV. [g] Reversible wave. [h] Corrected value (see text). [i] Wilson, C. A., unpublished results.

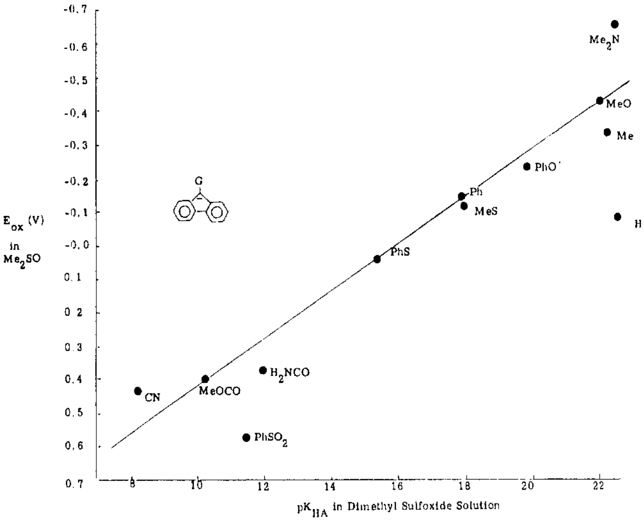


Figure 4. Plot of oxidation potentials (E_{ox}) vs. pK_{HA} in Me_2SO solution for 9-substituted fluorenide ions, 9-G–Fl⁻.

3-MeO, −1.0; 4-MeO, −1.3; 3-PhS, −0.63; 4-PhS, −0.68; 3-Me, −0.40; 4-Me, −0.56. Similar radical-stabilizing effects for these functions, as well as Ph and Me_2N substituents, are also indicated by Δ(AOP) values for 9-substituted fluorenes, as will be brought out in the next section.

The AOP method appears to be working well for detecting radical-stabilzing effects caused by para donor substituents. Its application to para acceptor substituents is less certain. The apparent lack of a stabilizing effect for the 4-Cl substituent [Δ(AOP) = +0.11 in Table III] is surprising since the $\sigma_\alpha\cdot$ and all seven $\sigma\cdot$ scales listed by Arnold and Dust indicate that *p*-Cl is radical-stabilizing. (Most suggest a stabilizing effect as large as Me, or larger.) Also, a recent measurement of Δ(AOP) for *p*-$CNC_6H_4CH_2CN$ failed to indicate the expected radical stabilization by *p*-CN.[13] It also needs to be emphasized that the AOP method assumes that substituent effects on the ground states of the acids can be neglected. This may not be a good assumption in all instances, particularly in view of the small size of remote substituent effects on radical stabilities.

The stabilizing effects of the para substituents Me_2N, MeO, Ph, and Me, on fluorenyl and arylcyanomethyl radicals are appreciable but are small compared to their effects on methyl radicals (Table I). In the next section, we will see that similar, but much larger, effects are observed for 9-substituents in fluorenyl radicals.

Δ(AOP) Values for 9-Substituted Fluorenide Ions. Oxidation potentials for the fluoradenide ion, fluorenide ion, and 11 9-substituted fluorenide ions, 9-G–Fl⁻, are presented in Table IV, together with the equilibrium acidities of their conjugate acids in Me_2SO solution.

Examination of Table IV shows that as the 9-G-Fl⁻ anions become less basic, they become more difficult to oxidize, as expected. A plot of E_{ox} vs. pK_{HA} (Figure 4) shows considerable scatter, however, compared to the linearity of Figure 2. Nevertheless, a line of the same slope as that in Figure 2 accommodates most of the points reasonably well, as shown. This suggests that CN, MeOCO, H_2NCO, PhS, Ph, MeS, PhO, MeO, and Me all stabilize the 9-Fl· radical to approximately the same degree, averaging about 4.5 kcal/mol for these nine substituents, relative to hydrogen. It must be remembered that this analysis does not take into account the effect of the substituents on the ground-state energies of the fluorenes, which could be appreciable in some instances. For that reason, we hesitate to use the Δ(AOP) values to define an order of radical-stabilizing effects for these sub-

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(12) (a) Streitweiser, A.; Hammons, J. H. *Prog. Phys. Org. Chem.* **1965**, *3*, 41–80. (b) Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503–507.

