$E_{ox}(A^-)$ values can be derived from the log k_{obsd} vs. $E_{ox}(A^-)$ plot (Figure 2) for 9-MeS-Fl$^-$ and 9-*i*-PrS-Fl$^-$ ions. These values are within ±25 mV of the measured values. The $E_{ox}(A^-)$ for 9-RS-Fl$^-$ ions would have to be more than 100 mV higher than observed for α-RS to be more stabilizing than α-RO.

Reactions of *t*-BuFl$^-$ Ion with c-C$_6$H$_{10}$(NO$_2$)Ts and with PhSO$_2$CH$_2$Br. Reactions of $R_2C(NO_2)X$ electron acceptors with 9-G-Fl$^-$ ions, where G = Me, C$_6$H$_5$ *p*-MeC$_6$H$_4$, and PhS, have been found earlier to give 60–80% yields of (9-G-Fl)$_2$ and (R$_2$CNO$_2$)$_2$ dimers together with small amounts of R$_2$CHNO$_2$.[24] Under the same conditions, with 150 mg (0.675 mmol) of *t*-BuFlH, 76 mg (0.675 mmol) of *t*-BuOK, and 191 mg (0.675 mmol) of c-C$_6$H$_{10}$(NO$_2$)Ts, a complex mixture was obtained from which 63 mg of *t*-BuFlH, 42 mg of c-C$_6$H$_{10}$(NO$_2$)Ts, 58 mg of (c-C$_6$H$_{10}$NO$_2$)$_2$, and 20 mg of c-C$_6$H$_{11}$NO$_2$ were recovered.

Also, 9-*t*-BuFl$^-$ ion was prepared in situ from 9-*t*-BuFlH by titration with CH$_3$SOCH$_2$K in Me$_2$SO and reacted with an equivalent amount of PhSO$_2$CH$_2$Br. Quenching with water, extraction with ether, and chromatography on silica gave principally 9-*t*-BuFlH in the first fraction and PhSO$_2$CH$_3$ in the second. The *t*-(BuFl)$_2$ dimer is presumably unstable under these conditions.

9-Isopropoxyfluorene. 9-Bromofluorene was refluxed in isopropyl alcohol until TLC tests indicated the absence of starting materials (120 h). Sublimation of the white solid formed by pouring the mixture into ice water gave coloreless flakes: mp 43–44 °C; NMR δ 1.15 (d, 6 H), 3.88 (sept 1 H), 5.6 (s, 1 H), 7.2–7.8 (m, 8 H). Anal. Calcd for C$_{10}$H$_{16}$O: C, 85.7; H, 7.2. Found: C, 85.8; H, 7.3.

Acidity Constant Measurements. Measurement of the acidities of 9-Ph$_2$CH-FlH and 9-Ph$_3$C-FlH are rendered difficult by the low solubility of these compounds in Me$_2$SO. Concentrations sufficient for pK_a measurements (2 mM) were obtained, however, after prolonged contact with the solvent (2 h and 10 days, respectively). The pK_a of 9-Ph$_2$CH-FlH is 20.9$_5$, which is the average of titrations made with (*m*-F$_3$CC$_6$H$_4$CH$_2$)$_2$SO$_2$ (pK_a = 20.97) and PhSCH$_2$SO$_2$Ph (pK_a = 20.34) as standard acids. The pK_a of 9-Ph$_3$C-FlH is 20.3 as determined by titration with (*m*-F$_3$CC$_6$H$_4$CH$_2$)SO$_2$. The trend in acidities for the series 9-MeFlH (22.3), 9-PhCH$_2$FlH (21.4), 9-Ph$_2$CHFlH (20.9$_5$), and 9-Ph$_3$C-FlH (20.3) indicates that the acid-strengthening inductive effect, aided perhaps by some relief of strain in forming the anion, prevails over steric inhibition of solvation.

The pK_a of 9-*i*-PrO-FlH was determined to be 21.43 ± 0.01 by titration at 565 nm with fluorene (pK_a 22.6) as a standard acid. Titration with PhSCH$_2$SO$_2$Ph (pK_a = 20.34) gave pK_a = 21.29 ± 0.05; average 21.36.

