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 10	E_p, mV/s 500	E_p (10) − E_p (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.

Acknowledgment. We thank Prof. R. W. Taft for suggesting the addition of a fluoradene point to Figure 5 and M. E. Mueller and C. A. Wilson for providing experimental results. This work was supported by the National Science Foundation. The Chemical Products Division of Crown Zellerbach provided a generous supply of dimethyl sulfoxide.

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

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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 (β = 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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Table I. Acidity-Oxidation-Potential (AOP) Values for Substituted 9-Phenylfluorenide Ions in Me_2SO at 25 °C

fluorenide ion	ΔE_{ox}, kcal[a]	ΔpK_{HA}, kcal[b]	Δ(AOP)[c]
9-phenyl	(0.0)	(0.0)	(0.0)
9-(4-methoxyphenyl)	−1.52	+0.89	−0.63
3-methyl-9-phenyl	−1.38	+1.1	−0.28
9-(4-methylphenyl)	−0.92	+0.55	−0.37
9-(3-chlorophenyl)	+2.07	−1.4	+0.63
2-bromo-9-phenyl	+3.09	−3.1	0.0
9-(4-(methylsulfonyl)phenyl)	+4.17	−3.7	+0.47
2-(phenylsulfonyl)-9-phenyl	+5.72	−5.6	+0.10

[a] Irreversible oxidation potentials measured by cyclic voltammetry.[9] [b] Calculated from the data given in Table II. [c] In kilocalories per mole.

equation (I) which relates the activation energy, $\Delta G^{\ddagger}$, to the free-energy change, ΔG°, and the intrinsic barrier, $\Delta G_0^{\ddagger}$, has proved useful in correlating rate data in many e_T^-s of this type.[6]

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left[1 + \frac{\Delta G^{\circ}}{4\Delta G_0^{\ddagger}}\right]^2 \qquad \text{(I)}$$

As several authors have pointed out, many reactions involving nucleophiles with electrophiles that have long been pictured as two-electron Lewis donor–acceptor-type combinations, including S_N2 reactions, can, in principle, involve single-electron-transfer mechanisms. In practice, it is often difficult to distinguish between these pathways. The identification of radical and/or radical anion species formed in eq II by trapping techniques or spectroscopic methods has provided direct experimental evidence for e_T^- to electron acceptors (EA) in several instances.[7]

$$\mathrm{Nu}^- + \mathrm{EA} \rightarrow \mathrm{Nu}\cdot + \mathrm{EA}^{-}\cdot \qquad \text{(II)}$$

