various mechanistic possibilities, which differ only in the timing of the two 1,2-shifts, and there is no guarantee that we have not overlooked still other possible mechanisms. These uncertainties, however, do not mollify our basic conclusions.

Conclusions

The demonstration that aceanthrylene, acephenanthrylene, and fluoranthene can be interconverted thermally constitutes the first strong evidence for the occurrence of benzene ring contractions at high temperatures. These interconversions furthermore represent the first examples of thermal rearrangements of aromatic hydrocarbons in which one benzenoid skeleton is transformed into another benzenoid skeleton. The mechanism by which these rearrangements occur appears to involve a carbon 1,2-shift and a hydrogen 1,2-shift, both across the same carbon–carbon bond but in opposite directions. The precise timing of these two shifts relative to each other remains uncertain.

Experimental Section

All gas chromatograms (GC) were recorded on a Vaian 1400 GC fitted with a 25 m broad bore (0.75 mm, SPB-5) capillary column. GC–MS analyses were performed on a Finnigan 4023 GC–MS operated by Roger Scholl. Aceanthrylene (**11**)[13] and acephenanthrylene (**13**)[14] were prepared by the literature methods of Scott, Roelofs et al. Fluoranthene (**15**) was purchased from Aldrich Chemical Co.

Pyrolysis of Aceanthrylene, Acephenanthrylene, and Fluoranthene. The title compounds were pyrolyzed in a horizontal quartz lined Lindberg tube furnace (purchased from Kontes Glass Inc.) packed with quartz chips. The contact time was controlled by varying the flow rate of nitrogen carrier gas and was typically held at 2 s. The sample was adsorbed on Pyrex wool and placed in an attached head. The head was warmed to 100 °C via an aluminum sleeve wrapped with heating tape. The sample was typically pyrolyzed in 10-mg batches, and the product was collected in a liquid-nitrogen trap. The sample was washed out of the trap with $CDCl_3$, and analysis was carried out via ^1H NMR (500 MHz), capillary GC, and GC–MS. The results are summarized in Table I. Mass balance typically ranged from 70% at 880 °C to 35% at 1200 °C.

Acknowledgment. We thank Gerd Reinhardt and Scott Fielder for early synthetic work and the National Science Foundation for financial support of this work. High-field ^1H NMR spectra (500 MHz) were obtained at the University of California, Davis Medical NMR Facility.

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Steric Effects on Acidities of 9-Alkyl-, 9-(Alkylthio)-, and 9-Alkoxyfluorenes and on the Electron-Transfer Abilities of Their Conjugate Bases

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Abstract: Perturbations caused by steric effects in 9-alkylfluorenes (9-R-FlH) account, in part, for the effects of changing alkyl size on acidities and, in turn, for the failure of the acidity–oxidation potential (AOP) method to provide reasonable estimates for the radical-stabilizing effects of large alkyl substituents, such as *t*-Bu, *t*-$BuCH_2$, and $PhC(Me)_2CH_2$. Increases in alkyl size along the series Me, Et, *i*-Pr, and *t*-Bu for 9-RS-FlH and 9-RO-FlH fluorenes cause progressive increases in acidities due to increases in polarizability effects, but the radical-stabilizing effects of these substituents on the 9-fluorenyl radical, as estimated by the AOP method, remain essentially contant at 5.4 ± 0.3 kcal/mol for RS and 6.5 ± 0.5 kcal/mol for RO. Rate constants (log k_{obsd}) for single-electron transfer to an electron acceptor from 9-R-Fl-, 9-RO-Fl-, 9-RS-Fl$^-$, and 9-R_2N-Fl$^-$ ions, where R is varied in size, plot linearly with their oxidation potentials, indicating that rates of electron transfer from these carbanions are much less subject to steric hindrance than are rates of S_N2 reactions of these anions with alkyl halides.

Investigations of the acidities and reactivities of fluorenes have provided a fertile field for studies of substituent effects for the past three decades.[1-8] Substituents at the 1, 2, 3, and 4 positions, although remote from the acidic hydrogen atoms in the 9-position, have large effects on acidity (the Hammett ρ is 7 for the "meta" 2-position) and substituents at the 9-position have very large effects.[8] The progressive decrease in acidity caused by 9-alkyl groups along the series Me, Et, *i*-Pr, and *t*-Bu, which has been observed in aqueous Me_2SO,[2] cyclohexylamine,[3] and Me_2SO,[5] has been attributed primarily to a polar effect based on a Taft correlation ($\rho^* = 4.5$) on the one hand,[3,7] and primarily to steric effects on the other.[5] The progressive decrease in S_N2 reactivities toward $PhCH_2Cl$ of 9-alkylfluorenide ions, 9-R-Fl$^-$, along the series Me, Et, *i*-Pr, and *t*-Bu, at the same basicities, has also been attributed to steric effects.[9] Recently, oxidation potentials, $E_{ox}(A^-)$, for 2-G-Fl$^-$, 3-G-Fl$^-$, and 9-G-Fl$^-$ carbanions have been measured for a variety of substituents and combined with pK_{HA} values of their conjugate acids to give acidity-oxidation-potential (AOP) values, which provide estimates of substituent effects on the relative bond dissociation energies (BDEs) or stabilities of 9-fluorenyl radicals.[10] The $E_{ox}(A^-)$ values for 12 2-G-Fl$^-$ and 2,7-G-Fl$^-$ ions were found to correlate directly with the pK_{HA} values of their conjugate acids, indicating that these remote ("meta") substituents had little or no ability to stabilize (or destabilize) the radical. Small increases in $E_{ox}(A^-)$ values beyond