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Registry No. 9-H-FlH, 86-73-7; 9-H Fl$^-$, 12257-35-1; 9-Me-FlH, 2523-37-7; 9-Me-Fl$^-$, 31468-21-0; 9-Et-FlH, 2294-82-8; 9-Et-Fl$^-$, 85535-23-5; 9-*i*-Pr-FlH, 3299-99-8; 9-*i*-Pr-Fl$^-$, 85535-24-6; 9-*t*-Bu-FlH, 17114-78-2; 9-*t*-Bu-Fl$^-$, 73838-69-4; 9-*t*-BuCH$_2$-FlH, 60147-52-6; 9-*t*-BuCH$_2$-Fl$^-$, 85535-25-7; 9-PhC(Me$_2$)CH$_2$-FlH, 109494-93-1; 9-PhC(Me$_2$)CH$_2$-Fl$^-$, 109494-94-2; 9-PhCH$_2$-FlH, 1572-46-9; 9-PhCH$_2$-Fl$^-$, 53629-11-1; 9-Ph$_2$CH-FlH, 4425-68-7; 9-Ph$_2$CH-Fl$^-$, 100859-14-1; 9-Ph$_3$C-FlH, 67635-27-2; 9-Ph$_3$C-Fl$^-$, 109494-95-3; 9-Ph-FlH, 789-24-2; 9-Ph-Fl$^-$, 31468-22-1; 9-MeS-FlH, 59431-17-3; 9-MeS-Fl$^-$, 100859-09-4; 9-EtS-FlH, 60147-53-7; 9-EtS-Fl$^-$, 109494-96-4; 9-*i*-PrS-FlH, 60147-54-8; 9-*i*-PrS-Fl$^-$, 85535-30-4; 9-*t*-BuS-FlH, 60147-55-9; 9-*t*-BuS-Fl$^-$, 85535-31-5; 9-PhS-FlH, 28114-92-3; 9-PhS-Fl$^-$, 71805-72-6; 9-MeO-FlH, 19126-15-9; 9-MeO-Fl$^-$, 71805-70-4; 9-EtO-FlH, 2868-70-4; 9-EtO-Fl$^-$, 109494-97-5; 9-*i*-PrO-FlH, 88655-92-9; 9-*i*-PrO-Fl$^-$, 109494-98-6; 9-*t*-BuO-FlH, 88655-93-0; 9-*t*-BuO-Fl$^-$, 109494-99-7; 9-PhO-FlH, 59431-17-3; 9-PhO-Fl$^-$, 73838-68-3; 9-*i*-Pr$_2$N-FlH, 109495-00-3; 9-*i*-Pr$_2$N-Fl$^-$, 109495-02-5; 9-*t*-Bu(2-Br)-FlH, 85535-38-2; 9-*t*-Bu(2-Br)-Fl$^-$, 85535-33-7; 9-Me(2,7-Br$_2$)-FlH, 73872-42-1; 9-Me(2,7-Br$_2$)-Fl$^-$, 73872-46-5; 9-*t*-Bu(2,7-Br$_2$)-FlH, 85535-39-3; 9-*t*-Bu(2,7-Br$_2$)-Fl$^-$, 85535-34-8; 9-Br-FlH, 1940-57-4; PhC(Me$_2$)CH$_2$Cl, 515-40-2; 9-PhC(Me$_2$)CH$_2$-Fl-OH, 109495-01-4; *c*-C$_6$H$_{10}$(NO$_2$)Ts, 41774-12-3; PhSO$_2$CH$_2$Br, 19169-90-5; fluorenone, 486-25-9.

Distinguishing between Polar and Electron-Transfer Mechanisms for Reactions of Anions with Alkyl Halides

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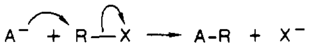
Abstract: 9-Substituted fluorenide carbanions in the series 9-MeFl$^-$, 9-MeO-Fl$^-$, and 9-Me$_2$N-Fl$^-$, which have nearly the same basicities but become progressively easier to oxidize, were selected as a test trio to probe for electron-transfer (e_T^-) components or radical-pair intermediates in reactions with alkyl halides. The trio members were shown to undergo e_T^- at progressively faster rates (>10^2 rate span) with two different types of single-electron acceptors, as expected. On the other hand, with PhCH$_2$Cl, *i*-BuBr, or *i*-BuI, S$_N$2 products were formed in a rate order that was the reverse of that established as characteristic of e_T^-. Reactions of the more sterically hindered 9-*i*-Pr$_2$N-Fl$^-$ ion with PhCH$_2$Cl or *i*-BuI to give S$_N$2 products were over 1400 times slower than those with 9-MeFl$^-$, whereas the e_T^- rate with *c*-C$_6$H$_{10}$(NO$_2$)Ts was eight times faster. On the other hand, reactions of the test trio with F$_3$CCH$_2$I, which is known to react slowly in S$_N$2 reactions, gave the reactivity order characteristic of e_T^-, and radical-type products were formed. For this reaction, a plot of log k_{obsd} vs. $E_{ox}(A^-)$ for seven 9-G-Fl$^-$ ions, wherein the bulk and radical-stabilizing ability of G was varied, was linear. This result shows that $E_{ox}(A^-)$ is a good measure of e_T^- ability and that e_T^- rates are insensitive to steric effects in either the donor or acceptor that cause large rate retardations in polar S$_N$2 reactions.

Displacement reactions of the type shown in eq 1 are among the most common in chemistry. The overall result is transfer of a single electron from a donor anion, A$^-$, to the leaving atom (or group), X, of an electron acceptor, RX. These reactions have been commonly represented as occurring, however, by attack of a lone pair from A$^-$ at the backside of R with the displacement of X$^-$, as shown in eq 1. Pross has emphasized recently that this representation is misleading because electrons shift singly, not in pairs.[1] Pross and Shaik prefer to represent synchronous displacements of this type in terms of eq 2,[2] where an electron from A$^-$ pairs with one from R and an electron from R is transferred to X, accompanied by fission of the R–X bond. In principle, this



$$A^- + R{-}X \longrightarrow A{-}R + X^- \qquad (1)$$

$$A^-{:} + R{\cdot\cdot}X \rightarrow A{\cdot\cdot}R + {:}X^- \qquad (2)$$

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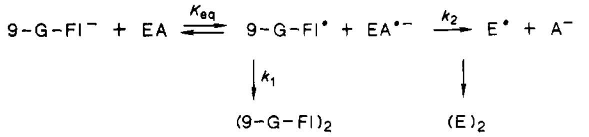
0002-7863/87/1509-5470$01.50/0

Scheme I



concerted ("polar") process can merge with a single-electron-transfer (SET or e_T^-) pathway wherein the AR product is formed by coupling of a geminate radical pair (eq 3).[1] In other words, the polar mechanism may contain an e_T^- component or involve a diradicaloid intermediate.