(13) Wilson, C. A., unpublished results.

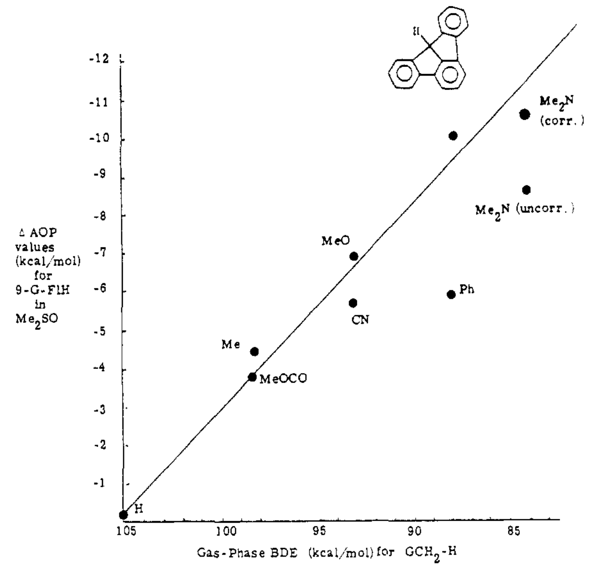
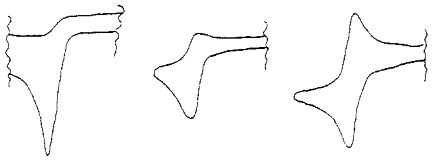


Figure 5. Plot of Δ(AOP) values in Me_2SO for 9-substituted fluorenes, 9-GFl–H, vs. gas-phase homolytic bond dissociation energies (BDE) for the corresponding methanes, GCH_2–H.



(a) (b) (c)

Figure 6. Cyclic voltammograms of 1 mM solutions of (a) 9-phenylfluorenide, (b) 9-(2-Me-4-$MeSC_6H_3$)fluorenide, and (c) 9-(2,4,6-$Me_3C_6H_2$)fluorenide ions in Me_2SO solution.

stituents, although the order Me_2N > MeO > Me > H appears secure. The $PhSO_2$ substituent appears to have little or no radical-stabilizing effect, but this result must be viewed with caution (see the Experimental Section). The Me_2N substituent appears to have an unusually strong radical-stabilizing effect, which is consistent with the electrochemistry of 9-Me_2N-Fl^-, as will be brought out in the next section.

A plot of Δ(AOP) values for 9-substituted fluorenes, 9-GFl–H, as a function of gas-phase BDEs (where available) for the corresponding substituted methanes, GCH_2–H (Figure 5), lends support to this interpretation of the data.

The correlation in Figure 5 is surprisingly good considering the 20 kcal/mol range in BDEs covered and the difference in the methods used. The slope of the line is about 0.5, which means that the stabilizing effects of MeO, Me, MeOCO, and CN substituents on fluorenyl radicals are about one-half as large as their effects on the corresponding methyl radicals. This is reasonable since the stabilizing effect of a given substituent, G, is expected to be smaller on the delocalized fluorenyl radical, 9-G-Fl·, than on the localized methyl radical, GCH_2·.

