Reactions of Carbanions with Electron Acceptors

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Second-order rate constants for reactions of families of 9-substituted fluorenide ions, 9-R-Fl⁻, and related carbanions in Me_2SO solution with the electron acceptors $PhSO_2CH_2Br$, $PhSO_2CH(Ph)Br$, $PhSO_2C(Me)(Ph)Br$, Me_2CBr_2, $Me_2C(NO_2)X$, $PhS(O)CH_2Cl$, $Me_2C(SO_2Ph)_2$, and $Ph_2I^+Cl^-$ have been measured. The carbanions used varied in basicity over a range of about 20 pK_{HA} units. For a given family, Brønsted plots of log k vs. pK_{HA} were linear, with slopes usually near unity. The relative order of rate constants correlated for the most part with the order of reduction potentials of the electron acceptors. The carbanions were converted by the electron acceptors to dimers, i.e., 9-R-Fl⁻ → (9-R-Fl)$_2$, by way of a single electron transfer (e⁻$_T$) mechanism. The Brønsted lines for the e⁻$_T$ reactions of the $GC_6H_4C(Me)CN^-$ ion family (G = *p*-Cl, H, and *p*-Me) and the 9-*t*-BuFl⁻ ion family were displaced below that of the 9-MeFl⁻ ion family (slower rates); the kinetic points for $PhC(Me)SO_2Ph^-$ and $Ph_2CSO_2Ph^-$ ions fell near the 9-*t*-BuFl⁻ ion family line. It is demonstrated that carbanions too weakly basic to undergo thermal e⁻$_T$ with a given electron acceptor can be made to undergo comparable e⁻$_T$ reactions under photostimulation.

In earlier papers we have shown that 9-substituted fluorenide carbanions, 9-R-Fl⁻, react in Me_2SO solution by single electron transfer (e⁻$_T$) mechanisms with electron acceptors of the type $PhSO_2CH_2X$ (X = I, Br, Cl) and $R_2C(NO_2)X$ (X = NO_2, CN, Ts; Ts = *p*-$MeC_6H_4SO_2$) to form fluorenyl dimers, (9-R-Fl)$_2$.[1] The reactions exhibited second-order kinetics, first order in both donor and acceptor, and Brønsted plots of log k vs. the acidity constant of the conjugate acid of the carbanion (pK_{HA}) were found to be linear with slopes near unity. It was suggested that this unusually high sensitivity of rates to changes in basicity might be characteristic of reactions proceeding by e⁻$_T$ mechanisms, with the corollary that the higher the basicity of a carbanion the greater its tendency to react by an e⁻$_T$ mechanism. In this paper we (a) report extension of the work to include rate studies with additional types of electron acceptors and additional types of carbanions, (b) make correlations of rates observed with these acceptors to their reduction potentials, and (c) examine the effect of photostimulation on the rates.

Results and Discussion

Structural Variation and Electron Accepting Ability. In previous papers we have presented kinetic evidence to show that the electron accepting ability in single electron transfer (e⁻$_T$) reactions decreases in the order c-$C_6H_{10}(NO_2)_2$ > $Me_2C(NO_2)_2$ > $PhSO_2CH_2Br$,

$PhSO_2CH_2I$ > c-$C_6H_{10}(NO_2)Ts$ > $Me_2C(NO_2)Ts$ > $PhSO_2CH_2Cl$ for reactions with 9-substituted fluorenide carbanions, 9-R-Fl⁻, that varied in basicity by about 5.5 pK_{HA} units. (The pK_{HA} values in Me_2SO solution ranged from about 16.8 for 9-(*m*-ClC_6H_4)Fl⁻ ion to 22.3 for 9-MeFl⁻ ion.) Brønsted plots of log k(where k is the second-order rate constant) vs. pK_{HA} for 9-PhFl⁻ ion and 9-MeFl⁻ ion families gave slopes near unity in all instances.[1] Further structural variations have now been made in the electron acceptors to extend the pK range of anions that can be used and to explore the acceptors' mode of action. The results of kinetic studies with these new electron acceptors ($PhSO_2CH(Ph)Br$, $PhSO_2C(Me)(Ph)Br$, Me_2CBr_2, Me_2C-$(NO_2)Br$, $PhS(O)CH_2Cl$, $Me_2C(SO_2Ph)_2$, and $Ph_2I^+Cl^-$) are compared in Table I with data obtained by using some of the earlier electron acceptors.

The acceptor series, $PhSO_2CH_2Br$, $PhSO_2CH(Ph)Br$, and $PhSO_2C(Me)(Ph)Br$ (see Table I) was chosen in an attempt to study a systematic increase in acceptor ability. Substitution of Ph for an α-hydrogen atom in $PhSO_2CH_2Br$ increased the accepting ability by a factor of about 1000, allowing rate studies to be made in the 13.2–15.4 pK_{HA} range using the 9-(PhS)Fl⁻ ion family. The kinetics were poorer with the better electron acceptor, however; an observation we thought might be associated with its greater acidity. Replacement of the acidic hydrogen by methyl resulted in an electron acceptor of intermediate strength, $PhSO_2C(Me)(Ph)Br$, but with no improvement in kinetics. 2,2-Dibromopropane, Me_2CBr_2, was found to be a weaker electron acceptor, since it requires

(1) (a) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1036; (b) *Ibid.* **1982**, *47*, 2510–2516.