$$A^- + RX \rightarrow \underline{A^{\bullet}RX^{\bullet -}} \rightarrow \underline{A{\cdot}R{\cdot}X^-} \rightarrow A\text{-}R + X^- \qquad (3)$$

The factors determining whether or not e_T^- is favorable for a particular donor–acceptor combination have been enumerated as being (a) the standard free energy change obtained from the two redox couples and (b) the molecular and solvent reorganization accompanying the e_T^-, the size of which can be estimated from the individual identity (self-exchange) reactions.[3] The radical pair mechanism (eq 3) has been recognized as a possibility for substitution reactions involving easily oxidized organometal nucleophiles by a variety of investigators.[4] Recently the S_N2 reaction between Me_3SnNa and 2-bromooctane in THF has been proposed to occur by eq 3, based on analogy with the reaction of Me_3SnNa with 6-bromo-1-heptene in THF, which was demonstrated to occur predominantly by a radical mechanism.[5]

For the past 6 years we have studied rates for S_N2 reactions of families of 9-substituted fluorenide carbanions, 9-G-Fl⁻, and related families of nitranions, oxanions, and thianions, with alkyl halides in Me_2SO solution. The second-order rate constants, log k, for these reactions plot linearly with the acidities of the conjugate acids of the anions in each family, pK_{HA}.[6] A recent analysis of the factors controlling the size of the slopes of these Brønsted plots, β_{Nu}, has led us to suggest that these S_N2 reactions take place in two stages. Formation of an ion–dipole complex occurs in the first stage, which may be of primary importance in determining the size of β_{Nu}. (β_{Nu} values range from about 0.2–0.5 for these S_N2 reactions.) Bond making and bond breaking occur in the second, rate-limiting stage of the reaction.[7] We have also found that for 9-G-Fl⁻ ion families reacting with single-electron acceptors, linear Brønsted plots, with β_{Nu} values near unity, are obtained for e_T^- reactions wherein the basicities of the 9-G-Fl⁻ ions are changed by introducing 2- and 2,7-substituents.[8] When basicities are changed by also introducing substituents into the 3- or 9-positions the correlation breaks down, however, because some of these substituents exert radical-stabilizing effects.[9b] But plots of log k_{obsd} vs. $E_{ox}(A^-)$ for e_T^- have been found to be linear for 9-G-Fl⁻ ions of all kinds, even when the 9-substituent size is varied.[10] It follows that $E_{ox}(A^-)$ provides a good model for e_T^- and that these transfers are not subject to steric effects of anywhere near the magnitude observed in S_N2 reactions. We can predict from these results that a progressive increase in rates of e_T^- should occur along the series 9-Me-Fl⁻, 9-MeO-Fl⁻, and 9-Me_2N-Fl⁻ since these anions all have nearly the same basicities, but they have $E_{ox}(A^-)$ values that become progressively more negative over a range of about 0.3 V (7 kcal/mol).[9a] Observation of a progressive increase in rates for reactions of these anions with an electrophile should then constitute a test for the presence of an e_T^- component or a radical pair intermediate, particularly since there is a progressive increase in the size of G along the series, which could lead to a reverse order of rates for an S_N2 type reaction.

Table I. Rates of Reactions of 9-Substituted Fluorenide Ions (9-G-Fl⁻) with Electron Acceptors (EA) in Me_2SO at 25 °C

G	EA	$pK_{HA}(Me_2SO)$	$E_{ox}(A^-)$[a]	k_{rel}
Me	c-$C_6H_{10}(NO_2)Ts$	22.3	−0.355	(1.0)[c]
MeO	c-$C_6H_{10}(NO_2)Ts$	22.1	−0.449	78
Me_2N	c-$C_6H_{10}(NO_2)Ts$	22.5	−0.56[b]	>100
Me	$PhSO_2CH_2Cl$	22.3	−0.355	(1.0)[d]
MeO	$PhSO_2CH_2Cl$	22.1	−0.449	27
Me_2N	$PhSO_2CH_2Cl$	22.5	−0.56[b]	154

[a] $E_{ox}(A^-)$ values (irreversible) in eV obtained by cyclic voltammetry in Me_2SO solution with use of a Pt working electrode and Ag/AgI reference electrode under the conditions described previously.[9] [b] Reversible potential; a 40–100 mV correction needs to be added for comparison with irreversible potentials. [c] $k_{obsd} = 2.0\ M^{-1}\ s^{-1}$. [d] $k_{obsd} = 1.4 \times 10^{-2}\ M^{-1}\ s^{-1}$.

Table II. Rate Constants for Reactions of 9-Substituted Fluorenide Ions (9-G-Fl⁻) with Benzyl Chloride and in Me_2SO Solution at 25 °C

G	pK_{HA}	k_{obsd} ($M^{-1}\ s^{-1}$)	k_{rel}	k_{rel}(corr)
Me_2N	22.5	1.31	(1.0)	(1.0)[b] MeO
MeO	22.1	14.5	11	(0.5)[b]
Me	22.3	67.7	52	(1.6)[b]
Me_2CH	23.2		(1.0)[a]	
$MeCH_2$	22.6		27[a]	
Me	22.3		33[a]	

[a] Rate data of Bordwell and Hughes (ref 6b), corrected for differences in basicity. [b] Corrected for differences in steric effects.