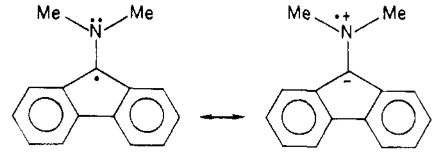
The stabilizing effect of the 9-Ph substituent on the fluorenyl radical is only 5.9 kcal/mol, as compared to about 17 kcal/mol for the Ph effect on the methyl radical. There is evidence showing that the phenyl ring in the 9-$PhFl^-$ ion is twisted about 30–40° out of the plane of the fluorene ring due to steric repulsions of the ortho hydrogen atoms in the phenyl ring and the 1- and 8-hydrogen atoms in the fluorene ring.[12] Since the 9-PhFl· radical should have similar steric demands, the stabilizing effect of the 9-phenyl substituent will be attenuated due to noncoplanarity with the half-filled orbital on the 9-carbon of the fluorene radical. The Ph moiety in fluoradene is attached to the 1- and 8-positions of the fluorene ring and is held nearly coplanar with this ring. As a consequence, the acidity of fluoradene is increased by 10 kcal/mol, relative to that of 9-phenylfluorene (Table IV). One would expect similar stabilization of the odd electron in the radical, and this was indeed realized; the observed Δ(AOP) value of −9.7 kcal/mol (Table IV) places the point for fluoradene in the expected region in Figure 5.

Table V. Data for Reversible and Irreversible Oxidation Potentials of Ions of 9-Arylfluorenes,[c] 1,2,3,4-Tetraphenylcyclopentadiene (Ph_4CpH_2), and 1,2,3,4,5-Pentaphenylcyclopentadiene (Ph_5CpH)

compound	pK_a	ΔE_{ox}-(calcd)[a]	E_{ox}, mV	ΔE_{ox}-(obsd)[c]	corr.[d]	$E_p - E_{p/2}$[g]
9-Ph–FlH	17.9	(0.0)	−219	(0.0)	(0.0)	50
9-(4-MeC_6H_4)FlH	18.3	−13	−259	−40	−27	50
9-(2-MeC_6H_4)FlH	18.8	−54	−168	+51	+105	50
9-(2-Me-4-MeS)-FlH	18.6	−42	−168	+51	+93[e]	50
9-(2,4,6-$Me_3C_6H_2$)-FlH	18.6	−42	−174[b]	+45	+87[f]	60
1,2,3,4-Ph_4CpH_2	13.7	(0.0)	+120	(0.0)	(0.0)	50
1,2,3,4,5-Ph_5CpH	12.5	+89	+295[b]	+175	+86	60

[a] E_{ox}(calcd) = ΔpK_a(kcal)/23.06 × 1000. [b] $E_{1/2}$ in millivolts. [c] Peak potential (E_p) in millivolts. [d] ΔE_{ox}(obsd) − ΔE_{ox}(calcd). [e] Uncorrected for the presumed anodic shift caused by the 4-MeS function. [f] Uncorrected for the anodic shift caused by the 4-Me function. [g] Peak potential − peak potential at half-height.

Reversible and Irreversible Oxidation Potentials. The oxidation potential for the 9-Me_2N–Fl^- ion differs from those other 9-G–Fl^- ions in being reversible; i.e., the wave breadth ($E_p - E_{p/2}$) is near 60 mV, and a cathodic wave comparable in peak height to the anodic wave is observed. Reversibility is no doubt realized in this instance because a large fraction of the spin density is on nitrogen (contributor **3b**) which inhibits dimerization.



3a **3b**

Rapid dimerization is presumably the cause of ireversibility of the oxidation potentials for the other 9-G–Fl^- ions. Irreversibility is known to lead to wave narrowing and cathodic shifts. For that reason, the E_{ox} value for 9-Me_2N–Fl^- needs to be corrected in order to compare it with the irreversible E_{ox} values for the other 9-G–Fl^- ions in Table IV. There are several ways to estimate the size of the correction. One way is by application of the Nicholson equation;[14] this leads to a value of 80 mV for the cathodic shift under the conditions of our experiment. Another and perhaps better way is to compare the E_{ox} values for a similar series of compounds where structural changes cause a change for reversible to irreversible behavior (Table V).