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Table I. Acidity and Acidity Oxidation Potential (Δ(AOP)) Values for 9-Alkylfluorenes (9-R-FlH) in Me_2SO at 25 °C

R	pK_{HA}[a]	ΔpK (kcal)[c]	$E_{ox}(A^-)$[d]	ΔE_{ox} (kcal)	Δ(AOP) (kcal)
H	22.6	(0.0)	−0.194	(0.0)	(0.0)
Me	22.3	−0.82	−0.355	−3.72	−4.5
Et	22.7	−0.27	−0.346	−3.50	−3.8
i-Pr	23.2	+0.41	−0.328	−3.10	−2.7[f]
t-Bu	24.35	+2.0	−0.284[e]	−2.07	−0.075[f]
t-$BuCH_2$	20.3	−3.56	−0.318	−2.86	−6.4[g]
$PhC(Me)_2CH_2$	20.3[b]	−3.56	−0.308	−2.63	−6.2[g]
$PhCH_2$	21.35	−2.12	−0.277	−1.94	−4.0
Ph_2CH	20.95[b]	−2.67	−0.182	+0.227	−2.4
Ph_3C	20.3[b]	−3.56	−0.141	+1.22	−2.3[h]

[a] Reported in previous papers unless otherwise noted. [b] Present study. [c] Statistically corrected for the number of acidic hydrogen atoms. [d] In eV; irreversible oxidation potentials measured by cyclic voltammetry as previously described.[10] [e] This value will become more negative by at least 25 mV when corrected for the partial reversibility observed in the wave. [f] Steric strain in the anion probably causes this value to be low (see text for discussion). [g] Steric relief of strain in forming the anion causes this value to be high (see text for discussion). [h] The value will be about −4 kcal/mol if one takes into account the reversibility of $E_{ox}(A^-)$, which will cause a cathodic shift of 30–100 mV.

Table II. Acidities of 9-Substituted Fluorenes (9-G-FlH) and Oxidation Potentials for 9-Substituted Fluorenide Ions (9-G-Fl$^-$) in Me_2SO at 25 °C

G	pK_{HA}[a]	ΔpK_{HA} (kcal)[d]	$E_{ox}(A^-)$[e]	ΔE_{ox} (kcal)	Δ(AOP) (kcal)
H	22.6	(0.0)	−0.194	(0.0)	(0.0)
Me	22.3	−0.82	−0.355	−3.72	−4.5[f]
Ph	17.9	−6.85	−0.153	+0.945	−5.9[f]
MeS	18.0	−6.7	−0.136	+1.34	−5.4[f]
EtS	17.5	−7.4	−0.118	+1.75	−5.6
i-PrS	16.9	−8.2	−0.085	+2.51	−5.7
t-BuS	15.9	−9.6	−0.004	+4.88	−5.2
PhS	15.4	−10.3	+0.026	+5.07	−5.2
MeO	22.1	−1.10	−0.449	−5.89	−7.0
EtO	22.0[b]	−1.23	−0.447	−5.83	−7.1
i-PrO	21.4[b]	−2.05	−0.422	−5.26	−7.3
t-BuO	21.3[c]	−2.17	−0.358	−3.78	−6.0
PhO	19.9	−4.11	−0.26	−1.43	−5.5[f]
$PhCH_2$	21.35	−2.12	−0.277	−1.94	−4.0

[a] Published in previous papers unless otherwise noted. [b] Present study. [c] G. E. Drucker, Ph.D. Dissertation, Northwestern University, 1978. [d] Statistically corrected for the number of acidic hydrogen atoms. [e] In eV; measured by cyclic voltammetry as previously described.[10] [f] Reference 10.

that predicted by the correlation line pointed to small radical-stabilizing effects for donor 3-G (para) substituents, e.g., 0.40, 0.63, and 1.0 kcal/mol for 3-Me, 3-PhS, and 3-MeO substituents, respectively. Much larger stabilizing effects were observed for 9-substituents, e.g., 4.5, 5.2, and 7.0 kcal/mol for 9-Me, 9-PhS, and 9-MeO, respectively.

In this paper oxidation potentials of 9-R-Fl$^-$, 9-RS-Fl$^-$, and 9-RO-Fl$^-$ ions have been measured in order to obtain estimates of the effect of the size of R on radical stabilities. We have also measured rates of single-electron transfer from these carbanions to an electron acceptor in order to determine the effect of alkyl size on the electron-transfer (e_T^-) ability.

Results and Discussion

Steric Effects on the Acidities of 9-Alkylfluorenes and on the Oxidation Potentials of Their Conjugate Bases. Oxidation potentials, $E_{ox}(A^-)$, were measured by cyclic voltammetry for 9-alkylfluorenide ions of varied size and combined with pK_{HA} values in the manner previously prescribed[10] to give Δ(AOP) values (Table I).