Results and Discussion

The proposed test for an e_T^- mechanism needed to be verified by carrying out reactions with known electron acceptors. Rates were first measured, therefore, with two of the electron acceptors that we have used previously[8] (Table I).

The e_T^- reactions in Table I are believed to occur by Scheme I, where EA is the electron acceptor.

Since the e_T^- in the first step is endergonic, this step is no doubt reversible, and k_{obsd} will therefore be determined by k_1K_{eq} and/or k_2K_{eq}. The overall rate spans in Table I are of the order of 10^2–10^3, which is smaller than the span of about 10^5 observed over a comparable 0.3-eV range for e_T^- reactions of 2-G-9-ArFl⁻ ions with c-$C_6H_{10}(NO_2)_2$.[9b]

Application of the Test to Benzyl Chloride. Rate constants for a number of 9-G-Fl⁻ ions with $PhCH_2Cl$ are summarized in Table II.

Examination of Table II shows that for S_N2 reactions of our test trio with benzyl chloride a *reverse* order of rates to that observed in e_T^-, i.e., Me > MeO > Me_2N, obtains. As mentioned earlier, e_T^- rates of 9-alkyl-, 9-alkoxy-, and 9-(dialkylamino)-fluorenide ions do not appear to be subject to steric effects.[10] On the other hand, rates of S_N2 reactions are known to decrease along the series 9-MeFl⁻, 9-EtFl⁻, 9-*i*-PrFl⁻, and 9-*t*-BuFl⁻.[6] In Table II rate constants for the S_N2 reactions along the series Me, $MeCH_2$, and Me_2CH, corrected for basicity effects,[6b] are used as models for the series Me, MeO, and Me_2N. When this correction is made the rate differences all but disappear (see k_{rel}(corr) in Table II). The test therefore fails to provide any evidence for the presence of an e_T^- component or a radical intermediate. It rules out the radical-pair mechanism (eq 3) since the kinetics should reveal the presence of the 9-G-Fl• radical even if it couples rapidly with the $PhCH_2^{\bullet}$ radical to form the S_N2 product, 9-G-$FlCH_2Ph$.

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Table III. Rate Constants for Reactions of 9-Substituted Fluorenide Ions (9-G-Fl$^-$) with Iosbutyl Bromide and Isobutyl Iodide in Me_2SO Solution at 25 °C

G	pK_{HA}	RX	k_{obsd} (M^{-1} s^{-1})	k_{rel}
Me_2N	22.5	*i*-BuBr	0.28	(1.0)
MeO	22.1	*i*-BuBr	1.74	6.2
Me	22.3	*i*-BuBr	2.75	9.8
Me_2N	23.2	*i*-BuI	11.4	(1.0)
i-Pr_2N	20.1	*i*-BuI	0.06	0.0053[a]
MeO	22.1	*i*-BuI	42.7	3.7
Me	22.3	*i*-BuI	85.0	7.5

[a] An almost identical decrease in rate constant (0.0052) was observed relative to that of 9-Me_2N-Fl$^-$ ion, for the reaction with $PhCH_2Cl$.

Table IV. Reactions of 9-G-Fl$^-$ Ions with Alkyl Iodides by Polar S_N2 and Electron-Transfer Mechanisms

G	pK_{HA}	RI	k (M^{-1} s^{-1})	k_{rel}
i-Pr_2N	20.8	*i*-$PrCH_2I$	0.06	(1.0)
Me_2N	22.5	*i*-$PrCH_2I$	11.4	190
MeO	22.1	*i*-$PrCH_2I$	42.7	712
Me	22.3	*i*-$PrCH_2I$	85.0	1417
i-Pr_2N	20.8	F_3CCH_2I	0.06	0.46
Me_2N	22.5	F_3CCH_2I	8.5	65.4
MeO	22.1	F_3CCH_2I	1.2	9.2
Me	22.3	F_3CCH_2I	0.13	(1.0)
$PhCH_2$	21.4	F_3CCH_2I	0.021[a]	
2-Br-$PhCH_2$	18.9	F_3CCH_2I	0.381[a]	
2,7-Br_2-$PhCH_2$	16.9	F_3CCH_2I	0.0442[a]	

[a] Reference 12.

The Effects of Steric Hindrance and Oxidation Potentials. It has been argued that increased steric hindrance will retard the reaction by the polar mechanism and will allow the e_T^- mechanism to emerge.[1] The formation of radical products from the reaction of *i*-Pr_2NLi and $(C_6H_5)_3CBr$ in THF was cited as an example. In Table III we present data for rates of reactions of the test trio of 9-G-Fl$^-$ ions, and that of the much more sterically hindered 9-*i*-Pr_2N-Fl$^-$ ion, with two alkyl halides, *i*-BuBr and *i*-BuI, that are perhaps more sterically hindered than $PhCH_2Cl$.

Examination of Table III shows that the relative rates with the test trio are in the same order as observed with $PhCH_2Cl$ (Table II), although the rate spread has been decreased somewhat. The rate constant for reactions of 9-*i*-Pr_2N-Fl$^-$ ion with *i*-BuI is decreased by 190-fold, relative to that of 9-Me_2N-Fl$^-$, which is almost identical with the decrease observed in the reactions of these two anions with $PhCH_2Cl$. These large rate decreases are comparable to that observed for the reaction of $PhCH_2Cl$ with 9-*t*-BuFl$^-$ ion, relative to 9-MeFl$^-$ ion, and are attributable to steric effects typical of the polar mechanism.[6b] In contrast, the rate constant for e_T^- from the 9-Me_2N-Fl$^-$ ion to the *c*-$C_6H_{10}(NO_2)Ts$ electron acceptor is 8-fold greater than that from the 9-MeFl$^-$ ion, which is more in line with their relative oxidation potentials.[10] We conclude that the presence of a large steric effect in Nu$^-$, coupled with a relatively negative oxidation potential, is not sufficient to allow the e_T^- mechanism to emerge for reaction with moderately hindered alkyl halides.