The CV waves for 9-$PhFl^-$ and 9-(4-MeC_6H_4)Fl^- are essentially superimposable, neither showing any evidence for a reverse, cathodic wave (Figure 6a). The 27-mV anodic shift in Table V for the 4-Me derivative, relative to the parent (after correcting for an anodic shift caused by its higher basicity), is believed to represent the stabilizing effect of Me on the 9-(4-MeC_6H_4)Fl· radical. [This 0.6 kcal/mol stabilizing effect is comparable to that in 3-MeFl· (0.4 kcal/mol) and 4-MeC_6H_4CHCN· (0.6 kcal/mol).] The E_{ox} peaks for the 9-(2-MeC_6H_4)Fl^- and 9-(2-Me-4-MeS)Fl^- ions are also nearly superimposable. They differ from those for the 9-$PhFl^-$ and 9-(4-MeC_6H_4)Fl^- ions, however, in that a cathodic wave is observed, which is about one-half the size of the anodic wave (Figure 6b). When steric hindrance to dimerization is increased still further by the presence of a second ortho methyl group [9-(2,4,6-$Me_3C_6H_2$)Fl^-] complete reversibility was observed (Figure 6c). The results with this series of fluorenes suggest that a correction of about 100 mV for the E_{ox} of the 9-Me_2N–Fl^- ion should be made for comparison with other 9-G–Fl^- ions. The comparison of the data for Ph_4CpH^- and Ph_5Cp^- ions (Table V) supports this conclusion. The pentaphenylcyclo-

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[14] Olmstead, M. L.; Hamilton, R. G.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 260–267.

pentadiene is more acidic than tetraphenylcyclopentadiene by 1.5 units (statistically corrected). The 86-mV cathodic shift observed for the Ph_4Cp^- ion is believed to be caused by the change from irreversible to reversible electrochemistry. This is probably a minimum figure since the $Ph_5Cp\cdot$ radical is likely to be more stable than the $Ph_4CpH\cdot$ radical, which should lead to an anodic contribution.

Comparison of Proximate Substituent Effects on Fluorene Anions and Radicals. The ΔpK_a and Δ(AOP) values summarized in Table IV provide estimates of anion- and radical-stabilizing effects of the 9-substituents, assuming that the ground-state effects in 9-G–FlH are relatively small. In general, we conclude that polar effects of G, aided by solvation as well as delocalization effects, stabilize 9-G-Fl^- anions but that polar effects unaccompanied by delocalization do not stabilize $9\text{-G-Fl}\cdot$ radicals. Since phenyl has only a small inductive effect ($\sigma_I = 0.1$), it stabilizes adjacent charges or odd electrons principally by delocalization, and its proximate effects on anions and radicals are similar. For 9-phenylfluorene, the stabilizing effect on the anion is about 7 kcal/mol vs. about 6 on the radical, while in fluoradene these effects are each about 10 kcal/mol (Table IV). For polar, π-delocalizing electron-withdrawing substituents such as H_2NCO, MeCO, and CN, the anion-stabilizing effects are about 15, 17, and 20 kcal/mol, respectively, compared to radical-stabilizing effects of about 5 kcal/mol. The $PhSO_2$ substituent is strongly anion stabilizing (~16 kcal/mol), but its radical-stabilizing ability is questionable. The MeS and PhS substituents are strongly anion stabilizing (about 7 and 10 kcal/mol, respectively) and are also strongly radical stabilizing (about 5 kcal/mol). The donor substituents Me, PhO, MeO, and Me_2N are weakly anion stabilizing (about 1, 4, 1, and 0.5 kcal/mol, respectively) and strongly radical stabilizing (about 5, 6, 7, and 11 kcal/mol, respectively).