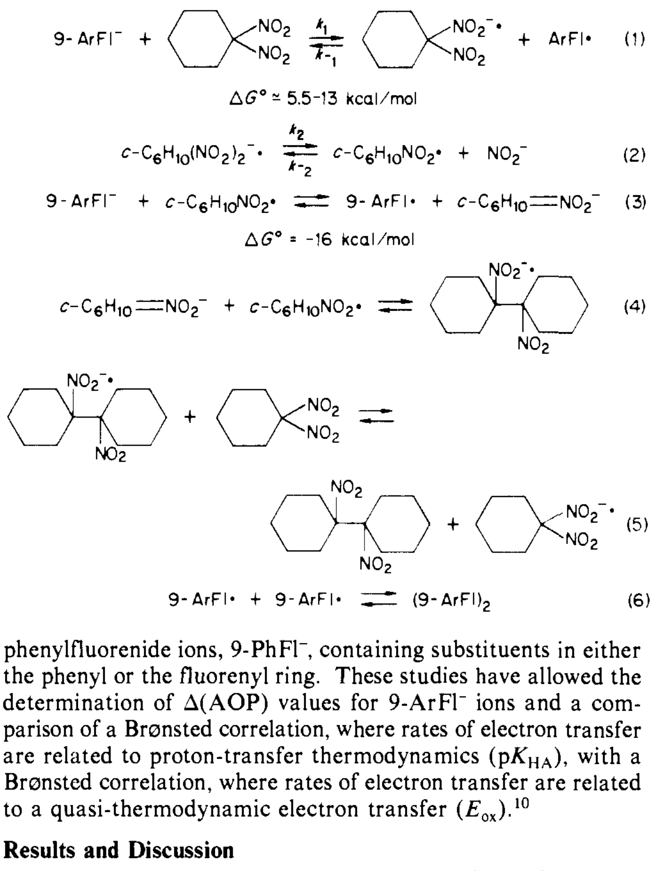
Carbanions have played a central role in the studies of organic e_T^- reactions from the outset,[1-4] and work in this area has intensified in recent years. Our research with families of 9-substituted fluorenide ions, 9-G–Fl⁻, reacting with a variety of electron acceptors has revealed the formation of dimers, $(9\text{-G–Fl})_2$, and other products characteristic of radical intermediates. The rates of these reactions (log k_{obsd}), which are, at least at the start, first order in [9-G–Fl⁻] and in [EA], have been shown to correlate linearly with the pK_{HA} values for the conjugate acids of the carbanions in the family. The slopes of the correlation lines (Brønsted β's) have been found to be generally near unity.[8] In the accompanying paper, it was reported that with a platinum electrode as the electron acceptor, the irreversible oxidation potentials (E_{ox}) for 2-substituted fluorenide ions, 2-G–Fl⁻, as well as those for meta-substituted arylcyanomethide ions (m-$GC_6H_4CHCN^-$), could be correlated with the pK_{HA} values of their respective conjugate acids to give plots with slopes near unity.[9] The points for Me_2N, MeO, MeS, PhS, Me, and Ph substituents located at para positions deviated from these lines, however, because of the ability of donor substituents to stabilize 3-G–Fl· and p-$GC_6H_4CHCN\cdot$ radicals. When the pK_{HA} and E_{ox} values for the meta- and para-substituted ions were combined and these acidity-oxidation-potential (AOP) values were related to those of the parents, Δ(AOP) values were obtained that provide estimates of the radical-stabilizing abilities of para substituents ranging from 0.4 to 3.9 kcal/mol. Application of this method to 9-substituted fluorenide ions revealed much larger effects, particularly for electron donor functions (4.5, 5.4, 7.0, and 10.7 kcal/mol for Me, MeS, MeO, and Me_2N, respectively[9]). In the present paper, we report the extension of this work to 9-phenylfluorenide ions, 9-PhFl⁻, containing substituents in either the phenyl or the fluorenyl ring. These studies have allowed the determination of Δ(AOP) values for 9-ArFl⁻ ions and a comparison of a Brønsted correlation, where rates of electron transfer are related to proton-transfer thermodynamics (pK_{HA}), with a Brønsted correlation, where rates of electron transfer are related to a quasi-thermodynamic electron transfer (E_{ox}).[10]

Table II. Rate Constants for Electron Transfer from 9-Phenylfluorenide Ions to 1,1-Dinitrocyclohexane in Me_2SO Solution at 25 °C

fluorenide ion	k[a]	E_{ox}, V[c]	pK_{HA}[d]
9-(4-methoxyphenyl)	215	−0.219	18.55
3-methyl-9-phenyl	195	−0.213	18.7
9-(4-methylphenyl)	93.3	−0.193	18.3
9-phenyl	17.5[b]	−0.153	17.9
9-(3-chlorophenyl)	0.607[b]	−0.063	16.85
2-bromo-9-phenyl	0.0820	−0.019	15.65
9-(4-(methylsulfonyl)phenyl)	0.0102	+0.028	15.2
2-(phenylsulfonyl)-9-phenyl	0.00082	+0.095	13.8

[a] Rate constants ($M^{-1}\ s^{-1}$) are averages of two or more runs usually with a reproducibility of ±10%. [b] Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1037. [c] E_{ox} values (irreversible) are in volts and were obtained by using a Pt working electrode and Ag/AgI reference electrode in Me_2SO solution, as described earlier. [d] Measured in Me_2SO solution.