The Effect of the Reduction Potential of the Alkyl Halide. The most likely explanation for the failure of the radical pair mechanism to occur for the 9-G-Fl$^-$ and RX combinations reported in Tables II and III appears to be an unsuitable match between $E_{ox}(A^-)$ and $E_{rd}(RX)$. We have found previously that single-electron transfer *does* occur between 9-G-Fl$^-$ ions with pK_{HA} values above 18 and $PhSO_2CH_2Br$ and $PhSO_2CH_2I$ halides.[8] The success of these e_T^-'s is the result of a more positive $E_{rd}(RBr)$ (−0.6 V)[8c] caused by the presence of the electron-withdrawing $PhSO_2$ moiety, coupled with the relative inertness of these halides to polar S_N2 reactions.[1] It seemed likely that F_3CCH_2I would also possess these two characteristics. It should be relatively inert to polar S_N2 reactions since F_3CCH_2Br and F_3CCH_2OTs have been shown to react with KI in acetone at rates about 6000 and 14000 times slower, respectively, than the corresponding RCH_2Br and RCH_2OTs analogues,[11] and the presence of the electron-withdrawing CF_3 moiety leads to an appreciably more positive E_{rd} (−1.3 V) than expected for *i*-BuI. Reaction of the test trio of 9-MeFl$^-$, 9-MeO-Fl$^-$, and 9-Me_2N-Fl$^-$ ions with F_3CCH_2I did indeed show the increasing reactivity order expected for reaction by an e_T^- mechanism. The rate constants for these reactions, together with those for the 9-*i*-Pr_2N-Fl$^-$ ion and a family of 9-$PhCH_2Fl^-$ ions, are given in Table IV.

Examination of Table IV shows that the 9-*i*-Pr_2NFl^- ion reacts 58 times slower with *i*-BuI in an S_N2 reaction than it does with F_3CCH_2I by an e_T^- reaction. But for 9-MeFl$^-$, the S_N2 reaction with *i*-BuI is 650 times *faster* than the e_T^- reaction with F_3CCH_2I, in part because of the smaller steric effect in the 9-MeFl$^-$ vs. 9-*i*-Pr_2N-Fl$^-$ in the S_N2 reaction and in part because of the lesser stabilization of the incipient 9-MeFl$^•$ radical than the 9-*i*-Pr_2N-Fl$^•$ radical in the e_T^- reaction. The kinetics of the reaction of 9-Me_2N-Fl$^-$ with F_3CCH_2I could be followed for less than 1 half-life spectrophotometrically because of interference from the strongly absorbing 9-Me_2N-Fl$^•$ radical being produced. Interference was worse in the 9-*i*-Pr_2N-Fl$^-$ reaction with F_3CCH_2I, but fortunately the 9-*i*-Pr_2N-Fl$^•$ radical is persistent and absorbs more strongly at 620 nm than does the 9-*i*-Pr_2N-Fl$^-$ anion (λ_{max} = 510 nm), so that the rate of appearance of the radical could be monitored. The rate of e_T^- for 9-*i*-Pr_2N-Fl$^-$ to *c*-$C_6H_{10}(NO_2)Ts$ was found to be only about 2 times slower than the minimum rate estimated for 9-Me_2N-Fl$^-$.

Product studies for the reactions of F_3CCH_2I with 9-MeO-Fl$^-$ and 9-$PhCH_2Fl^-$ ions revealed that the reactions were occurring by radical mechanisms. With 9-MeO-Fl$^-$ ion, the major product was $(9\text{-MeOFl})_2$ derived by coupling of the 9-MeO-Fl$^•$ radical. With 9-$PhCH_2Fl^-$ ion about 20% of the $(9\text{-}PhCH_2Fl)_2$ dimer was formed, accompanied by about 20% of 9-$PhCH_2FlH$ and 40% of 9-PhCH=Fl. The latter products are apparently formed by disproportionation and by hydrogen atom loss from the 9-$PhCH_2Fl^•$ radical, e.g.,

$$9\text{-}PhCH_2Fl^• + 9\text{-}PhCH_2Fl^• \rightarrow 9\text{-}PhCH_2FlH + 9\text{-}PhCH{=}Fl$$

$$9\text{-}PhCH_2Fl^• + F_3CCH_2^• \rightarrow [F_3CCH_3] + 9\text{-}PhCH{=}Fl$$

No products containing the CH_2CF_3 moiety were observed in either case.

Analysis of the products formed from the reaction of the 9-*i*-Pr_2N-Fl ion with F_3CCH_2I showed 9-*i*-Pr_2N-FlH to be the major product, accompanied by small amounts of at least five other products. Formation of 9-*i*-Pr_2N-FlH in the product study probably occurs by hydrogen atom abstraction from the solvent by the persistent 9-*i*-$Pr_2NFl^•$ radical. Reaction of this radical (or 9-*i*-Pr_2N-FlH) with $F_3CCH_2^•$ radicals apparently gives rise to three isomeric 9-(diisopropylamino)fluorenes containing a single F_3CCH_2 moiety and two containing two F_3CCH_2 moieties (see the Experimental Section).