Estimates of the relative effects of a number of proximate substituents on incipient radical stabilities have been made by measuring the relative rates of thermolysis of azo compounds.[15] The rates for donor substituents were found to be in the order CH_3 (1.0) < CH_3O (22) < C_6H_5S (7×10^3) < CH_3S (1.9×10^4). The order CH_3S > PhS is similar to that in the present work, but the order for RO and RS substituents is reversed. The CN substituent is slightly more stabilizing than the CH_3 substituent and much more stabilizing than the $PhSO_2$ substituent, which is in agreement with the present results.

Summary and Conclusions

The pK_a values for a variety of fluorenes bearing remote substituents (2-, 3-, and 7-positions) or proximate substituents (9-position) have been combined to give relative acidity-oxidation-potential values Δ(AOP), which provide a method of measuring relative BDEs and, in turn, relative radical-stabilizing effects of substituents in Me_2SO solution. Para, but not meta, remote donor substituents (Me, MeO, MeS, Me_2N, and Ph) have been found to have mild stabilizing effects (0.5–3 kcal/mol), in agreement with literature reports.[11] Proximate substituents in 9-substituted fluorenes have been found to have much larger effects (about 5 kcal/mol), which correlate well with gas-phase BDEs (Figure 5). This AOP method gives promise of providing an important method for measuring the relative anion-stabilizing and radical-stabilizing effects for numerous substituents.

Experimental Section

General. NMR spectra were obtained by using Varian EM-360 and EM-390 spectrometers. EPR spectra were obtained by John Cline, using a Varian Assoc. Model E-4 spectrometer. Melting points are uncorrected and were determined by using a Thomas-Hoover Unimelt capillary melting-point apparatus.

The purification of Me_2SO and the preparation and standardization of $CH_3SOCH_2^-K^+$ (potassium dimsyl solution), as well as the method for the pK_a determinations, have been described previously.[7]

Materials. The syntheses and sources of the 9-arylfluorenes have been described elsewhere,[16] except for 9-(4-methoxyphenyl)fluorene, which was prepared according to the method of Cockerill and Lamper,[12] and 3-methyl-9-phenylfluorene, which appears to be a new compound. It was prepared from a 1-g sample of 3-methylfluorenone (synthesized by G. J. McCollum) by reaction with 3 mL of phenyllithium (2.7 M) in toluene at 0 °C. After stirring for 1.5 h, the reaction mixture was hydrolyzed with 2 N HCl, extracted with ether, washed with water, and dried with anhydrous Na_2SO_4. The crude carbinol obtained by evaporation of the ether was reduced with iodine and H_3PO_2 in acetic acid by the method described earlier for 2-chloro-9-methylfluorene.[16] The hydrocarbon was crystallized from acetone/water and hexane; the white fluffy sample method at 104 °C: NMR ($CDCl_3$) 2.5 (3 H, s, CH_3), 5.0 (1 H, s, 9-H proton), 7.0–7.8 (12 H, m, aryl protons).

1,2,3,4,5-Pentaphenyl-1,4-cyclopentadiene was prepared according to the method of Niem and Rausch.[17] The white product was recrystallized from benzene and melted at 255 °C (lit.[17] mp 259–260 °C).

Electrochemical Techniques. Cyclic voltammetric experiments were performed by using a three-electrode Bioanalytical Systems Inc. (BAS) apparatus, Purdue Research Park, W. Lafayette, IN. Voltammograms were recorded on a Bausch & Lomb X-Y recorder. A platinum disk (BAS, polished with silica between runs) was used as the working electrode, a platinum wire (BAS) was used as the auxiliary electrode, and a Ag/AgI electrode was used as a reference electrode. Experiments were conducted in standard glass cells (cleaned with acetone between runs) provided by BAS. Cells were fitted with a three-way stopcock similar to that described previously.[7] Tetraethylammonium tetrafluoroborate (analytical grade, sublimed before use) was used as the supporting electrolyte. Anhydrous Me_2SO (purification described previously),[7] 0.1 M in tetraethylammonium tetrafluoroborate, was used as the solvent.