Scheme I



Results and Discussion

AOP Values for 9-Phenylfluorenide Ions. Acidity and oxidation potential data for 9-phenylfluorenide ions in which substituents have been introduced into either the fluorene ring or the phenyl ring are summarized in Table I. Examination of Table I shows that the presence of the 3-methyl substituent in the fluorene ring and the 4-methyl and 4-methoxy substituents in the phenyl ring give negative Δ(AOP) values (−0.3, −0.4, and −0.6, respectively). In contrast, the 2-Br and 2-$PhSO_2$ substituents in the fluorene ring give near zero values, and the 3-Cl and 4-$MeSO_2$ substituents in the phenyl ring give positive Δ(AOP) values (+0.6 and +0.5, respectively). These results are consistent with those obtained earlier with 2- and 3-substituted fluorenide ions and with 3- and 4-substituted arylcyanomethide ions.[9] The negative Δ(AOP) values for 3-Me, 4-Me, and 4-MeO indicate mild stabilization of the radical. The stabilizing effect for the 9-(4-MeOC_6H_4)Fl· and $4\text{-MeOC}_6H_4CHCN\cdot$ radicals (1.0 and 1.3 kcal/mol, re-

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(8) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1037; **1982**, *47*, 2510–2516; **1985**, *50*, 1151–1156.

(9) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

(10) We suggest that any plot of a kinetic parameter (log k, E_a, $\Delta G^{\ddagger}$, etc.) vs. a thermodynamic parameter (pK_a, E_{ox}, ΔG°, etc.) be termed a Brønsted plot.

spectively[9]), and the Me-stabilizing effects in 3-Me-9-PhFl· and 9-(4-MeC_6H_4)Fl· radicals are also slightly smaller than previously observed in 3-MeFl· and 4-MeC_6H_4CHCN· radicals (0.3 and 0.4 vs. 0.4 and 0.55 kcal/mol). The near zero Δ(AOP) effects for 2-Br and 2-$PhSO_2$ are similar to those observed earlier,[9] and the positive Δ(AOP) values for 9-(3-ClC_6H_4)Fl· and 9-(4-$MeSO_2C_6H_4$)Fl· are also consistent with the previous findings.[9]

Rate Constants and Mechanisms for Reactions of 9-Phenylfluorenide Ions with 1,1-Dinitrocyclohexane. Rate constants for reactions of the eight substituted 9-phenylfluorenide ions in e_T^- reactions with 1,1-dinitrocyclohexane are summarized in Table II along with E_{ox} and pK_{HA} values. The steps previously suggested as occurring in these reactions are given in Scheme I (eq 1–7).[8] Further information concerning the mechanism was obtained by a determination of the (irreversible) reduction potential of 1,1-dinitrocyclohexane ($E_{red} \simeq -0.5$ V). Subtracting the oxidation potential values for the 9-$ArFl^-$ ions from this value shows that the first step in these reactions (eq 4) is uphill thermodynamically, the $\Delta G°$ values ranging from about 13 kcal/mol for the reaction of the least basic ion, 2-(phenylsulfonyl)-9-phenylfluorenide ion, to 6.6 kcal/mol for the 3-methyl-9-phenylfluorenide ion.

The reactions in Scheme I offer likely routes for the formation of the major products identified previously in the reaction of the 9-$PhFl^-$ ion with $c\text{-}C_6H_{10}(NO_2)_2$, namely, $(9\text{-}PhFl)_2$, $(c\text{-}C_6H_{10}NO_2)_2$, and $c\text{-}C_6H_{10}{=}NO_2^-$.[8] The endergonic nature of the eq 1, established by electrochemistry, appears to ensure that k_{-1} will be near the diffusion-controlled limit and that the rate of disappearance of the 9-$ArFl^-$ ion, which is being monitored spectroscopically, will depend on the position of this equilibrium (K) and the rates of reactions of the resulting ArFl· radical and/or $c\text{-}C_6H_{10}(NO_2)_2^-\cdot$ radical anion. The cleavage of the latter to $c\text{-}C_6H_{10}NO_2\cdot$ and NO_2^- in step 2 appears likely to be the rate-limiting step. Since the exergonic e_T^- in step 3 (k_3) should occur at near the diffusion-controlled limit, the $c\text{-}C_6H_{10}NO_2\cdot$ radical will be scavenged immediately by the $ArFl^-$ ion, which is in large excess at the start of the reaction. This would lead to $k_{obsd}/2 = Kk_2$ and would account for the second-order kinetics observed for the first few half-lives of the reaction. During the first few half-lives, the concentration of the $c\text{-}C_6H_{10}{=}NO_2^-$ ion will build up and that of the 9-$ArFl^-$ ion will decrease. At some point, the $c\text{-}C_6H_{10}{=}NO_2^-$ ion will begin to compete with the 9-$ArFl^-$ ion for the $c\text{-}C_6H_{10}NO_2\cdot$ radical. Reactions 4 and 5 constitute propagation steps in a chain reaction to produce the $(c\text{-}C_6H_{10}NO_2)_2$ dimer. The $c\text{-}C_6H_{10}(NO_2)_2^-\cdot$ radical ion formed as part of this chain adds to the supply of this radical ion formed in step 1 and changes the kinetic order of the reaction. Reaction 7 may also be occurring and changing the kinetic order.