Although the decrease in acidities for 9-alkylfluorenes along the series Me, Et, *i*-Pr, and *t*-Bu correlates with Taft σ^* constants ($\rho^* \simeq 4$),[3,7] there is both experimental[11,15] and theoretical[12] evidence to indicate that these alkyl groups all have essentially zero field ("inductive") effects ($\sigma_F = -0.01$, relative to $H = 0.0012$), as originally suggested by Ritchie.[13] The decrease in acidities for 9-alkylfluorenes in Me_2SO solution, like that along the series MeOH, EtOH, *i*-PrOH, and *t*-BuOH,[14] is believed to be caused primarily by a progressive increase in steric inhibition of solvation in the anions. On the other hand, the increase in acidity with alkyl size along the series of 9-alkylfluorenes $MeCH_2$, $EtCH_2$, *i*-$PrCH_2$, and *t*-$BuCH_2$ is believed to be caused, at least in part, by a polarizability effect.[5] The striking increase in acidity of 4 pK_a units for 9-neopentylfluorene vs. 9-*tert*-butylfluorene is probably due in part also to relief of steric strain in forming the 9-neopentylfluorenide ion. An increase in acidity with alkyl size is observed when the CH_2 moiety in 9-RCH_2FlH is replaced by either O or S to give 9-RO-FlH or 9-RS-FlH fluorenes. As mentioned in the introduction, in the absence of radical stabilization by substituents, there is a direct relationship between anion basicities and oxidation potentials. For example, the plot of pK_{HA} vs. $E_{ox}(A^-)$ for 2-G-Fl$^-$ ions is linear with a slope near unity.[10a] Substitution of a hydrogen atom in the methyl group of the 9-MeFl$^-$ ion by Ph follows this pattern in that it causes a 1.3-kcal/mol decrease in basicity accompanied by a roughly equal decrease in the oxidation potential (1.8 kcal/mol, see Table I). On the other hand, successive substitutions of methyl groups for hydrogen atoms in the 9-MeFl$^-$ ion to produce the series 9-$MeCH_2$Fl$^-$, 9-Me_2CHFl$^-$, and 9-Me_3CFl$^-$ cause progressive increases in basicity by 0.55, 1.2, and 2.8 kcal/mol, respectively, accompanied by progressive *decreases* in $E_{ox}(A^-)$ by 0.22, 0.62, and 1.6 kcal/mol, respectively. The result is an apparent decrease in radical-stabilizing effects (Δ(AOP) values) from 4.5 kcal/mol for Me to 0.075 kcal/mol for *t*-Bu (Table I). In contrast, substitution of *t*-Bu and $PhC(Me)_2$ groups for a hydrogen atom in the 9-MeFl$^-$ ion to give 9-*t*-$BuCH_2$Fl$^-$ and 9-$PhC(Me)_2CH_2$Fl$^-$ ions causes a 2.7-kcal/mol decrease in basicity in each instance (relative to the 9-MeFl$^-$ ion), but $E_{ox}(A^-)$ values decrease by only 0.86 and 1.1 kcal/mol, respectively. The result is an apparent increase in the radical-stabilizing ability of these groups by 1.9 and 1.7 kcal/mol, relative to Me. The resulting Δ(AOP) values for 9-*t*-BuFlH, 9-*t*-$BuCH_2$FlH, and 9-$PhC(Me)_2$CH2FlH of −0.075, −6.4, and −6.2 kcal/mol, respectively, are unreasonable. The breakdown of the AOP method in these instances is consistent with our conclusion that the effects of these substitutions on acidities are not polar but steric in nature. The success of the AOP method depends on the relative basicities and relative $E_{ox}(A^-)$ values being unperturbed by steric effects. For 9-*t*-BuFl$^-$ ion, steric inhibition of solvation and perhaps steric strain are increasing the basicity, leading to an apparent high $+\Delta pK_a$ and a small negative Δ(AOP) value. The steric effect of the *tert*-butyl group inhibits dimerization of the radical causing partial reversibility of the oxidation peak and a cathodic shift in the $E_{ox}(A^-)$ value. This also contributes to the small size of Δ(AOP). On the other hand, for 9-*t*-$BuCH_2$Fl$^-$ and 9-$PhC(Me)_2CH_2$Fl$^-$ ions, relief of steric strain and polarizability effects decrease the basicity, leading to a large $-\Delta pK_a$ and artificially large negative Δ(AOP) values. These perturbation caused by steric effects render the AOP method unsatisfactory for judging the effect of size on the stability of 9-R-Fl$^\bullet$ radicals. This is not true for 9-RS and 9-RO fluorenes, however, as we will see in the next section.

Anion-Stabilizing and Radical-Stabilizing Effects of 9-(Alkylthio) and 9-Alkoxy Substituents in Fluorenes. The data in Table II allow estimates of anion-stabilizing effects of 9-RS and 9-RO substituents in fluorenes, relative to H, to be made from ΔpK_{HA} values and estimates of radical-stabilizing effects to be made from $\Delta E_{ox}(A^-)$ and Δ(AOP) values. Data for 9-Me, 9-Ph, and 9-$PhCH_2$

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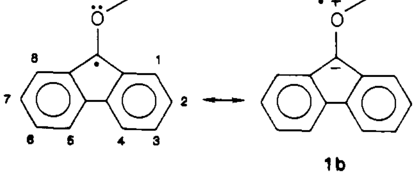
substituents are included for purposes of comparison.

Examination of Table II shows that replacement of Me in 9-MeFlH by MeS increases the acidity by 5.9 kcal/mol. This change is due largely to an increase in anion stability resulting from the much greater polarizability of MeS than Me. Changes in the alkyl moiety along the series MeS, EtS, *i*-PrS, and *t*-BuS lead to a further progressive increase in anion stability, covering a range of 2.9 kcal/mol. This too is attributable to enhanced polarizability of the group with increasing size.[5] The acidity increases are comparable in size to those observed for increasing the size of R in 9-RCH_2FlH fluorenes (3.1 kcal/mol),[5] which now appear to be caused by polarizability effects coupled, at least in some instances, with a diminution of steric strains in forming the anions. Relief of steric strain conceivably could occur in forming, say, 9-*t*-BuS-Fl^- ion, but the observation of a similar, although somewhat smaller, acidifying effect for $RSCH_2CN$ compounds (1.9 kcal/mol),[5] where steric factors cannot play a role, supports the view that polarizability is the dominant factor.