A typical 9-ArFl^- E_{ox} value was determined in the following way. About 5 mg of the 9-ArFl-H acid whose 9-ArFl^- anion was to be oxidized was added to the cell. This cell was evacuated and flushed with argon at least 3 times. About 7 mL of Me_2SO (0.1 M in $Et_4N^+BF_4^-$) was then added to the cell via a Hamilton air-tight syringe, giving about a 2–3 mM solution. The cell and its contents were then transferred to the CV apparatus, and argon was bubbled into the solution for about 2 min. At this point, enough dimsyl anion was added to the solution, also via an air-tight syringe, in order to generate a 1 mM solution of the 9-ArFl^- anion. Argon bubbling into the solution served to distribute the dimsyl anion throughout the cell; upon addition of the dimsyl, the Me_2SO solution took on the characteristic color of the 9-ArFl^- carbanion, indicative of an oxygen-free environment. (As evidenced by this color, in the electrochemical cell, the 9-ArFl^- solutions were stable for days, when kept under argon.) After dimsyl addition, the cell and its contents were further blanketed with argon for about 1 min, immediately preceding the E_{ox} determinations.

Voltammograms were recorded at sweep rates of 100 mV/s, between −1.5 V and +1.5 V (vs. Ag/AgI reference electrode). In our systems, an $E_{1/2}$ value of 0.875 V was observed for the ferrocene–ferrocinium redox couple.

Irreversible and Reversible Oxidation Potentials. The oxidations of nearly all the fluorenide ions with 2-, 3-, or 9-substituents, as well as the arylcyanomethide ions, were remarkably free of side reactions as judged by the similarity in appearance and breadth of the waves, the reproductibility of the peak potentials, and the effects of changing the scan rate on the peak potentials. As brought out in Figure 6a, many of the irreversible oxidation potentials are similar to the point of being superimposable. The irreversible waves all exhibit the narrowness (50 ± 5 mV) characteristic of rapid follow reactions, probably dimerizations.[18] On the other hand, the reversible waves for 9-(dimethylamino)fluorenide, 9-mesitylfluorenide, and 1,2,3,4,5-pentaphenylcyclopentadienide ions have wave breadths comparable to that of ferrocene (60 ± 5 mV). The peak potentials are reproducible to ±3 mV for successive runs, ±6 mV for runs made by the same investigator after several days (or weeks) and ±10 mV for different investigators. This compares favorably with investigations with (more basic) diphenylmethide ions in DME,[4] cyclopentadienide, and benzyl ions (Li salts in THF)[5] and alkylmetals in CH_3CN,[6] where reproducibilities of ±5 (consecutive runs), ±20, and ±50 mV have been reported. Increasing the scan rate causes a cathodic shift in peak potential for the irreversible potentials, as expected. The effect of changing the scan rate from 10 to 500 mV/s for representative fluorenide ions is shown in Table VI. For the ion exhibiting irreversible potentials, the shift observed was 55 ± 4 mV for fluorenide ions with different types of substituents in various positions. The shift was less (48 mV) for the partially reversible 9-(2-methylphenyl)fluorenide ion (Figure 6) and almost negligible for the reversible 9-mesitylfluorenide and

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[15] Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856–5862. Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150. Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268–270.

[16] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314–3320.

[17] Niem, R.; Rausch, M. D. *J. Org. Chem.* **1977**, *42*, 275–279.