$$c\text{-}C_6H_{10}{=}NO_2^- + c\text{-}C_6H_{10}(NO_2)_2 \rightleftarrows c\text{-}C_6H_{10}NO_2\cdot + c\text{-}C_6H_{10}(NO_2)_2^-\cdot \quad (7)$$

The $(9\text{-}ArFl)_2$ dimer is believed to be formed by coupling of 9-ArFl· radicals. The absence of any appreciable quantity of the product of cross coupling of 9-ArFl· and $c\text{-}C_6H_{10}NO_2\cdot$ radicals is intriguing. A possible explanation is that the $c\text{-}C_6H_{10}NO_2\cdot$ radical is so efficiently scavenged by the 9-$ArFl^-$ and $c\text{-}C_6H_{10}{=}NO_2^-$ ions present in the solution that the $c\text{-}C_6H_{10}NO_2\cdot$ radical is never present in high enough concentration to form the cross-coupling product.

A Brønsted plot of the rate constants (log k_{obsd}) in Table II vs. pK_{HA} is linear with scatter (Figure 1). An improved plot is obtained by plotting log k_{obsd} vs. E_{ox} (Figure 2) because relative oxidation potentials provide a better measure of e_T^- rates from an anion than do relative anion basicities. Nevertheless, the Brønsted plot is remarkably good, and it follows that a plot of pK_{HA} vs. E_{ox} must be equally good. Similar good correlations of pK_{HA} and E_{ox} values have been observed previously in our laboratory and elsewhere.[9]

In Figure 2, log k_{obsd} values for the e_T^- reactions are plotted as a function of the respective E_{ox} values for the 9-$ArFl^-$ ion donors. All the 9-$ArFl^-$ ion data points, spanning a range in E_{ox} of 0.314 V (7.2 kcal/mol) and a range in rates of over 2.5 × 10^5, fall on or near a line of slope 0.0618. Converting the x axis of this Brønsted plot to log units gives a β value of 1.04 ($R^2 = 0.999$).[11] The excellent correlation of the reaction rates with E_{ox} values is further evidence that reactions between 9-$ArFl^-$ carbanions and 1,1-dinitrocyclohexane are proceeding by initial electron transfer. At the same time, the correlation provides further evidence that the oxidation potentials for these fluorenide ions, although irreversible, are giving meaningful relative values.[9] The scatter observed in the log k_{obsd} vs. pK_{HA} plot (Figure 1) is no longer present in the log k_{obsd} vs. E_{ox} plot (Figure 2). Deviations from the log k_{obsd} vs. pK_{HA} plot for the 3-$MeFl^-$, 9-(4-MeC_6H_4)Fl^-, and 9-(4-$MeOC_6H_4$)Fl^- ion points are expected since the Δ(AOP) values for these ions indicate that the e_T^- rate will be enhanced because the radical being formed is stabilized by these remote substituents (Table I). Note that the rate constant for e_T^- from the 9-(4-$MeOC_6H_4$)Fl^- ion is 1.1 times *greater* than that with the 3-Me-9-$PhFl^-$ ion, whereas the relative basicities of these carbanions leads one to expect the latter to be more reactive. Although the meaning of the Brønsted coefficient obtained from a Brønsted plot for e_T^- rate vs. H_T^+ thermodynamics is difficult to concep-