Table I. Second-Order Rate Constants and Brønsted Coefficients for Reactions of Carbanions with Electron Acceptors in Me_2SO Solution at 25 °C

carbanion	$pK_{HA}{}^a$	electron acceptor[b]	$10k$ $(M^{-1} s^{-1})^d$
9-$(p$-$MeC_6H_4)Fl^-$	18.3	$PhSO_2CH_2Br^c$	8.14 ± 0.34
9-$C_6H_5Fl^-$	17.9	$PhSO_2CH_2Br^c$	3.03 ± 0.12
9-$(m$-$ClC_6H_4)Fl^-$	16.8	$PhSO_2CH_2Br^c$	0.158 ± 0.008
			$\beta = 1.15$
9-$(C_6H_5S)Fl^-$	15.4	$PhSO_2CH(Ph)Br$	133 ± 10
9-$(p$-$BrC_6H_4S)Fl^-$	14.8	$PhSO_2CH(Ph)Br$	58 ± 5
2-Br-9-$(C_6H_5S)Fl^-$	13.2	$PhSO_2CH(Ph)Br$	0.92 ± 0.12
			$\beta = 1.1$
9-$(m$-$ClC_6H_4)Fl^-$	16.8	$PhSO_2C(Me)(Ph)Br$	10.3 ± 1.3
9-$(p$-$BrC_6H_4S)Fl^-$	14.8	$PhSO_2C(Me)(Ph)Br$	0.2 ± 0.08
			$\beta = 0.86$
9-$MeFl^-$	22.3	Me_2CBr_2	33–76
9-$MeFl^-$	22.3	$PhSO_2CH_2Cl^c$	0.14 ± 0.01
9-$MeFl^-$	22.3	$PhS(O)CH_2Cl$	1.77 ± 0.28
2-Br-9-$MeFl^-$	20.0	$PhS(O)CH_2Cl$	0.044 ± 0.0376
			$\beta = 0.7$
9-$(p$-$MeOC_6H_4)Xn^-$	28.4	$Me_2C(SO_2Ph)_2$	206.3 ± 2
9-$C_6H_5Xn^-$	27.9	$Me_2C(SO_2Ph)_2$	58.6 ± 6.7
9-$(m$-$ClC_6H_4)Xn^-$	26.6	$Me_2C(SO_2Ph)_2$	3.72 ± 0.13
			$\beta = 0.97$
9-$MeFl^-$	22.3	c-$C_6H_{10}(NO_2)Ts^c$	18.2 ± 0.9
2-Br-9-$MeFl^-$	20.0	c-$C_6H_{10}(NO_2)Ts^c$	0.061 ± 0.002
			$\beta = 1.1$
9-$(PhS)Fl^-$	15.4	$Ph_2I^+Cl^-$	too fast
2-Br-9-$(PhS)Fl^-$	13.2	$Ph_2I^+Cl^-$	167 ± 50
2,7-Br_2-9-$(PhS)Fl^-$	11.1	$Ph_2I^+Cl^-$	1.56 ± 0.39
			$\beta = 0.97$
9-$(CO_2Me)Fl^-$	10.35	$Ph_2I^+Cl^-$	1.39 ± 0.14
2-Br-9-$(CO_2Me)Fl^-$	8.2	$Ph_2I^+Cl^-$	0.042 ± 0.007
			$\beta = 0.71$

$^a pK_a$ of the conjugate acid of the anions in Me_2SO at 25 °C.
^{b} Used in excess (2- to 400-fold). ^{c} Data from ref 1. ^{d} The results of two–five runs with varying amounts of electron acceptor.

a stronger base for reaction (9-$MeFl^-$, $pK_{HA} = 22.3$). Chloromethyl phenyl sulfoxide proved to be a somewhat better acceptor toward 9-$MeFl^-$ ion than the corresponding sulfone, judging from the higher observed reaction rate exhibited by the former. The dimer (9-$MeFl)_2$ was isolated from the reactions of 9-$MeFl^-$ ion with $PhSOCH_2Cl$ and Me_2CBr_2 in yields of 54% and 64%, respectively.

The electron accepting ability of 2,2-bis(phenyl-sulfonyl)propane, $Me_2C(SO_2Ph)_2$, is less than those of $PhSO_2CH_2Br$, $PhSO_2CH_2I$, or $R_2C(NO_2)X$ since it fails to react with the 9-$PhFl^-$ and 9-$MeFl^-$ ion families (pK_{HA} ranges 16.8–18.3 and 17.7–22.3, respectively). Reactions of the strongly basic 9-arylxanthenide ion family (pK_{HA} range 26.6–28.4) with this acceptor were found to resemble the reactions of more weakly basic ion families with stronger acceptors, the rates being highly sensitive to changes in donor basicity ($\beta = 0.98$). A quantitative estimate of the electron acceptor properties of this compound can be made from the observation that the rate constant for 9-$(m$-$ClC_6H_4)Xn^-$ ion reacting with $Me_2C(SO_2Ph)_2$ is 3.8 fold smaller than that for the 9-$MeFl^-$ ion reacting with $Me_2C(NO_2)Ts$,[1] despite the 4.3 pK unit lower basicity of the latter ion. Extrapolation indicates that a 9-$MeFl^-$ ion family member with a pK_{HA} of 26.6 would react with $Me_2C(NO_2)Ts$ about 7.6 × 10^4 faster than does 9-$(m$-$ClC_6H_4)Xn^-$ with $Me_2C(SO_2Ph)_2$. This comparison demonstrates the powerful ability of NO_2 vs. $PhSO_2$ to enhance electron accepting ability. The products isolated from the reaction of 9-$PhXn^-$ ion with $Me_2C(SO_2Ph)_2$ included a 75% yield of (9-$PhXnO)_2$ and a 55% yield of Me_2CHSO_2Ph. This product distribution is similar to that found for reaction of 9-$PhFl^-$ ions with $PhSO_2CH_2Br$ or of the 9-$MeFl^-$ ion with $PhSO_2CH_2Cl$. The reaction sequence with 9-$PhXn^-$ ion is believed to be

$$9\text{-}PhXn^- + Me_2C(SO_2Ph)_2 \rightarrow$$
$$9\text{-}PhXn\cdot + Me_2C(SO_2Ph)_2{}^-\cdot$$
$$Me_2C(SO_2Ph)_2{}^-\cdot \rightarrow PhSO_2{}^- + Me_2CSO_2Ph\cdot \xrightarrow{(+H\cdot)} Me_2CHSO_2Ph$$
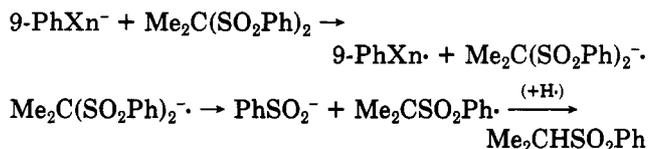
The solvent is the presumed hydrogen atom donor to the $Me_2CSO_2Ph\cdot$ radical. Experimental support for this presumption was obtained by carrying out a reaction of the acceptor $PhSO_2CH_2Br$ with 9-$TolFl^-$ ion in Me_2SO-d_6. The methyl phenyl sulfone product obtained was trideuterated, $PhSO_2CD_3$. Rapid deuterium exchange with $PhSO_2CH_2Br$ to give $PhSO_2CD_2Br$ is expected under the reaction conditions.[2] The third deuterium is incorporated by reaction of the $PhSO_2CD_2\cdot$ radical with Me_2SO-d_6.