In the absence of appreciable changes in radical-stabilizing ability for RS substituents, we can expect the progressive decreases in basicities with increases in the size of R to be paralleled by decreases in oxidation potentials. Examination of the ΔE_{ox} column in Table II shows that this is essentially what happens. As a consequence, the Δ(AOP) values remain constant at 5.4 ± 0.3 kcal/mol, suggesting that there is little or no change in 9-RS-$Fl^\bullet$ radical stabilities (or 9-RSFl-H BDEs) along the series. Evidently, increasing the size and polarizability of the alkyl group in 9-RS-$Fl^\bullet$ radicals has little or no effect on radical stability. This is consistent with our view that it is the negative charge on the anion that induces polarization of the alkyl group and enhances anion stability.[15]

The effect of substitution of MeO for Me in 9-MeFlH on both the acidity and oxidation potential contrasts strikingly with that of MeS substitution. The acidity increase is negligible, suggesting that stabilization of the anion by the appreciable field-inductive effect of MeO is being offset by an equally large π-donor repulsive effect. Changes in the size of the alkyl group in RO along the series Me, Et, *i*-Pr, and *t*-Bu are still acid strengthening, but the alkyl polarizatility effects are smaller than in the RS series (ΔpK = 1.1 kcal/mol for MeO vs. *t*-BuO compared to 2.9 for MeS vs. *t*-BuS). It would appear that the presence of the sulfur atom is enhancing the polarizability of the alkyl groups. We concluded earlier that a similar synergistic effect occurs for the PhS group, which helps to make it have a more powerful stabilizing effect on an adjacent carbanion than does even a Ph group.[5]

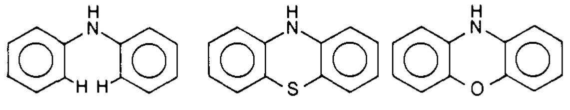
The change from Me to MeO causes a 2.2-kcal/mol increase in the oxidation potential, whereas the change from Me to MeS causes a 1.3-kcal/mol decrease. We have seen, however, that the latter decrease is associated with a basicity decrease, which is only partially compensated by the slightly greater radical-stabilizing effect of MeS vs. Me. The increased $E_{ox}(A^-)$ for 9-MeO-Fl^- vs. 9-$MeFl^-$ is associated with an appreciably greater radical-stability ability (Δ(AOP) = 7.0 vs. 4.5 kcal/mol) due to the π-donor delocalizing ability of MeO (e.g., contributors **1a** and **1b**). The radical-stabilizing effects of RO substituents are about 1.5 kcal/mol greater than those for comparable RS substituents, probably because of the better overlap, caused by a closer equality in orbital size, for contributors of the type **1a** and **1b** for RO than for RS.



1a **1b**

Our conclusion that an α-MeO function is about 1.6 kcal/mol better than an α-MeS function at stabilizing an odd electron on an adjacent carbon atom is consistent with 1.5, 1.6, and 0.8 greater stabilizing effects observed for EtO, *i*-PrO, and *t*-BuO, respectively, compared to the corresponding RS functions (Table II), and with slightly larger ΔAOP value for 9-PhO-FlH (−5.5 kcal/mol) than for 9-PhS-FlH (−5.2 kcal/mol).

For similar types of molecules it is possible to make estimates of the radical-stabilizing effects of structural changes by comparing AOP values. For example, the AOP values of diphenylamine, phenothiazine, and phenoxazine are 34.4, 28.6, and 26.2, respectively, suggesting that insertion of S into diphenylamine by replacing two ortho hydrogen atoms stabilizes the $Ph_2N^\bullet$ radical by about 5.8 kcal/mol. Replacement of the sulfur atom by oxygen leads to an apparent further stabilization by about 2.4 kcal/mol. These comparisons are rough since they ignore differences in ground-state energies of the molecules, but they are consistent with our other data, indicating a greater stabilizing effect on radicals by oxygen than by sulfur.



pK_a = 34.2 kcal/mol	pK_a = 31.1	pK_a = 29.7
$E_{ox}(A^-)$ = 0.2 kcal/mol	$E_{ox}(A^-)$ = −2.5	$E_{ox}(A^-)$ = −3.5
AOP = 34.4 kcal/mol	AOP = 28.6	AOP = 26.2

Other Evidence Concerning the Radical-Stabilizing Abilities of Alkylthio and Alkoxy Substituents. In sharp contrast to the conclusion just drawn from a consideration of the ΔAOP data, most data in the literature suggest that RS functions are better than RO functions at stabilizing radicals. For example, a comparison of rates of thermolysis of $GC(Me)_2N{=}NC(Me)_2G$ compounds has shown that the reactions are accelerated by only 10-fold when G = MeO, relative to Me, as compared to about 10^4 fold for G = MeS or PhS.[16] Also, the rearrangement of 3-(*p*-GC_6H_4)-2,2-dimethylmethylenecyclopropanes occurs 2.67-fold more rapidly than the parent when G = MeS,[17a] whereas a 2.38-fold acceleration relative to the parent was observed when G = MeO.[17b] Rates of reactions wherein radicals are formed are known to be often dominated by polar effects, however,[18] which suggests the possibility that the larger rate accelerations observed for RS than for RO may be caused by a polarizability, rather than a radical-stabilizing, effect. Also, interpretation of the thermolysis studies is clouded somewhat by the observation of negative entropies of activation for the reactions of the MeS and PhS compounds.[16a]