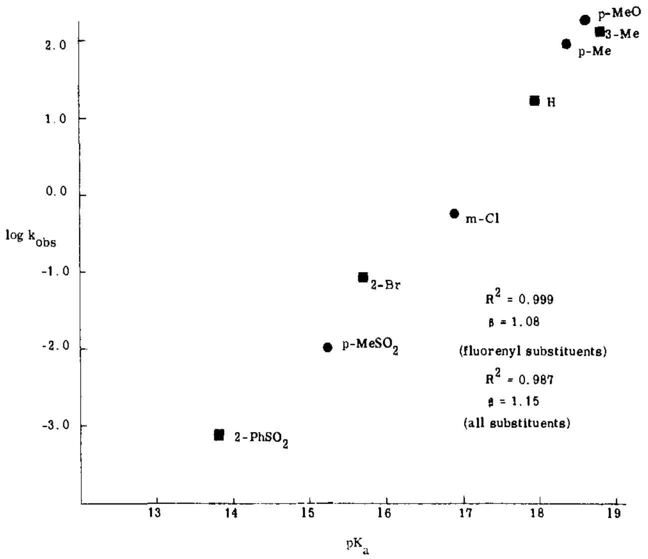

Figure 1. Plot of rate constants (log k_{obsd}) for electron transfer to 1,1-dinitrocyclohexane from substituted 9-phenylfluorenide ions vs. their pK_{HA} values in Me_2SO solution at 25 °C.

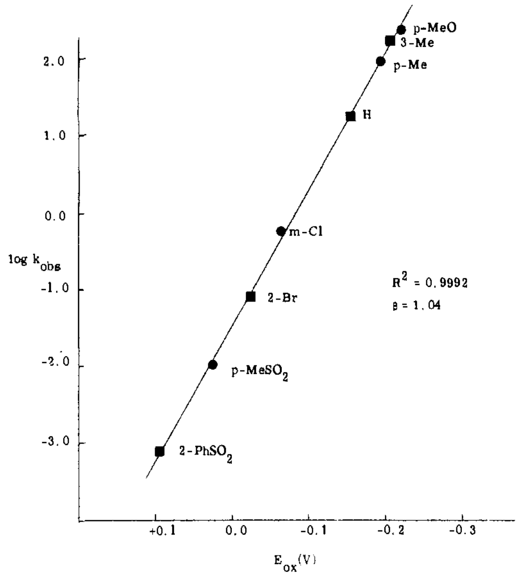

Figure 2. Plot of rate constants (log k_{obsd}) for electron transfer to 1,1-dinitrocyclohexane from substituted 9-phenylfluorenide ions vs. the oxidation potentials for the ions in Me_2SO solution at 25 °C.

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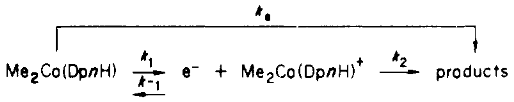
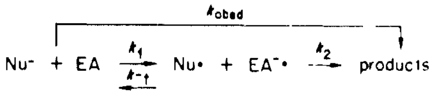
[11] At 25 °C, 1 V = 23.06 kcal/mol and 1 pK_a unit = 1.37 kcal/mol.

Scheme II



Scheme III



tualize, a Brønsted plot[10] of e_T^- rate vs. E_{ox} can be examined in the context of the Marcus equation (1).

Scheme I and the Marcus Equation. The strict linearity of Figure 2 over a reactivity range of 7.2 kcal/mol might at first sight appear to be a contradiction of the Marcus equation, which has had considerable success in correlating data for electron-transfer reactions. The Marcus equation requires that $\Delta G^{\ddagger}$ have a quadratic dependence on ΔG°, which means that a Brønsted plot such as that in Figure 2 should be curved if the data are taken over a sufficient range of ΔG°. The linearity of this plot may be rationalized, however, by an analysis (Scheme II) applied by Klingler and Kochi to the study of outer-sphere electron transfer from an organometallic compound, $Me_2Co(DpnH)$.[12]

In Scheme II, k_e is the experimental rate constant and k_1 is the intrinsic rate constant for the forward direction. Klingler and Kochi were able to sort out k_1, k_{-1}, and k_2 from k_e. A plot of log k_1 vs. E_{ox} showed Marcus curvature with $\beta = 0.5$ at $\Delta G^{\circ} = 0$. On the other hand, a plot of log k_e vs. E_{ox} also showed Marcus curvature in the exergonic region, but in the endergonic region, the curve flattened and a linear portion with the unit slope was observed. The electron transfer studied in the present work can be represented similarly (Scheme III).

In Scheme III, the 9-ArFl⁻ ions are represented by Nu^- and the 1,1-dinitrocyclohexane electron acceptor by EA. The rate constants for the succeeding steps are represented by k_2. The intrusion of the chain reaction in Scheme I requires that the pseudo-first-order rate constant for the disappearance of Nu^- (k_{obsd}) be monitored for only one or two half-lives. The linearity of the plot of log k_{obsd} vs. E_{ox} (Figure 2) is analogous to that observed by Klingler and Kochi in the endergonic region.