The 9-$PhXn\cdot$ radical is stabilized by resonance delocalization and tends to be persistent by virtue of steric hindrance to dimerization. It apparently exists in the reaction mixture primarily as the dimer since the mixture is not highly colored, but the dimer evidently dissociates readily enough to react with oxygen during the workup, since 9-phenylxanthenyl peroxide is the product isolated.

$$(9\text{-}PhXn)_2 \rightleftharpoons 2(9\text{-}PhXn\cdot) \xrightarrow{O_2} (9\text{-}PhXnO)_2$$
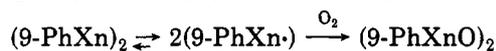
The reactions of carbanions with the acceptors $PhSO_2CH_2Br$ and $Me_2C(SO_2Ph)_2$ differ from those with $R_2C(NO_2)X$ in that the $PhSO_2CH_2\cdot$ and $PhSO_2C(Me)_2\cdot$ radicals formed by loss of Br^- ion from the radical ion are not scavenged by substrate anions, as happens, for example, with $R_2CNO_2\cdot$ radicals and 9-R-Fl^- anions (eq 1).

$$9\text{-}R\text{-}Fl^- + R_2CNO_2\cdot \rightleftharpoons 9\text{-}R\text{-}Fl\cdot + R_2C{=}NO_2{}^- \quad (1)$$

Experimental evidence showing that the $PhSO_2CH_2\cdot$ radical is not scavenged by 9-R-Fl^- ions comes from the observation that a full equivalent of electron acceptors is required to discharge the color of 9-R-Fl^- anion with $PhSO_2CH_2Br$ as acceptor, whereas with acceptors of the type $R_2C(NO_2)_2$, one-half of an equivalent will suffice.[1] This difference in behavior can be explained by the much greater basicity of $R_2CSO_2Ph^-$ compared to $R_2C{=}NO_2{}^-$ ($\sim$14 pK units), which results in a great difference in the positions of equilibria (as indicated by the relative lengths of the arrows) for reactions 1 and 2.

$$9\text{-}R\text{-}Fl^- + R_2CSO_2Ph\cdot \rightleftharpoons 9\text{-}R\text{-}Fl\cdot + R_2CSO_2Ph^- \quad (2)$$
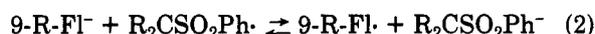
The high basicity of $PhSO_2CH_2{}^-$ argues against a $Br^+{}_T$ mechanism, since the reaction shown as eq 3 must have a very small equilibrium constant.
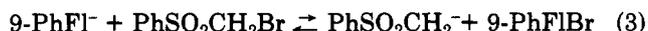
$$9\text{-}PhFl^- + PhSO_2CH_2Br \rightleftharpoons PhSO_2CH_2{}^- + 9\text{-}PhFlBr \quad (3)$$
$$pK_{HA} = 17.9 \qquad pK_{HA} = 29$$

In a search for more powerful electron acceptors our attention was attracted to $C(NO_2)_4$ and $Ph_2I^+Cl^-$. The latter has been shown to be a phenylating agent for the relatively weakly basic ion derived from ethyl 1-oxo-cyclohexane-2-carboxylate ($pK_{HA} = 14.2$ in Me_2SO).[3] Tetranitromethane proved to be unsuitable for spectrophotometric kinetic studies because of the immediate formation of an intense yellow color on dissolving it in Me_2SO. Diphenyliodonium chloride proved to be the most powerful electron acceptor examined to date, but unfortunately, the second-order rate constants of reactions em-

(2) Branca, J. C., Ph.D. Dissertation, Northwestern University, 1979, observed that base-catalyzed deuterium exchange occurred readily between Me_2SO-d_6 and carbon acids that were weaker by as much as 15 pK units.

(3) Beringer, F. M.; Forgione, P. S. *J. Org. Chem.* **1963**, *28*, 714–717. Beringer, F. M.; Galton, S. A.; Huang, S. J. *J. Am. Chem. Soc.* **1962**, *84*, 2819–2823.

Table II. Reduction Potentials for Electron Acceptors in Dimethyl Sulfoxide Solution at Ambient Temperature

electron acceptor	reduction potential,[a] V
$Ph_2I^+Cl^-$	+0.16
$Me_2C(NO_2)_2$	-0.50
$PhSO_2CH_2I$	-0.50
$PhSO_2CH_2Br$	-0.60
$c\text{-}C_6H_{10}(NO_2)Ts$	-0.87
$c\text{-}C_6H_{10}(NO_2)CN$	-0.91
$Me_2C(NO_2)Ts$	-0.97
$Me_2C(NO_2)Br$	-1.0
$PhSO_2CH_2Cl$	-1.5
$Me_2C(SO_2Ph)_2$	-1.6

[a] Irreversible potentials obtained with a hanging mercury drop working electrode, a $Ag/AgI/Me_2SO$ reference electrode, and 0.1 M $Et_4N^+BF_4^-$ in Me_2SO as a supporting electrolyte at a scan rate of 25 V/s.

ploying it showed large standard deviations, and complex mixtures of products were formed. Its reactions with two members of the 9-(PhS)Fl⁻ ion family (pK_{HA} = 13.2–15.4) did exhibit the high sensitivity to changes in anion basicity characteristic of e^-_T reactions, however (β = 0.97; Table I), and a reaction was observed even with the weakly basic 2-Br-9-(CO₂Me)Fl⁻ ion (pK_{HA} = 8.2). One would anticipate a mechanism of the type

$$9\text{-}(PhS)Fl^- + Ph_2I^+ \rightarrow 9\text{-}(PhS)Fl\cdot + Ph_2I\cdot$$

$$Ph_2I\cdot \rightarrow PhI + Ph\cdot$$

$$9\text{-}(PhS)Fl^- + Ph\cdot \rightarrow 9\text{-}(PhS)FlPh^- \xrightarrow{e^-} 9\text{-}(PhS)Fl\text{-}Ph$$
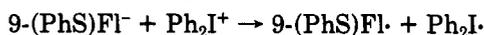
Iodobenzene and 9-(PhS)FlPh were identified among the complex mixture of products formed. If we assume that β = 1 over the total pK range covered in Table I, the corresponding e^-_T rate variation for the carbanions would be about 10^{20}.