Electron spin resonance (ESR) data indicate that alkylthio are better than alkoxy functions at delocalization of spin density of odd electrons to substituents. For example, Arnold and his students have found the *p*-MeS group to be the most effective of all the para substituents studied in its ability to delocalize the spin of the odd electrons, as judged by hyperfine splitting constants of benzyl radicals.[19] In other words, the *p*-MeS substituent has the highest value in Arnold's $\sigma_\alpha^\bullet$ scale, an assessment that agrees with that of Creary's scale.[17] On the other hand, the AOP method indicates that the 3-MeS and 3-MeO ("para") functions stabilize the fluorenyl radical to about the same extent (ca. 1 kcal/mol).[10a]

An analysis of ESR hyperfine coupling constants for $CH_2{=}CHCHG^\bullet$, $HC{\equiv}CCHG^\bullet$, $CNCHG^\bullet$, and $CH_3O_2CCHG^\bullet$ radicals, where G = RS or RO, indicates that spin density is delocalized onto RS groups more effectively than to RO groups. The analysis also indicates that the barrier for rotation around the C_α–S bond in the (adamantylthio)methyl radical, AdS-$CH_2^\bullet$, is greater

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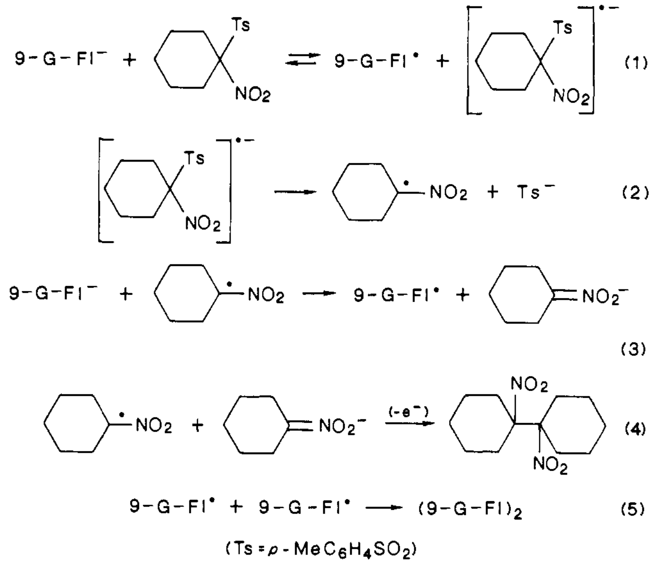
Scheme I



than that around the C_α–O bond in the AdO-CH_2• radical.[20] These conclusions are, of course, at odds with the ΔAOP values in Table II. We do not understand why the ESR and ΔAOP values give different orders for the relative abilities of α-RS and α-RO functions to stabilize adjacent radicals. One possibility is that the ESR method, for some reason, overestimates alkylthio stabilizing effects. Alternatively, it is possible that enhanced solvation of 9-RO-Fl⁻ ions may lead to abnormally low basicities for these ions and, therefore, apparent high radical-stabilizing effects.[21] We do know that the relative $E_{ox}(A^-)$ values for 9-RSFl⁻ and ROFl⁻ ions give an accurate measure of their rates of electron transfer to an electron acceptor, however, as will be brought out in the next section. Also, recent ab initio calculations indicate that $HOCH_2$• radicals are more stable than $HSCH_2$• radicals by 1.5 kcal/mol,[23] which is consistent with the ΔAOP order.

Steric Effects in 9-Substituted Fluorenide Ions on Their Electron-Transfer Abilities. We have seen in previous sections that variation in the size of 9-alkyl substituents can cause changes in their acidities by as much as 4 pK_{HA} units (Table I). Changes in basicity over this range caused by introducing substituents in the 2- and 2,7-positions have been found to cause a change in rate constants for single-electron transfer by as much as 4 powers of 10.[10b] In the present instance, however, the basicities have been changed by substitution directly at the acidic site (9-position) and are associated, in part, with steric effects. Measurements of rates of single-electron transfer from a number of these fluorenide ions to c-$C_6H_{10}(NO_2)$Ts were made to determine whether or not a steric effect on the rates would be observed. The reactions involved are shown in Scheme I and the results are summarized in Table III.

A discussion of Scheme I has been presented in an earlier paper.[10b] It was concluded that steps 1 and 3 controlled the rate of disappearance of 9-G-Fl⁻, which is being monitored. The kinetics are first order in [9-G-Fl⁻] and first order in [c-C_6H_{10}-(NO_2)Ts] but are not of high accuracy, presumably because of interference from reaction 4.

The data in Table III are arranged in order of decreasing oxidation potentials (and decreasing rate constants). A plot of log k_{obsd} vs. pK_{HA} is shown in Figure 1.