Steric Effects in Intermolecular Electron Transfers. It has been demonstrated in several studies that, for certain radical anions, electron transfers can occur rapidly by intramolecular routes over distances as large as 10 Å, apparently via σ bonds.[13] Coupling of radicals and ions, such as $p\text{-}NO_2C_6H_4C(Me)_2^•$ with $(CH_3)_2C{=}NO_2^-$, to give a sterically crowded radical anion (**1**) followed by the rapid *intermolecular* electron transfer from **1** to an electron acceptor to form a new radical anion (**2**) are also known to occur as part of radical chain substitution reaction eq 4.[14]

It would appear from these examples that rapid electron transfers can occur either intra- or intermolecularly from radical

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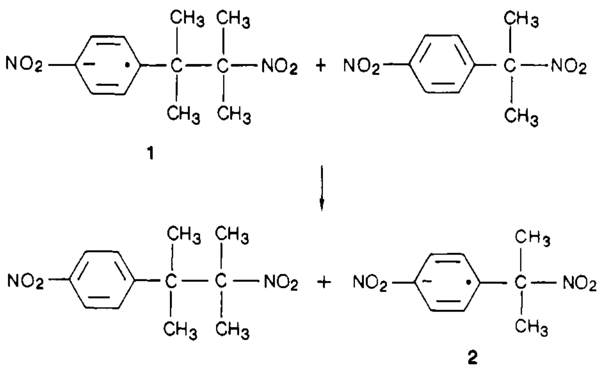
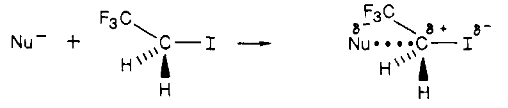


(4)

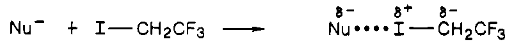
anions with seemingly little or no steric constraints. In the accompanying paper we found that a linear plot of log k_{obsd} for e_T^- to c-$C_6H_{10}(NO_2)Ts$ vs. $E_{ox}(A^-)$ for 9-G-Fl⁻ ions, where G included R, RO, RS, and R_2N groups of varying sizes, was obtained. There was no indication of a steric retarding effect in these e_T^- reactions, although rates of the corresponding S_N2 reactions between these carbanions and $PhCH_2Cl$ were severely retarded in some instances. Further information of this kind was obtained in the present instance by plotting log k_{obsd} for e_T^- to F_3CCH_2I vs. $E_{ox}(A^-)$ for the 9-MeFl⁻, 9-$PhCH_2$Fl⁻, 9-MeO-Fl⁻, 9-Me_2N-Fl⁻, and 9-i-Pr_2NFl⁻ ions (Figure 1).

Examination of Figure 1 shows no evidence for a steric effect. The order of rates is that expected from the oxidation potentials, i.e., 9-Me_2N-Fl⁻ > 9-i-Pr_2N-Fl⁻ > 9-MeOFl⁻ > 9-MeFl⁻. The steric effects observed in the reaction of iodide ion with F_3CCH_2Br and F_3CCH_2OTs[11] are nowhere to be seen. Evidently e_T^- to electron acceptors is not deterred by either steric constraints in the donor or the acceptor of the type that retard S_N2 reactions. The striking difference in the effects for these two types of reactions is no doubt due in part to the mode of approach of the donor in forming the initial ion–molecule complex. In the S_N2 reaction the complex must be formed by approach to the carbon end of the C–I dipole, where "steric" interference is encountered in the form of the lone pairs on the fluorine atoms (eq 5). In contrast, the donor can approach the iodine end of the C–I dipole in the e_T^- reaction (eq 6).



(5)

(ion-molecule complex for S_N2)



$$\mathrm{Nu^- + I{-}CH_2CF_3 \longrightarrow \overset{\delta-}{Nu}\cdots\overset{\delta+}{I}{-}\overset{\delta-}{CH_2CF_3}} \qquad (6)$$

(ion-molecule complex for e_T^-)

Summary and Conclusions. Reactions of the trio of equally basic 9-MeFl⁻, 9-MeO-Fl⁻, and 9-Me_2N-Fl⁻ ions with $PhCH_2Cl$, i-BuBr, or i-BuI occurred at progressively slower rates due to increasing steric effects in the polar S_N2 reaction. The order of rates was reversed, however, for reactions of the trio with c-$C_6H_{10}(NO_2)Ts$, $PhSO_2CH_2Cl$, or F_3CCH_2I, in keeping with the progressively increasing oxidation potentials of these ions. The latter reactions gave products derived from the 9-G-Fl• and the c-$C_6H_{10}NO_2$• (or $PhSO_2CH_2$•) (or F_3CCH_2•) radicals formed. Our test has thus failed to reveal evidence for an e_T^- component or a radical pair intermediate in reactions of simple alkyl halides with 9-G-Fl⁻ ions that have sizable oxidation potentials. A switch to an e_T^- mechanism has been achieved, however, with halides that have more positive reduction potentials and also offer hindrance to polar S_N2 reactions, e.g., $PhSO_2CH_2Cl$ and F_3CCH_2I.

Experimental Section

General Procedures. Measurements of $E_{ox}(A^-)$ and rate constant values were determined by methods described in earlier papers.[6-10] The sources or syntheses of materials have also been described earlier. Mass spectra were run by H. L. Hung on a HP5984 GC/MS system.