Reduction Potentials of Electron Acceptors. Measurement of the reduction potentials for the electron acceptors studied (Table II) shows that they cover a range of 1.76 eV (40.5 kcal/mol) and fall in the order expected based on our kinetic results. This provides strong support for the single electron transfer mechanism proposed for reactions of carbanions with these acceptors.

Structural Variation and Electron Donor Ability. The earlier work with 9-substituted fluorenide carbanions has now been supplemented by rate measurements with several α-cyano and α-sulfonyl carbanions (Table III).

Examination of Table III shows that the rates of reactions of the $GC_6H_4C(Me)CN^-$ ion family (G = p-Me, H, p-Cl) with the acceptors $Me_2C(NO_2)Ts$ and $c\text{-}C_6H_{10}(NO_2)Ts$ exhibited the same high sensitivity to changes in basicity (β = 0.97 and 1.0, respectively) shown by the 9-MeFl⁻ ion family reacting with $R_2C(NO_2)Ts$, or the 9-PhFl⁻ ion family reacting with $PhSO_2CH_2Br$, $PhSO_2CH_2I$, or $R_2C(NO_2)_2$ (Table I). We have seen above that the 9-PhXn⁻ ion family reacting with $Me_2C(SO_2Ph)_2$ and the 9-(PhS)Fl⁻ ion family reacting with $Ph_2I^+Cl^-$ also conform to this pattern. These results provide further support for our earlier conclusion that a Brønsted β near unity is characteristic of e^-_T reactions of carbanions with electron acceptors. In this section we will examine the effect of variation of carbanion structure on the rate of e^-_T. These comparisons must be regarded as rough because of the limited amount of data available permitting comparisons with a single acceptor and the consequent need for extrapolations.

Since the kinetic point for the 9-(PhS)Fl⁻ ion reacting with $c\text{-}C_6H_{10}(NO_2)_2$ can be shown to fall reasonably near to the extrapolated two-point Brønsted line defined by the 9-PhFl⁻ and 9-(m-ClC₆H₄)Fl⁻ ions reacting with this ac-

Table III. Effects of Variation of Carbanion Structure on Rates of Single Electron Transfer Reactions in Me₂SO Solution at 25 °C

carbanion	pK_{HA} (Me_2SO)[a]	electron acceptor[b]	$10k$ (M^{-1} s^{-1})[d]
$p\text{-}MeC_6H_4C(Me)CN^-$	24.1	$c\text{-}C_6H_{10}(NO_2)Ts$	72.1 ± 8.6
$C_6H_5C(Me)CN^-$	23.0	$c\text{-}C_6H_{10}(NO_2)Ts$	3.80 ± 0.44
$p\text{-}ClC_6H_4C(Me)CN^-$	21.7	$c\text{-}C_6H_{10}(NO_2)Ts$	0.334 ± 0.06
			β = 0.97
$p\text{-}MeC_6H_4C(Me)CN^-$	24.1	$Me_2C(NO_2)Ts$	56.2 ± 5.5
$C_6H_5C(Me)CN^-$	23.0	$Me_2C(NO_2)Ts$	3.07 ± 0.65
$p\text{-}ClC_6H_4C(Me)CN^-$	21.7	$Me_2C(NO_2)Ts$	0.282 ± 0.018
			β = 1.0
$9\text{-}(C_6H_5)Fl^-$	17.9	$c\text{-}C_6H_{10}(NO_2)_2$[c]	175 ± 23
$9\text{-}(m\text{-}ClC_6H_4)Fl^-$	16.8	$c\text{-}C_6H_{10}(NO_2)_2$[c]	6.07 ± 0.78
			$\beta \simeq 1$
$9\text{-}(C_6H_5S)Fl^-$	15.4	$c\text{-}C_6H_{10}(NO_2)_2$	0.120
Ph_2CCN^-	17.4	$Me_2C(NO_2)Br$	>100
Ph_2CCN^-	17.4	$c\text{-}C_6H_{10}(NO_2)_2$	0.0951 ± 0.0032
$9\text{-}PhFl^-$	17.4	$Me_2C(NO_2)_2$[c]	66 ± 8.2
$PhC(Me)SO_2Ph^-$	25.7	$c\text{-}C_6H_{10}(NO_2)Ts$	165 ± 1
$Ph_2CSO_2Ph^-$	22.3	$c\text{-}C_6H_{10}(NO_2)Ts$	0.0685
$9\text{-}t\text{-}BuFl^-$	24.35	$c\text{-}C_6H_{10}(NO_2)Ts$	7.14 ± 0.32
$2\text{-}Br\text{-}9\text{-}t\text{-}BuFl^-$	21.7	$c\text{-}C_6H_{10}(NO_2)Ts$	0.0546 ± 0.3332
			β = 0.81

[a] pK_a of the conjugate acid of the anions in Me_2SO at 25 °C. [b] Used in excess (2- to 400-fold). [c] Data from ref 1. [d] The results of two–five runs with varying amounts of electron acceptor.

ceptor, it would appear that changing the 9-substituent from 9-Ph to 9-PhS does not cause a large change in anion reactivity at comparable basicities. Comparison of the rates for the $p\text{-}ClC_6H_4C(Me)CN^-$ ion (pK_{HA} = 21.7) and the 9-MeFl⁻ ion (pK_{HA} = 22.3) reacting with the $c\text{-}C_6H_{10}(NO_2)Ts$ acceptor shows the 9-MeFl⁻ ion to be 55 times more reactive. When corrected for the difference in basicities of the ions, the difference decreases to a factor of only 13, however, indicating that the reactivities of these rather different kinds of carbanions are not greatly different. A pronounced difference is found, however, when one compares 9-PhFl⁻ ion (pK_{HA} = 17.9) reacting with $Me_2C(NO_2)_2$ vs. Ph_2CCN^- ion (pK_{HA} = 17.4) reacting with $c\text{-}C_6H_{10}(NO_2)_2$, where the fluorenide ion is seen to be 1840 times more reactive. The fluorenide ion is 0.5 pK unit more basic, but it is here reacting with a somewhat poorer electron acceptor, so the reactivity difference is clearly of the order of 10^3. These data suggest the following order of e^-_T donor ability for families of ions of equal basicity: 9-MeFl⁻ > $C_6H_5C(Me)CN^-$ and 9-PhFl⁻ ≫ Ph_2CCN^-.