Table III. Rate Constants for Electron Transfer from 9-Substituted Fluornide Ions (9-G-Fl⁻) to 1-((p-Methylphenyl)sulfonyl)-1-nitrocyclohexane in Me_2SO at 25 °C

G	pK_{HA}[a]	$E_{ox}(A^-)$	k_{obsd}[d]
MeO	22.1	−0.449	176 ± 30
i-PrO	21.4	−0.442	120 ± 30
i-Pr_2N	20.5[b]	−0.360[c]	16 ± 0.5
t-BuO	21.3	−0.358	4.2 ± 0.2
Me	22.3	−0.355	2.0 ± 0.1
t-$BuCH_2$	20.3	−0.318	0.78 ± 0.05
$PhC(Me)_2CH_2$	20.3	−0.308	0.74 ± 0.30
t-Bu	24.35	−0.284	0.71[e]
MeS	18.0	−0.136	(5.8×10^{-3})[f]
t-Bu (2-Br)	21.7	−0.131	(5.5×10^{-3})[e]
i-PrS	16.9	−0.085	(5.8×10^{-4})
Me (2,7-diBr)	17.7	−0.056	$(7.2 \pm 4 \times 10^{-4})$[e]
t-Bu (2,7-diBr)	19.4	+0.025	$(5.3 \pm 3 \times 10^{-5})$[e]

[a] From Table II or previous papers unless otherwise noted. [b] Present study. [c] Reversible potentials; if corrected for the cathodic shift caused by reversibility this value could be more negative by as much as 100 mV. [d] Average of three or more runs reproducible to ±10% or better unless otherwise noted. [e] Data of M. E. Mueller. [f] Standard deviation ±2.7.

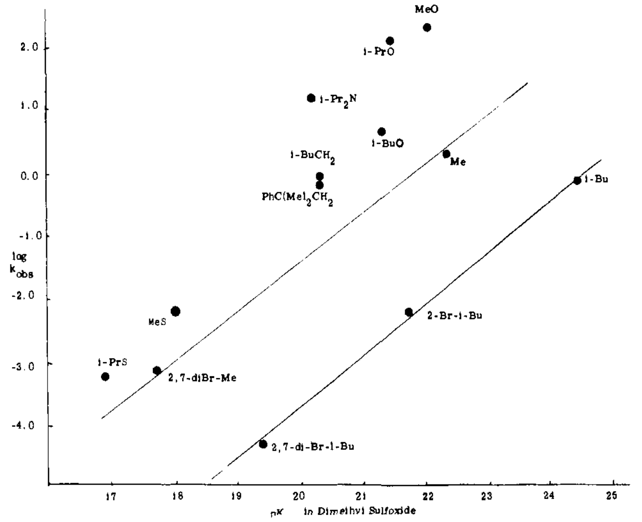


Figure 1. Rates of electron transfer (log k_{obsd}; Table III) from 9-substituted fluorenide ions, 9-G-Fl⁻, to 1-((p-methylphenyl)sulfonyl)-1-nitrocyclohexane plotted vs. the pK_{HA} values of their conjugate bases, both in Me_2SO solution at 25 °C.

Examination of Figure 1 shows that for the 9-*t*-Bu-Fl⁻ ion family, where the basicity is changed by introducing 2-Br and 2,7-Br_2 substituents, a reasonably good 3-point plot of log k_{obsd} vs. pK_{HA} is obtained. A 2-point plot of similar slope is also obtained for 9-MeFl⁻ and its 2,7-Br_2 derivtive reacting with the electron acceptor. These plots with slopes near unity are similar to those obtained in earlier studies of rates of electron transfer from fluorenide carbanions.[24] It is now clear that their linearity and unit slope are a consequence of the absence of radical stabilizing (or destabilizing) effects of substituents when placed at the 2- or 2,7-positions on the fluorene ring.[10a] The spread between the 9-Me and 9-*t*-Bu family lines is caused primarily by steric hindrance to solvation effects, which lead to abnormally high pK_{HA} values for members of the 9-*t*-BuFl⁻ ion family. On the other hand, the positioning of the neopentyl and neophyl points about 3 log units above the 9-*t*-BuFl⁻ ion family line is caused, in part, by steric strain and polarizability effects, which lead to abnormally low pK_{HA} values for these alkyl substituents. (These effects have been discussed in a previous section.) The large deviations of the points for RS, RO, and R_2N substituents from the 9-MeFl⁻ ion and 9-*t*-BuFl⁻ family lines are caused by failure of pK_{HA} to take account of the additional radical-stabilizing ability of these substituents.[10] This conclusion is supported by the greatly improved

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(21) This possibility is being checked by measuring the acidities of 9-RS-FlH and 9-RO-FlH in the gas phase.[22]

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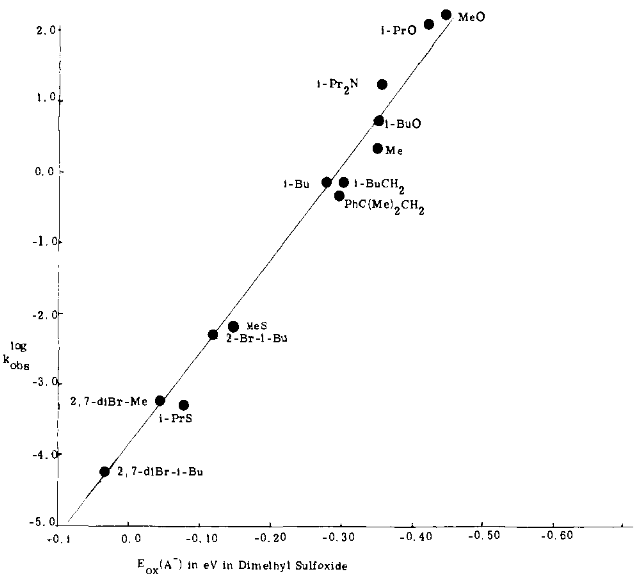

Figure 2. Rates of electron transfer (log k_{obsd}; Table III) from 9-substituted fluorenide ions, 9-G-Fl$^-$, to 1-((*p*-methylphenyl)sulfonyl)-1-nitrocyclohexane plotted vs. $E_{ox}(A^-)$ values, both in Me_2SO solution at 25 °C.

line obtained when log k_{obsd} is plotted against $E_{ox}(A^-)$ values (Figure 2).