Product Studies. The formation of S_N2 products from reactions of 9-G-Fl⁻ ions in Me_2SO solution with $PhCH_2Cl$, n-BuBr, and other simple alkyl halides has been observed in numerous earlier studies. A few additional studies carried out in instances where it seemed possible that S_N2-type products might be replaced by radical-type products are listed below.

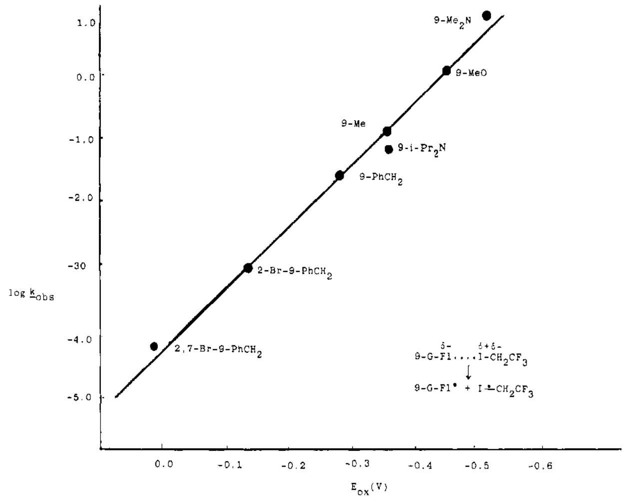


Figure 1. Plot of log k_{obsd} for electron transfer from 9-substituted fluorenide ions, 9-G-Fl⁻, to 2-iodo-1,1,1-trifluoroethane in Me_2SO solution at 25 °C. The deviation of the 9-i-Pr_2N-Fl⁻ ion point is caused, at least in part, by the reversibility of its oxidation potential, which causes a cathodic shift relative to the irreversible potentials of the other anions.

Table V

ret. time	area (%)	m/e	suggested structure
3.12	6.0	180	?
4.26	1.4	262	?
5.51	14.8	347	9-i-Pr_2N-$FlCH_2CF_3$
6.66	48.5	265	9-i-Pr_2N-FlH
7.29	7.0	347	9-i-Pr_2N-$FlCH_2CF_3$
7.70	18.8	347	9-i-Pr_2N-$FlCH_2CF_3$
8.37	1.2	429	9-i-Pr_2N-$Fl(CH_2CF_3)_2$
8.65	2.3	429	9-i-Pr_2N-$Fl(CH_2CF_3)_2$
	100		

9-(Diisopropylamino)-9-isobutylfluorene. A 152-mg sample of 9-i-Pr_2N-FlH in Me_2SO under argon was treated with 1 equiv of CH_3SOCH_2K in Me_2SO to effect complete deprotonation. Excess i-BuI was added and the solution allowed to stand for 48 h. Quenching in H_2O, Et_2O extraction, and rotoevaporation gave 144 mg of crude product containing ca. 90% of 9-i-Pr_2N-9-i-BuFl (by TLC). The NMR was complicated by the presence of diastereotopic protons; MS (m/e) 321 (61%), 264 (loss of C_4H_9, 24%), 306 (loss of CH_3, 3%), 221 (loss of C_3H_7 + C_4H_9, 43%), 179 (loss of C_3H_6 + C_3H_7 + C_4H_9, 93%), 165 (loss of $(C_3H_7)_2N$ and C_4H_8, 100%).

9-MeOFl⁻ Ion with F_3CCH_2I and with c-$C_6H_{10}(NO_2)Ts$. Titration of 156 mg (0.796 mmol) of 9-MeO-FlH with CH_3SOCH_2K in Me_2SO followed by treatment with excess F_3CCH_2I gave, after standing overnight and the usual workup, 146 mg (94%) of crude $(9\text{-MeO-Fl})_2$ dimer. After washing the mixture with EtOH a colorless solid, mp 255–260 °C, was obtained (lit.[15] mp 274–276 °C); NMR δ 2.98 (s, 6 H), 7.2–8.0 m, 16 H); MS (70 eV) no parent peak;[15] 195 (100%, 9-MeOFl), 328 (0.5%; Fl=Fl), 180 (26.7%), 165 (3.1%). This dimer was also formed by reaction of 9-MeO-Fl⁻ ion with c-$C_6H_{10}(NO_2)Ts$ (identified by the δ 2.9 peak in the NMR).

9-$PhCH_2$Fl⁻ Ion with F_3CCH_2I. An ^1H NMR analysis of the product obtained from a reaction run under comparable conditions with 9-$PhCH_2$Fl⁻ and F_3CCH_2I indicated the presence of about 20% of 9-$PhCH_2$FlH, 20% of $(9\text{-}PhCH_2Fl)_2$, and 40% of 9-PhCH=Fl.[12]

9-i-Pr_2N-Fl⁻ Ion Reaction with F_3CCH_2I in Me_2SO Solution. A 151-mg (0.571 mmol) sample of 9-i-Pr_2N-FlH was titrated with CH_3SOCH_2K in Me_2SO and stirred overnight with a 0.2 mL of F_3CCH_2I. Workup gave 175 mg of a complex mixture. An NMR of the crude product indicated the presence of about 50% of i-Pr_2N-FlH, multiple CH_2 peaks at δ 2.8–3.5, and the splitting of the isopropyl methyl peaks, suggesting that several compounds with slightly different chemical shifts

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were present. GC analysis gave 8 peaks, the largest of which was identified as 9-*i*-Pr_2N-FlH.