The reaction of Ph_2CCN^- ion with $Me_2C(NO_2)Br$ occurs

$$2Ph_2CCN^- + 2Me_2C(NO_2)Br \xrightarrow{Me_2SO} (Ph_2CCN)_2 + (Me_2CNO_2)_2$$
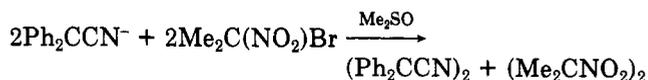
very rapidly to give high yields of dimeric products. No cross products were isolated. The products are suggestive of an e^-_T mechanism, but the $\sim10^3$ slower rate for Ph_2CCN^- reacting with $c\text{-}C_6H_{10}(NO_2)_2$ is surprising in view of the 0.5 V more positive reduction potential of $Me_2C(NO_2)_2$ compared to $Me_2C(NO_2)Br$ (Table II). This suggests that an alternative mechanism is operative, perhaps one involving Br_T^+, which would be slightly exergonic with regard to the relative basicities of the anions.[4]

$$Ph_2CCN^- + Me_2C(NO_2)Br \xrightarrow[Me_2SO]{Br^+_T} Ph_2C(CN)Br + Me_2C=NO_2^-$$
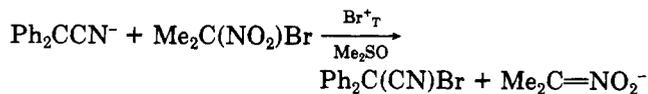
$$pK_{HA} = 17.4 \qquad pK_{HA} = 16.9$$

Further examination of Table III shows that the rate constant for 9-MeFl⁻ ion reacting with c-C₆H₁₀(NO₂)Ts is 2.5 times that for 9-*t*-BuFl⁻ reacting with this acceptor. At equal basicities the relative rates are about 250 to 1. The difference in reactivities toward c-C₆H₁₀(NO₂)Ts for 9-MeFl⁻ and Ph₂CSO₂Ph⁻ ions, which have the same basicities, is almost as large (209 fold). Similarly, the PhC-(Me)SO₂Ph⁻ ion is 218 times less reactive than the 9-MeFl⁻ ion toward this acceptor when comparisons are made at the same basicity. These effects are similar to those reported earlier in the S_N2 reactions of 9-*t*-BuFl⁻ and H₂CSO₂Ph⁻ ions with PhCH₂Cl, where the reaction rates relative to 9-MeFl⁻, corrected for basicity differences, are both about 400-fold slower for steric reasons.[5] (The PhC(Me)SO₂Ph⁻ ion reactivity toward PhCH₂Cl is only retarded by a factor of 4, however.[5]) Additional work is under way to determine whether these retarding effects in e^-_T reactions have steric or electronic origins.

Photostimulation of Electron Transfer Reactions.
Most, but not all, chain e^-_T reactions of carbanions with electron acceptors of the type R₂C(NO₂)X,[6] *p*-NO₂C₆H₄C(X)R₂,[7] or ArX[8] require photostimulation. On the other hand, the e^-_T reactions from the carbanions reported here are thermally promoted. The need for photostimulation found in earlier studies appears to stem primarily from the lower basicity of many of the carbanions used. We have shown that 9-PhFl⁻ or 9-PhS⁻ ions react rapidly with α,p-dinitrocumene to give Kornblum substitution products *without* photostimulation.[1] The high sensitivity of e^-_T reactions to changes in basicity means that carbanions of low basicity have a relatively small inherent ability to act as donors in e^-_T reactions and that, within a family of carbanions, the donor ability will decrease rapidly with a decrease in basicity. For example, the rate constant for reaction of Me₂C(NO₂)Ts with 9-MeFl⁻ ion (pK_{HA} = 22.3) is 1.43 M⁻¹ s⁻¹, but with 2,7-Br₂-9-MeFl⁻ ion, which has a pK 4.6 units lower; it should be about 3.6×10^{-5} M⁻¹ s⁻¹, which is too low for convenient rate measurements. If we assume that ions such as (CN)₂CH⁻ and (CH₃CO)₂CH⁻ will show donor effects toward this acceptor similar to those of 9-MeFl⁻ ions,[9] the expected rate constants will be about 10^{12} and 10^9 smaller than this, respectively, assuming $\beta \simeq 1$, since the pK_{HA} values for their conjugate acids are 11.1 and 13.3, respectively. It is not surprising, then, that reactions with weakly basic carbanions may require photostimulation. The reaction of 9-(PhS)Fl⁻ ion (pK_{HA} = 15.4) with c-C₆H₁₀(NO₂)₂ has a rate constant of 0.0120 M⁻¹ s⁻¹ at 25 °C. Extrapolation from this value, assuming a linear correlation with basicity and β = 1, indicates that the rate constant for 9-(CO₂Me)Fl⁻ ion reacting with this acceptor should be less than 10^{-7} M⁻¹ s⁻¹. No reaction was detected between 9-(CO₂Me)Fl⁻ ion and c-C₆H₁₀(NO₂)₂ in the dark, which is

not surprising since the half-life should be several months. However, a qualitative test showed that intermittent irradiation of a 1 mM solution of 9-(CO₂Me)Fl⁻ in Me₂SO containing 0.6 mM of c-C₆H₁₀(NO₂)₂ over a period of 4 h caused substantial discharge of the indicator color. Photostimulation appears not to initiate a chain reaction, however, since the reaction stopped immediately when irradiation ceased.