Examination of Figure 2 shows that the 9-MeFl$^-$ and 9-*t*-Bu-Fl$^-$ family lines now essentially coalesce and that the 9-*t*-BuCH$_2$Fl$^-$ and 9-PhC(Me)$_2$CH$_2$Fl$^-$ ion points fit close to this line. The points for 9-*i*-PrS-Fl$^-$, 9-MeS-Fl$^-$, 9-*t*-BuO-Fl$^-$, and 9-MeO-Fl$^-$ ions fit the line within the experimental error of the rate measurements. The point for 9-*i*-Pr$_2$N-Fl$^-$ falls above the line, but a correction of 30–100 mV needs to be made for the cathodic shift in $E_{ox}(A^-)$ expected in view of its reversibility. When this corrections is made the point will fall on, or below, the line. The plot is remarkably good considering that (a) k_{obsd} is determined not only by the size of K_{eq} in step 1 of Scheme I but also by the rate at which the radical ion and/or the radical produced in step 1 is converted to product(s) in steps 2–4 and 5 and (b) several reactions can occur that interfere with the kinetic order.[10b] The figure brings out the wide disparity in both oxidation potentials and rates of electron transfer between RS-Fl$^-$ and RO-Fl$^-$ ions. Note that the rate of e_T^- from 9-MeO-Fl$^-$ is 10^4 times that from 9-MeS-Fl$^-$. The good agreement between the $E_{ox}(A^-)$ and rate data lends support to the evidence for a superior ability of α-RO than α-RS functions at stabilizing radicals. Similar linear correlations of $E_{ox}(A^-)$ values with rates of e_T^- reactions of 9-ArFl$^-$ ions[10b] and of substituted phenothiazinide ions[10c] have been made previously.

It is noteworthy that highly hindered carbanions, such as 9-*t*-BuFl$^-$ and 9-*i*-Pr$_2$N-Fl$^-$, which react with alkyl halides in S_N2 reactions at rates more than 10^3 times slower than do 9-MeFl$^-$ ions,[9,25] react in e_T^- at rates predicted by their oxidation potential (Figure 2). Rapid intermolecular single-electron transfers are known to occur between sterically congested radical anions and electron acceptors, such as *p*-$NO_2C_6H_4C(Me)_2C(Me)_2NO_2^{\bullet}$ and *p*-$NO_2C_6H_4C(Me)_2NO_2$,[26] but to our knowledge, this is the first evidence of a relative lack of steric hindrance to intermolecular e_T^- from an anion to an electron acceptor in an endergonic process. Exergonic intramolecular electron transfers are known to occur over distances as large as 10 Å,[27] but exergonic intermolecular electron transfers have been shown to decrease exponentially with distance in a rigid organic solid.[28]

Summary and Conclusions

Relief of strain in forming the anion and stabilization of the anion by its polarization of the adjacent *t*-Bu moiety account for the 4 pK_a unit increase in acidity for 9-*t*-BuCH$_2$FlH vs. 9-*t*-BuFlH. Perturbations caused by steric effects render the AOP method unsatisfactory for judging the effect of size on the stability of 9-R-Fl$^{\bullet}$ radicals. The AOP values remained essentially constant as R was changed along the series Me, Et, *i*-Pr, and *t*-Bu for 9-RO-FlH and 9-RS-FlH, indicating that the polarizability effects of R exert little or no radical-stabilizing effect in these RX-Fl$^{\bullet}$ radicals. The radical-stabilizing effects of α-RO groups are greater than those of α-RS groups and oxygen stabilizes the phenoxazine radical more than sulfur stabilizes the phenothiazine radical, but *p*-MeO and *p*-MeS effects in H-Fl$^{\bullet}$ radicals are similar in size. These results contrast with the conclusions that α-RS functions stabilize radicals better than α–RO functions that have been drawn previously from kinetic data and from ESR hyperfine coupling constants. Rates of electron transfer to the c-$C_6H_{10}(NO_2)$Ts acceptor for 13 9-R-Fl$^-$, 9-RO-Fl$^-$, 9-RS-Fl$^-$, and R$_2$N-Fl$^-$ ions with R varying in size give a good linear correlation with oxidation potential, indicating that these reactions are much less subject to steric effects than are S_N2 reactions of these anions with alkyl halides. The rates of electron transfer from 9-RO-Fl$^-$ ions are much greater than those for 9-RS-Fl$^-$ ions, which is consistent with the order of radical stabilities 9-RO-Fl$^{\bullet}$ > 9-RS-Fl$^{\bullet}$ deduced by the ΔAOP method. Recent ab initio calculations also support this order.

Experimental Section

The methods used for determination of pK_a's,[14,29] rate constants,[24] and $E_{ox}(A^-)$ values[10a] have been described in earlier publications.