GC/MS analysis gave 8 peaks with the retention times, areas, and *m/e* values shown in Table V.

The structures of the compounds with *m/e* of 347 and 429 were supported further by the MS fragments associated with them:

$$347 \xrightarrow{(-i\text{-}Pr_2N)} FlCH_2CF_3\ (247,\ 100\%) \xrightarrow{(-CF_3)} FlCH_2\ (178,\ 27.8\%) \xrightarrow{(-CH_2)} HFlH\ (165,\ 4\%)$$

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Registry No. 9-Me-Fl^-, 31468-21-0; 9-MeO-Fl^-, 71805-70-4; 9-Me_2N-Fl^-, 83936-70-3; 9-*i*-Pr_2N-Fl^-, 109495-02-5; 9-$PhCH_2$-Fl^-, 53629-11-1; 2-Br-9-$PhCH_2$-Fl^-, 103422-01-1; 2,7-Br_2-9-$PhCH_2$-Fl^-, 109528-77-0; c-$C_6H_{10}(NO_2)Ts$, 41774-12-3; $PhSO_2CH_2Cl$, 7205-98-3; $PhCH_2Cl$, 100-44-7; *i*-BuBr, 78-77-3; *i*-BuI, 513-38-2; CF_3CH_2I, 353-83-3.

An Experimental and Theoretical Evaluation of the Intramolecular Reactions of Cyclohexyne

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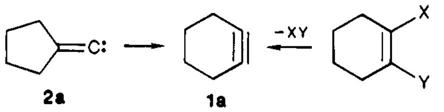
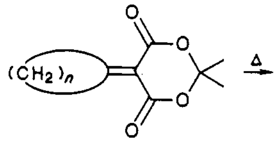
Abstract: The intramolecular reactions of cyclohexyne (**1a**) have been explored theoretically by using ab initio calculations at the MP2/6-31G* level and experimentally by examining the ring expansion of cyclopentylidenecarbene (**2a**) at elevated temperatures. The calculations indicate that **1a** is more stable than **2a** by 19.0 kcal/mol and that the barrier for **1a** → **2a** is 26.4 kcal/mol. Carbene **2a** can rearrange to bicyclo[3.1.0]hex-5-ene and thence to cyclohexadiene with a barrier of 38.9 kcal/mol. A higher energy reaction of **1a** is cleavage to ethylene and butatriene in a retro-Diels–Alder reaction, which is calculated to have a barrier of 46.8 kcal/mol. This retro-Diels–Alder reaction is observed experimentally when **2a** is generated by the pyrolysis of the cyclopentylidene adduct of Meldrum's acid.

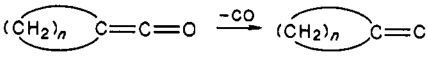
Although cycloalkynes with eight or more carbons[1] and certain substituted cycloheptynes[2] are isolable, the chemistry of the smaller ring cycloalkynes has mainly been inferred from intermolecular trapping reactions.[3] Consequently, there is little known about the intramolecular reactivity of these interesting species. In this paper, we report a theoretical and experimental evaluation of the intramolecular chemistry of cyclohexyne (**1a**). Methods of preparing cyclohexynes include β-elimination reactions of substituted cyclohexenes[4] and ring expansion of cyclopentylidenecarbene (**2a**) as illustrated in eq 1.[5] Thus, carbene **2a**, when generated by elimination, ring expands to cyclohexyne (**1a**), which may then be trapped with a suitable reagent.[5] An interesting pyrolytic method of preparing cycloalkylidenecarbenes (**2**) in which the cycloalkylidene derivatives of Meldrum's acid (**3**) are thermolyzed via methylene ketenes (**4**) to give **2** (eq 2) has been reported by Baxter and Brown.[6] However, pyrolysis of Meldrum's acid adduct **3a** gave only 1,3-cyclohexadiene (**5**) and benzene (**6**) (from decomposition of **5**). Since ring expansion of **2a** is observed when this carbene is generated at lower temperatures,[5] these data imply that this ring expansion may be reversible and that a low-energy intramolecular pathway for **1a** may simply be ring contraction to carbene **2a** followed by rearrangement to **5**. Rearrangement of **2a** to **5** is thought to involve an initial C–H insertion to give bicyclo[3.1.0]hex-5-ene (**7**), which subsequently ring opens to 2-cyclohexenylidene (**8**) followed by rearrangement to **5** (eq 3).



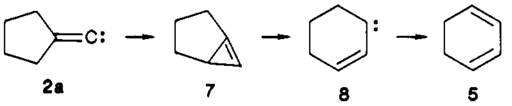
2a **1a** (1)



3a, *n* = 4
b, *n* = 5
c, *n* = 6
d, *n* = 7



4 **2** (2)



2a **7** **8** **5** (3)

In order to investigate the feasibility of rearrangement of **1a** to 1,3-cyclohexadiene, we have carried out an ab initio molecular orbital study of the energetics of this system. Since these calculations predict an additional first-order pathway for **1a**, we have also reinvestigated the pyrolysis of **3a** in order to search for this process.

Results

Molecular Orbital Calculations. In these ab initio calculations, which utilized the GAUSSIAN 82 program,[7] geometries were optimized with the 3-21G basis set and single-point calculations were made at the 6-31G, the 6-31G*, the MP2/6-31G, and the

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