In another experiment, a 1 mM solution of 9-(PhS)Fl⁻ was allowed to react with a 0.7 mM solution of c-C₆H₁₀-(NO₂)₂ with exposure to light until the color was discharged (∼1 h). An 80% yield of (9-(PhS)-Fl)₂ together with a 65% combined yield of (c-C₆H₁₀NO₂)₂ and c-C₆H₁₀=NO₂⁻ ion was obtained. In the dark this reaction would be expected to require about 200 h to reach 4 half-lives. These experiments demonstrate that nonchain (or short chain) e^-_T dimerization of carbanions by electron acceptors is susceptible to photostimulation. Furthermore, the identity in kind and distribution of products formed in the light and dark reactions indicates that the mechanisms are similar, as Fukui has suggested.[10]

Summary and Conclusions. By adding the weaker electron acceptor, (PhSO₂)₂CMe₂, and the stronger electron acceptor, Ph₂I⁺Cl⁻ to the list of those studied earlier, a series of electron acceptors is available to cover a pK range in Me₂SO solution of about 20 units for e^-_T reactions with carbanions (pK_{HA} = 8.2–28.4). Since the Brønsted β values approach unity in most instances, this means that the total possible measurable rate span for these reactions would be about 10^{20}. The relative reduction potentials for the electron acceptors correlate with their electron accepting ability as measured by reaction rates. The electron transfers are all believed to occur by nonchain mechanisms. The mechanisms for reactions using R₂C(X)SO₂Ph and Ph₂I⁺ as electron acceptors differ from those with R₂C-(X)NO₂ acceptors in that the R₂CSO₂Ph· and PhI₂· radicals formed are not scavenged by the carbanion reagents, as happens with R₂CNO₂· radicals. The rate constants for reactions of ArC(Me)CN⁻ carbanions indicate that they are poorer electron donors toward R₂C(NO₂)Ts than are 9-MeFl⁻ ions of the same basicity by a factor of about 10. 9-*t*-BuFl⁻ and Ph₂CSO₂Ph⁻ ions also undergo e^-_T much more slowly than 9-R-Fl⁻ ions of comparable basicity. The high sensitivity of these e^-_T reactions to changes in basicity ($\beta \simeq 1$) means that the higher the basicity of a carbanion the more likely it is to undergo electron transfer in preference to following an alternative pathway. Strongly basic carbanions can evoke nonchain electron transfers to R₂C-(NO₂)₂ acceptors, but weakly basic carbanions require photostimulation.

Experimental Section

General Procedures. NMR spectra were obtained with either a Varian T-60 or FM-360 spectrometer. Mass spectra were run by Ms. H. L. Hung on an HP5984 GC/MS system. Melting points were determined with a Thomas-Hoover Unimelt capillary melting apparatus and are uncorrected.

Materials. The syntheses and sources of 9-substituted fluorenes and xanthenes, and of the Me₂C(NO₂)'Ts and c-C₆H₁₀(NO₂)Ts electron acceptors, have been described in earlier publications.

Chloromethyl phenyl sulfone was prepared from chloromethyl phenyl sulfide[11] by cautious oxidation with a hydrogen peroxide in acetic acid mixture at slightly below reflux. After short-path distillation and crystallization from EtOH/H₂O a 29% yield of sulfone, mp 52–53 °C, was obtained (lit.[12] mp 52–53 °C).

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(9) This is not an unreasonable assumption for the (CN)₂CH⁻ ion, since it has been found that the kinetic points for α-cyano carbanions reacting with the PhCH₂Cl electrophile in S_N2 reactions fit near the extended 9-MeFl⁻ ion family line over a range of about 18 pK units.[4] It seems likely that in the *endergonic region* the slopes of Brønsted plots for e^-_T reactions may remain constant over an equally large range.

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Table IV. Dimerization Products Formed from Carbanions by Reactions with Electron Acceptors in Dimethyl Sulfoxide Solution

carbanion	acceptor[a]	dimer	(yield, %)[e]	other product	(yield, %)[e]
9-MeFl⁻	PhSO₂CH₂Br	(9-MeFl)₂	(70)[f]	PhSO₂CH₃	(32)
9-p-TolFl⁻	PhSO₂CH₂Br	(9-p-TolFl)₂	(65)[g]	PhSO₂CH₃	(32)
9-p-TolFl⁻	PhSO₂CH₂Br[b]	(9-p-TolFl)₂	(88)[g]	PhSO₂CD₃	(86)[i]
9-MeFl⁻	PhSO₂CH₂Cl[c]	(9-MeFl)₂	(71)[f]	PhSO₂CH₃	(40)
9-MeFl⁻	PhS(O)CH₂Cl[c]	(9-MeFl)₂	(54)[f]		
9-MeFl⁻	Me₂CBr₂	(9-MeFl)₂	(64)[f]		
9-PhXn⁻	Me₂C(SO₂Ph)₂	(9-PhXnO)₂	(75)[h]	PhSO₂CHMe₂	(55)
p-ClC₆H₄C(Me)CN⁻	c-C₆H₁₀(NO₂)Ts	[p-ClC₆H₄C(Me)CN]₂	(85)[i]	(c-C₆H₁₀NO₂)₂	(45)
9-PhFl⁻	Me₂C(NO₂)₂[b]	(9-PhFl)₂	(60)[f]	(Me₂CNO₂)₂	(31)[m]
9-p-TolFl⁻	Me₂C(NO₂)₂[c]	(9-p-TolFl)₂	(74)[g]	(Me₂CNO₂)₂	(25)[m]
9-PhFl⁻	c-C₆H₁₀(NO₂)₂	(9-PhFl)₂	(93)[f]	(c-C₆H₁₀NO₂)₂	(72)[n]
Ph₂CCN⁻	Me₂C(NO₂)Br	(Ph₂CCN)₂	(85)[j]	(Me₂CNO₂)₂	(65)
9-(PhS)Fl⁻	c-C₆H₁₀(NO₂)₂[d]	(9-(PhS)Fl)₂	(80)[i,k]	(c-C₆H₁₀NO₂)₂ ⎫ c-C₆H₁₀=NO₂⁻ ⎭	(65)