[18] Both fluorenide and arylcyanomethide ions have been observed to undergo dimerization when treated with electron acceptors.[19]

Table VI. Shifts in Peak Potentials for the Oxidation of Carbanions on Changing Sweep Rates in Cyclic Voltammograms from 10 to 500 mV/s

anion	E_p, mV/s		E_p (10) − E_p (500)
	10	500	
fluorenide	−0.220	−0.169	0.051
9-*tert*-butylfluorenide	−0.309	−0.250	0.059
2,7-dibromo-9-methylfluorenide	−0.083	−0.024	0.059
9-(3-chlorophenyl)fluorenide	−0.088	−0.032	0.056
9-(methoxycarbonyl)fluorenide	+0.354	+0.408	0.054
9-phenoxyfluorenide	−0.278	−0.220	0.058
9-(benzhydryl)fluorenide	−0.234	−0.179	0.055
9-(2-methylphenyl)fluorenide	−0.117	−0.067	0.048
9-mesitylfluorenide	−0.151	−0.141	0.010
pentaphenylcyclopentadienide	+0.325	+0.333	0.008

1,2,3,4,5-pentaphenylcyclopentadienide ions.

The CV of the 9-(phenylsulfonyl)fluorenide ion was unusual in that it exhibited two small additional peaks of lower intensity following the main peak. These peaks were absent in the spectra of 2-$PhSO_2$– and 3-$PhSO_2FlH^-$ ions (Table VI). Radicals of the type $PhSO_2CR_2\cdot$, when produced in e_T^- reactions, appear to be much more reactive than $CNCR_2\cdot$ or $NO_2CR_2\cdot$ radicals in that they abstract a hydrogen atom from the Me_2SO solvent rather than dimerize.[19] Therefore, the E_{ox} value for 9-$PhSO_2Fl^-$ in Table IV may not be strictly comparable with the other values. The data now in hand suggest that neither α-$PhSO_2$ or *p*-$PhSO_2$ functions stabilize radicals, but there is not sufficient evidence to indicate a destabilizing effect.

The peak potential for ferrocene changed gradually with time, apparently due to aging of the Ag/AgI electrode. This did not affect the relative peak potentials for our carbanions since they are corrected for changes in the ferrocene peak potential, which was monitored continually. The Ag/AgI electrodes were replaced after about 6 months use.

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Registry No. $C_6H_5CHCN^-$, 18802-89-6; 4-$Me_2NC_6H_4CHCN^-$, 64764-37-0; 4-$MeOC_6H_4CHCN^-$, 64764-34-7; 4-$MeC_6H_4CHCN^-$, 64764-31-4; 3-$MeC_6H_4CHCN^-$, 42117-18-0; 4-$FC_6H_4CHCN^-$, 61057-17-8; 3-$MeOC_6H_4CHCN^-$, 64764-33-6; 4-$PhC_6H_4CHCN^-$, 64764-32-5; 4-$ClC_6H_4CHCN^-$, 64764-38-1; 3-$FC_6H_4CHCN^-$, 100859-02-7; 4-$PhSC_6H_4CHCN^-$, 100859-03-8; 3-$ClC_6H_4CHCN^-$, 100859-04-9; 3-$CF_3C_6H_4CHCN^-$, 100859-05-0; 3-$NCC_6H_4CHCN^-$, 64764-40-5; 3,4-$Cl_2C_6H_3CHCN^-$, 100859-06-1; 3-$PhSO_2C_6H_4CHCN^-$, 100859-07-2; 4-$CF_3C_6H_4CHCN^-$, 100859-08-3; Fl^-, 12257-35-1; 3-MeO-F^-, 100858-84-2; 3-Me-F^-, 100858-85-3; 2-Me-Fl^-, 100858-86-4; 2,7-$(MeO)_2$-Fl^-, 100858-87-5; 2-MeO-Fl^-, 100858-88-6; 3-F-Fl^-, 100858-89-7; 3-MeS-Fl^-, 100858-90-0; 2-F-Fl^-, 100858-91-1; 4-aza-Fl^-, 100858-92-2; 2-Br-Fl^-, 85535-20-2; 3-PhS-Fl^-, 100858-93-3; 2-MeS(O)-Fl^-, 100858-94-4; 2-PhCO-Fl^-, 100858-95-5; 2-$MeSO_2$-Fl^-, 100858-96-6; 2-NC-Fl^-, 100858-97-7; 2-$PhSO_2$-Fl^-, 100858-98-8; 2,7-Br_2-Fl^-, 85535-21-3; 3-$PhSO_2$-Fl^-, 100858-99-9; 2,7-$(NC)_2$-Fl^-, 100859-00-5; 2,3-benzo-Fl^-, 100859-01-6; 1,2-benzo-Fl^-, 85535-22-4; 9-Me_2N-Fl^-, 83936-70-3; 9-MeO-Fl^-, 71805-70-4; 9-PhO-Fl^-, 73838-68-3; 9-Me-Fl^-, 31468-21-0; 9-Ph-Fl^-, 31468-22-1; 9-MeS-Fl^-, 100859-09-4; 9-PhS-Fl^-, 71805-72-6; 9-H_2NCO-Fl^-, 79366-83-9; 9-MeOCO-Fl^-, 100859-10-7; 9-NC-Fl^-, 12564-43-1; 9-$PhSO_2$-Fl^-, 71805-74-8; 9-(4-MeC_6H_4)-Fl^-, 42730-14-3; 9-(2-MeC_6H_4)-Fl^-, 85535-26-8; 9-(2-Me-4-$MeSC_6H_3$)-Fl^-, 100859-11-8; 9-(2,4,6-$Me_3C_6H_2$)-Fl^-, 85535-28-0; 1,2,3,4-Ph_4CpH^-, 100859-12-9; 1,2,3,4,5-Ph_5Cp^-, 100859-13-0; 2,7-dibromo-9-methylfluorenide, 73872-46-5; 9-(3-chlorophenyl)fluorenide, 73872-45-4; 9-*tert*-butylfluorenide, 73838-69-4; 9-(benzhydryl)fluorenide, 100859-14-1; 3-methyl-9-fluorenone, 1705-89-1.