Our data can also be analyzed in terms of the Rehm–Weller equation (8), a Marcus-like equation that some chemists feel more accurately describes solution intermolecular e_T^- kinetic–thermodynamic relationships.[13]

$$\Delta G^{\ddagger}(\Delta G^{\ddagger} - \Delta G^{\circ}) = (\Delta G_0^{\ddagger})^2 \quad (8)$$

Rehm–Weller and other[14] free-energy relationships differ from the Marcus equation in their description of the kinetics in the exergonic region. When the exergonicity is increased, Marcus theory predicts an "inverted region",[15] while Rehm–Weller theory predicts that the Brønsted slope asymptotically approaches zero. The Rehm–Weller equation predicts a Brønsted slope of unity in the endergonic limit. This is a possible explanation of the near unity slope observed in our study. Other investigators have attributed β values of near unity to reversibility in the electron transfer.[16] Since we have no knowledge of k_1, k_{-1}, and k_2 in Scheme III, our explanation of $\beta = 1.04$ (Figure 2) depends on both the endergonicity and reversibility of the electron transfer.

Summary and Conclusions

The measurement of Δ(AOP) values for seven substituted 9-phenylfluorenide ions has revealed that the 3-Me-9-Fl·, 9-(4-MeC_6H_4)Fl·, and 9-(4-$MeOC_6H_4$)Fl· radicals are stabilized by remote substituents. These radical-stabilizing effects cause deviations in a Brønsted plot of rates of e_T^- vs. pK_{HA} because the relative basicities of the ions fail to take into account the radical-stabilizing effects of *p*-Me and *p*-MeO substituents. On the other hand, a Brønsted plot[10] of rates of e_T^- vs. E_{ox} is strictly linear (Figure 2) because the substituent effects on the rates of electron transfer are exactly mirrored by the substituent effects on the quasi-thermodynamic electron transfers measured by oxidation potentials.

Experimental Section

General. NMR spectra were obtained by using Varian EM-360 and EM-390 spectrometers. Melting points were determined by using a Thomas-Hoover unimelt capillary melting-point apparatus and are uncorrected.

The purification of Me_2SO and the preparation of potassium dimsyl ($CH_3SOCH_2^-K^+$) as well as the methods for measuring rate and equilibrium constants spectrophotometrically have been described earlier.

Reactions of 9-Arylfluorenide Ions with 1,1-Dinitrocyclohexane. Product analyses from the reactions of 9-phenyl- and 9-*p*-tolylfluorenide ions with 1,1-$C_6H_{10}(NO_2)_2$ have been described earlier. The $(9\text{-PhFl})_2$ and $(9\text{-}p\text{-TolFl})_2$ dimers obtained are difficult to purify because they dissociate readily and form peroxides in the presence of oxygen. The NMR spectra of the $(9\text{-PhFl})_2$ dimer in the crude product was identical with that of an authentic sample obtained by the reaction of 9-PhFl⁻ with 1,2-dibromocyclohexane.[17]

Electrochemistry. Cyclic voltammetric experiments were carried out as described earlier.[9]

Acknowledgment. We are grateful to the National Science Foundation for support of this research. We thank C. A. Wilson and M. Chehel-Amiran for measuring several of the redox potentials. Crown Zellerbach, Inc., Vancouver, WA, provided us with a generous supply of dimethyl sulfoxide. We are grateful to a referee for perceptive and helpful comments.

Registry No. 9-PhFl⁻, 31468-22-1; 9-(*p*-$MeOC_6H_4$)Fl⁻, 42730-16-5; 3-Me-9-PhFl⁻, 100859-19-6; 9-(*p*-MeC_6H_4)Fl⁻, 42730-14-3; 9-(*m*-ClC_6H_4)Fl⁻, 73872-45-4; 2-Br-9-PhFl⁻, 100859-20-9; 9-(*p*-$MeSO_2C_6H_4$)Fl⁻, 73872-44-3; 9-Ph-2-$PhSO_2$Fl⁻, 73872-40-9; 1,1-dinitrocyclohexane, 4028-15-3.

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