[a] Used in equivalent amount or slight excess unless otherwise noted. [b] In 1.5-fold excess. [c] In 2-fold excess. [d] The reaction was carried out under photostimulation for 1 h. [e] Isolated yield of product unless otherwise noted. [f] Reference 1. [g] mp 205 °C dec; lit.[22] mp 216 °C; NMR (CDCl₃) δ 2.15 (s, 3 H), 6.8–7.3 (m, 12 H). [h] The (9-PhXn)₂ dimer is evidently converted to the peroxide by oxygen during workup. [i] Yield estimated by NMR. [j] The dimer had mp 215–216 °C; lit. mp's 210–213 °C (ref 13a), 218 °C (ref 23b). [k] mp 218 °C; lit.[24] mp 229–231 °C. [l] Experiment carried out in Me₂SO-d₆. [m] It is likely that Me₂C=NO₂⁻ ion is also formed. [n] A 26% yield of c-C₆H₁₀=NO₂⁻ was isolated from the aqueous solution on treatment with an acidic buffer.

Bromomethyl phenyl sulfone was prepared by a method similar to that of Otto.[13] A stirred solution of sodium benzenesulfinate (2.0 g, 0.0122 mol) and dibromomethane (2.1 g, 0.0122 mol) in 50 mL of DMF was kept at 85 °C for 10 h. Quenching with water and extraction with ether gave 2.2 g of crude sulfone, which was crystallized from EtOH; mp 47–48 °C (lit.[13] mp 46–48 °C). **Iodomethyl phenyl sulfone** was prepared in a similar manner from diiodomethane; mp 64–65 °C (lit.[14] mp 64.5 °C).

α-Bromobenzyl phenyl sulfone was prepared from (phenylsulfonyl)acetic acid by the method of Bordwell and Jarvis.[15]

α-Bromo-α-methylbenzyl phenyl sulfone was prepared from α-methylbenzyl phenyl sulfone (1.23 g, 5 mmol) by addition of a 1.5 molar excess of n-BuLi to an ether solution at −78 °C, followed by dropwise addition of a solution of bromine in ether until the bromine color remained. After being warmed to −10 °C; the ether solution was washed with bisulfite solution, dried over MgSO₄, and evaporated. Two crystallizations from chloroform gave colorless crystals: mp 133–134 °C; NMR (CDCl₃) δ 2.25 (s, 3 H), 7.20 (m, 10 H).

2,2-Bis(phenylsulfonyl)propane was prepared from bis(phenylsulfonyl)methane in 75% yield by the method of Fromm.[16] Diphenyliodonium chloride and 2,2-dibromopropane were commercial samples.

α-Methyl-p-chlorophenyl- and α-methyl-p-methylphenylacetonitriles were prepared by phase-transfer methylation of the parent phenylacetonitriles.[17] The liquid products were purified by two or more Kugelrohr distillations. GLC analysis indicated the presence of small amounts of dimethylated products but, since these would not interfere with the kinetics, further purification was not necessary.

Chloromethyl phenyl sulfoxide was prepared in 30% yield by treating chloromethyl phenyl sulfide[11] with 1 equiv of 30% aqueous hydrogen peroxide in acetic acid. Three products were formed and separated by column chromatography on silica gel. Elution with 10% Et₂O/90% hexane brought through the required sulfoxide as a pale yellow liquid. Elution with hexane gave diphenyl sulfide; the third product, eluted with ether, was not identified. Repeated Kugelrohr distillations (0.9 mm, 120 °C) gave chloromethyl phenyl sulfoxide as a white solid, mp 28 °C (lit.[18] mp 28–29 °C).

2-Bromo-2-nitropropane was prepared by addition of bromine (16.1 g, 100 mM) to a vigorously stirred solution of 2-nitropropane

(8.9 g, 100 mM) in 40 mL of 2.5 M NaOH at 0–5 °C. After 45 min the solution was extracted with Et₂O (3 × 50 mL), washed with 1 M NaOH solution and H₂O, dried (MgSO₄), and concentrated in vacuo to give a yellow liquid. Repeated distillation (bp 151 °C (760 mm) gave 2-bromo-2-nitropropane as a pale yellow liquid (14.5 g, 84%).[19]

Kinetic Measurements. The kinetic methods for standard runs have been described previously.[1] Experiment showed that 1 equiv of Me₂C(SO₂Ph)₂ acceptor was required to discharge the 9-PhXn⁻ anion color.[1] The quality of the kinetics can be judged by the square of the correlations of the kinetic plots. "Good kinetics" are characterized by R^2 values of 0.999 or better. "Poor kinetics" are indicated by R^2 values of 0.99 or less.

Photochemical Reactions. The reaction of 9-(CO₂Me)Fl⁻ ion with PhSO₂CH₂Br may be regarded as a typical example. Two milliliters of a 2 mM Me₂SO solution of 9-(CO₂Me)Fl⁻ ion in a 1-cm photospectrometer cuvette was treated with a 7-fold excess of a Me₂SO solution of PhSO₂CH₂Br. On mixing the reactants under normal lighting conditions there is no observable reaction after 25 min. The absorbance reading was constant at 0.841 during this time. On irradiation for 80 s with a 600-W light source placed 1 in. from the cuvette containing the reactants the anion color intensity dropped from 0.766 to 0.550 and remained constant at this level until the next irradiation 30 min later. Eventually, after five irradiations totaling 320 s, the anion color was essentially all discharged (0.126 absorbance reading). Similar results were obtained with 9-(CO₂Me)Fl⁻ and 2-Br-9-(PhS)Fl⁻ ions reacting with c-C₆H₁₀(NO₂)₂.

A solution of 9-(CO₂Me)Fl⁻ ion alone was subjected to similar treatment and shown not to be affected by the photostimulation. (The color was discharged on photostimulation, however, if oxygen was present.) The effect of a 2-min exposure to our light source on the temperature of the solution within the cuvette was found to be negligible (<1 °C increase).