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Correlation of Electron-Transfer Rate Constants of Carbanions with Their Oxidation Potentials and Basicities

Frederick G. Bordwell* and Mark J. Bausch

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received August 30, 1985*

Abstract: Acidity-oxidation-potential (AOP) values for seven 9-substituted fluorenide ions, 9-$ArFl^-$, relative to that of fluorene, have revealed the presence of small radical-stabilizing effects for 4-MeO and 4-Me substitutents in the aryl ring and a 3-Me substituent in the fluorene ring and their absence for 3-Cl and 4-$MeSO_2$ substituents in the aryl ring and 2-Br and 2-$PhSO_2$ substituents in the fluorene ring. Measurements of redox potentials have shown that electron-transfer (e_T^-) reactions of these 9-$ArFl^-$ ions with 1,1-dinitrocyclohexane are endergonic by 6.6–13 kcal/mol. A Brønsted-type plot of log k_{obsd} for these reactions vs. pK_{HA} was linear with scatter. A Brønsted-type plot of log k_{obsd} vs. E_{ox} gave an improved plot ($\beta = 1.04$; $R^2 = 0.999$) that covered a rate range of $>10^5$ and an E_{ox} range of 7.3 kcal/mol. Mechanistic schemes are presented to account for the products formed in the e_T^- reaction and to reconcile the strict linearity of the latter plot with the Marcus equation.

Single electron transfer (e_T^-) from alkali metals to unsaturated organic compounds has been of synthetic importance for many years (e.g., Bouveault–Blanc and zinc reductions, Birch reductions, acyloin condensations, etc.) The recognition that e_T^- can also occur readily from organic nucleophiles, Nu^-, is of more recent origin, however.[1] The realization that nucleophilic e_T^- substitutions occur by chain mechanisms[2] and that the scope of these reactions can be broadened to include aryl halide electron acceptors[3] led to a wealth of new chemistry.[4] In the meantime, inorganic chemists were involved in elucidating the mechanisms of inner-sphere and outer-sphere e_T^- from coordination compounds.[5] The Marcus

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