Fluorenes. The syntheses of 9-methylfluorene,[30] 9-ethylfluorene,[30] 9-isopropylfluorene,[30] 9-*tert*-butylfluorene,[30] 9–neopentylfluorene,[30] 9-propylfluorene,[30] 9-*sec*-butylfluorene,[30] 9-(methylthio)fluorene,[30] 9-(ethylthio)fluorene,[30] 9-(isopropylthio)fluorene,[30] 9-*tert*-butylthio)-fluorene,[30] 9-(phenylthio)fluorene,[30] 9-benzylfluorene,[9] 9-(diphenylmethyl)fluorene,[31] 9-(triphenylmethyl)fluorene,[31] and 9-phenoxyfluorene[31] have been described previously.

9-Methoxy-,[32] 9-ethoxy-,[33] 9-isopropoxy-,[34] and 9-*tert*-butoxyfluorenes[35] were prepared by refluxing 9-bromofluorene in the appropriate alcohol solvent for 5 h, 4 days, 5 days, and 2 months, respectively.

9-(2-Methyl-2-phenylpropyl)fluorene was prepared by reaction of fluorenone with the Grignard reagent prepared from 1-chloro-2-methyl-2-phenylpropane, followed by hydrogenolysis of the resulting alcohol:[36] mp 96–97 °C; NMR ($CDCl_3$, Me_4Si) δ 1.6 (s, 6 H), 2.2 (d, 2 H), 3.7 (t, 1 H), 6.8–7.7 (m, 13 H). Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.32; H, 7.43.

Cyclic Voltammetry. The cyclic voltammograms were recorded in Me_2SO solution at 100 mV/s under the conditions previously described.[10] Since the ESR data reported in the literature suggest that α-RS carbanions should be more readily oxidized than α-RO carbanions, the $E_{ox}(A^-)$ values for 9-*t*-BuS-Fl$^-$ and 9-*t*-BuO-Fl$^-$ ions were measured also at scan rates of 50 and 500 mV/s. Under these conditions the $\Delta E_{ox}(A^-)$ values were 42 and 60 mV, respectively, and the $\Delta(E_p - E_p/2)$ values were 47 and 45 mV, respectively. These values are typical of those for other fluorenide ions.[10c] Also, the $\Delta E_{ox}(A^-)$ values with platinum and glassy carbon electrodes agreed to within 6 mV. We conclude, therefore, that there is nothing unusual in the electrochemical behavior of 9-*t*-BuS-Fl$^-$ and 9-*t*-BuO-Fl$^-$ ions, since both showed similar sensitivities to changes in sweep rates, both were insensitive to the nature of the working electrode (Pt or C), and both exhibited similar wave widths. Also, the

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$E_{ox}(A^-)$ 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-$C_6H_{10}(NO_2)$Ts and with $PhSO_2CH_2Br$. Reactions of $R_2C(NO_2)X$ electron acceptors with 9-G-Fl^- ions, where G = Me, C_6H_5 *p*-MeC_6H_4, and PhS, have been found earlier to give 60–80% yields of $(9\text{-G-Fl})_2$ and $(R_2CNO_2)_2$ dimers together with small amounts of R_2CHNO_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-$C_6H_{10}(NO_2)$Ts, a complex mixture was obtained from which 63 mg of *t*-BuFlH, 42 mg of c-$C_6H_{10}(NO_2)$Ts, 58 mg of (c-$C_6H_{10}NO_2)_2$, and 20 mg of c-$C_6H_{11}NO_2$ were recovered.

Also, 9-*t*-BuFl⁻ ion was prepared in situ from 9-*t*-BuFlH by titration with CH_3SOCH_2K in Me_2SO and reacted with an equivalent amount of $PhSO_2CH_2Br$. Quenching with water, extraction with ether, and chromatography on silica gave principally 9-*t*-BuFlH in the first fraction and $PhSO_2CH_3$ 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_2CH-FlH and 9-Ph_3C-FlH are rendered difficult by the low solubility of these compounds in Me_2SO. 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_2CH-FlH is 20.9_5, which is the average of titrations made with $(m\text{-}F_3CC_6H_4CH_2)_2SO_2$ (pK_a = 20.97) and $PhSCH_2SO_2Ph$ (pK_a = 20.34) as standard acids. The pK_a of 9-Ph_3C-FlH is 20.3 as determined by titration with $(m\text{-}F_3CC_6H_4CH_2)SO_2$. The trend in acidities for the series 9-MeFlH (22.3), 9-$PhCH_2$FlH (21.4), 9-Ph_2CHFlH (20.9_5), and 9-Ph_3C-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 $PhSCH_2SO_2Ph$ (pK_a = 20.34) gave pK_a = 21.29 ± 0.05; average 21.36.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for financial support. We thank M. E. Mueller for providing the data for the base lines in Figure 1.

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_2CH-FlH, 4425-68-7; 9-Ph_2CH-Fl^-, 100859-14-1; 9-Ph_3C-FlH, 67635-27-2; 9-Ph_3C-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_2N-FlH, 109495-00-3; 9-*i*-Pr_2N-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$(Me_2)CH_2Cl$, 515-40-2; 9-PhC$(Me_2)CH_2$-Fl-OH, 109495-01-4; *c*-$C_6H_{10}(NO_2)$Ts, 41774-12-3; $PhSO_2CH_2Br$, 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_2N-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 $PhCH_2Cl$, *i*-BuBr, or *i*-BuI, S_N2 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_2N-Fl^- ion with $PhCH_2Cl$ or *i*-BuI to give S_N2 products were over 1400 times slower than those with 9-MeFl^-, whereas the e_T^- rate with *c*-$C_6H_{10}(NO_2)$Ts was eight times faster. On the other hand, reactions of the test trio with F_3CCH_2I, which is known to react slowly in S_N2 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_N2 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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