Electrochemistry. All cyclic voltammetric experiments were carried out at room temperature, data being collected by a Raytheon R.D.S. 500 computer system. The 9-R-Fl⁻ anion solutions for electrochemical study were prepared under an argon atmosphere by using the same general procedure used in normal kinetic runs.[1] An amount of 9-R-FlH, calculated to give a 2–4 mM solution of anion when made up to 10 mL, was dissolved in approximately 2 mL of Me₂SO. Sufficient potassium dimsyl/Me₂SO solution was added so as to just convert all of the 9-R-FlH to its corresponding anion, as evidenced by the failure of one further drop of base solution to increase the color intensity (measured spectrophotometrically) of the 9-R-Fl⁻ anion solution. This was then added to a previously prepared solution of tetraethylammonium tetrafluoroborate (0.217 g, 1 mmol) in Me₂SO (8 mL) to give the electrochemical sample.

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The reduction potential samples were prepared by adding tetraethylammonium tetrafluoroborate (0.217 mg, 1 mM) and the electron acceptor (in an amount calculated to give a final concentration of 2-4 mM) together in one cell, evacuating, flushing with argon 3 times, and then injecting Me₂SO (10 mL) from an argon flushed syringe.

Product Studies. The product studies were carried out by the method previously described using equivalent amounts of reactants.[1] Product isolations were effected by column chromatography. For example, the product from the reaction of 9-MeFl⁻ ion and PhSO₂CH₂Br was isolated by quenching with water, ether extraction, and adsorption on silica gel; elution with Et₂O/hexane (5/95) gave (9-MeFl)₂ as colorless crystals, identical by NMR with a known sample.[1] Elution with 10% Et₂O/hexane gave PhSO₂CH₃, mp 84 °C; identical by NMR and mmp with an authentic sample. The products formed from reactions with electron acceptors are summarized in Table IV.

Quenching the reaction mixture from 9-PhXn⁻ ion and Me₂C(SO₂Ph)₂ gave a white solid, mp 219 °C dec, identified as (9-PhXnO)₂ by NMR: the reported mp is 219 °C.[20] The residue was adsorbed onto alumina. Elution with 2% Et₂O/hexane gave more (9-PhXnO)₂; elution with 20% Et₂O/hexane brought through Me₂CHSO₂Ph as a colorless liquid; mass spec (70 eV) m/e 184 (M⁺), 141 (SO₂Ph); the NMR agreed with that previously reported.[21]

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In the reactions with PhSOCH₂Cl and Me₂CBr₂ with 9-MeFl⁻ the dimer was isolated, but the products derived from the electron acceptors were intractable mixtures.

Registry No. 9-(PhS)Fl⁻, 71805-72-6; 9-(p-BrC₆H₄S)Fl⁻, 73838-77-4; 2-Br-9-(PhS)Fl⁻, 73838-76-3; 9-(m-ClC₆H₄)Fl⁻, 73872-45-4; 9-MeFl⁻, 31468-21-0; 2-Br-9-MeFl⁻, 81255-42-7; 9-(p-MeOC₆H₄)Xn⁻, 94929-75-6; 9-PhXn⁻, 94929-76-7; 9-(m-ClC₆H₄)Xn⁻, 85554-38-7; 2,7-Br₂-9-(PhS)Fl⁻, 81245-84-3; 9-(CO₂Me)Fl⁻, 12565-94-5; 2-Br-9-(CO₂Me)Fl⁻, 73838-71-8; p-MeC₆H₄C(Me)CN⁻, 94929-77-8; PhC(Me)CN⁻, 56751-34-9; p-ClC₆H₄C(Me)CN⁻, 85535-18-8; Ph₂CCN⁻, 31468-22-1; PhC(Me)SO₂Ph⁻, 85554-41-2; Ph₂CSO₂Ph⁻, 85554-40-1; 9-t-BuFl⁻, 73838-69-4; PhSO₂CH(Ph)Br, 15296-88-5; PhSO₂C-(Me)(Ph)Br, 94929-78-9; Me₂CBr₂, 594-16-1; PhS(O)CH₂Cl, 7205-94-9; Me₂C(SO₂Ph)₂, 39863-09-7; c-C₆H₁₀(NO₂)Ts, 41774-12-3; Me₂C(NO₂)Ts, 21272-86-6; c-C₆H₁₀(NO₂)₂, 4028-15-3; Me₂C-(NO₂)Br, 5447-97-2; Ph₂I⁺Cl⁻, 1483-72-3; Me₂C(NO₂)₂, 595-49-3; PhSO₂CH₂I, 65492-21-9; PhSO₂CH₂Br, 19169-90-5; c-C₆H₁₀-(NO₂)CN, 58102-55-9; ClCH₂SPh, 7205-91-6; PhSO₂Na, 515-42-4; Br₂CH₂, 74-95-3; PhCH(CH₃)SO₂Ph, 24422-78-4; I₂CH₂, 75-11-6; p-ClC₆H₄CH₂CN, 140-53-4; p-MeC₆H₄CH(CH₃)CN, 75920-45-5; CH₃CH(NO₂)CH₃, 79-46-9; 2-Br-9-t-BuFl⁻, 85535-33-7.

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Conformational Analysis, Synthesis, and Carbon-13 Spectroscopy of 9,9-Dimethylbicyclo[3.3.1]nonane Derivatives

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A series of 9,9-dimethylbicyclo[3.3.1]nonanes substituted in position 3 and/or 7 has been synthesized. Their conformational properties have been studied by force field calculations and ¹³C NMR. These studies indicate that, in most of the compounds, the dimethyl bridge substitution forces the two cyclohexane rings in the chair conformation. The steric compression imposed on carbons 3 and 7 by this double chair conformation is found to displace their carbon-13 chemical shifts to high field.

Introduction

Compounds possessing the bicyclo[3.3.1]nonane skeleton have been the subject of numerous conformational and spectrometric studies.[1-11] Interest in these compounds

arises from their twin cyclohexane structure giving rise to chair-boat interchanges and from the close spatial proximity of carbons 3 and 7, the endo substituents of which being able to initiate conformational changes or intramolecular transannular reactions.[5,11]

Naturally the conformation of the bicyclic skeleton depends on the size of the endo 3,7-substituents and most previous studies consider the chair to boat transformation as a result of the steric interaction of the endo substituents.

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