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Carbon Acidity. 75. The Effects of Hetero-Substituted Pendant Groups on Carbanion Reactivity. Kinetic Acidities of 9-Substituted Fluorenes in Tetrahydrofuran. The Importance of Free Ions in the Reactions of Delocalized Carbanion Salts

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Abstract: For a series of 9-substituted fluorenes (substituents: $CH_3OCH_2CH_2$–, **1**; $(CH_3)_2NCH_2CH_2$–, **2**; $CH_3SCH_2CH_2$–, **3**; and $CH_3CH_2CH_2CH_2$–, **4**), the second-order rate constants for deprotonation by triphenylmethyllithium (TPMLi) have been determined in THF at 25 °C with UV-vis spectroscopy. Since TPMLi is significantly ionized in dilute THF solution (10^{-3} to 10^{-5} M), both free ions and ion pairs are involved in the deprotonations. Dissociation constants for the lithium salts of the substituted fluorenes are presented. Rates of deprotonation by the free triphenylmethyl anion and its solvent-separated ion pair lithium salt give the same order of kinetic reactivity: **3** > **1** > **2** > **4**. Brønsted analysis of the rate–pK_a relationships indicates that precoordination of the Li^+ to the hetero-substituted pendant groups is not important in these deprotonations. Brønsted α's of about 1 are observed, indicating that the substituents equally stabilize the transition states and product salts. The anomalous α value is explained as a result of transition-state charge localization near the substituent. Reactions of free ions can play a significant role in dilute THF solutions of delocalized carbanions.

The previous paper considered the effects of hetero-substituted pendant groups on the thermodynamic stabilities of some lithium–carbanion salts in tetrahydrofuran (THF).[1] Here, we discuss the effects of such pendant groups on the kinetic acidities of carbon acids. Carbanionic intermediates utilized in synthetic pathways are often generated under conditions leading to kinetically rather than thermodynamically favored products.[2] As a result, kinetic acidities are of great interest to synthetic organic chemists. Recent studies have noted that nonconjugated but nearby heteroatoms can have dramatic effects on the kinetic reactivities of carbon acids.[3-10] This topic has been reviewed recently by Beak and Meyers.[11]

Our accompanying study of the effects of coordinating pendant groups on the relative stabilities of contact and solvent separated ion pairs provides an opportunity to study comparable effects in kinetic acidities. We present here the kinetic acidities of fluorenes substituted in the 9-position with the following substituents: $CH_3OCH_2CH_2$–, **1**; $(CH_3)_2NCH_2CH_2$–, **2**; $CH_3SCH_2CH_2$–, **3**; $CH_3CH_2CH_2CH_2$–, **4**. This is a useful series because all of the fluorenes have fairly similar steric requirements around the acidic proton. Fluorene itself and the fluorene with a bidentate pendant group were not included in this study because differences in their steric bulk could influence the relative rates. Test studies with fluorene indicated that the deprotonation rate was much faster than that for the 9-substituted fluorenes. Throughout this study, triphenylmethyllithium (TPMLi) was employed as the base for deprotonations. This salt is well characterized in THF and yields rates that can be conveniently monitored by our techniques.[12,13] TPMLi exists primarily as monomeric solvent separated ion pairs (SSIP's) in dilute THF solution. The absence of TPMLi aggregation is evident in the kinetic acidity studies presented below, and it significantly simplifies the data analysis.

Table I. Dissociation Constants of Organolithium Salts[a]

	10^6K_d (M)[b]	f_{FI} at 10^{-4} M
1	2.9	0.16
2	1.1	0.10
3	13.4	0.30
4	10.7	0.28
TPMLi[d]	23.4	0.38

[a] In THF at 25.00 ± 0.02 °C. [b] Estimated error is ±25%. [c] Equivalent conductance at infinite dilution. Units are $cm^2\ \Omega^{-1}\ M^{-1}$. [d] Triphenylmethyllithium.

During the deprotonation, the pendant group heteroatom may coordinate the lithium cation of the incoming base and lead to a transition-state stabilization.[4,14] On the other hand, the heteroatom may increase the rate by inductively stabilizing the dipolar transition state without coordinating the cation. If precoordination is important, then the fluorenes with the coordinating pendant groups will benefit and react relatively faster than those with noncoordinating pendant groups. Brønsted analysis[15-22] of the

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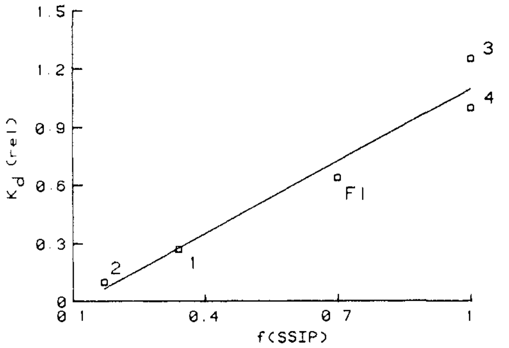

Figure 1. Plot of dissociation constant relative to 9-*n*-butylfluorenylllithium versus f_{SSIP}.

relationship between the kinetic and equilibrium acidities[1] is a useful tool for studying mechanisms and can be used in this system to characterize the role of the pendant groups during the deprotonations. Furthermore, Brønsted analysis measures the importance of the substituent in stabilizing the deprotonation transition state with respect to the product salt.

Finally, a body of Russian work indicates that free ions can make important contributions in the reactions of delocalized carbanion salts in ethereal solvents.[23-25] In addition, Chan and Smid[26] have considered the importance of free ions in the deprotonation of triphenylmethane by a polystyrylsodium salt. To characterize the free ion concentrations, the relationship between the electrical conductance and salt concentration may be employed. This technique has been applied successfully to a number of carbanion salts in THF and 1,2-dimethoxyethane (DME) with use of UV-vis spectroscopy to obtain concentrations.[23,26-29] For the present study, our results on ionic dissociation of triphenylmethyllithium in THF[29] were used to dissect the deprotonation rates into ionic and ion pair contributions.

Results and Discussion

For the lithium salts of the 9-substituted fluorenes, the dissociation constants, K_d, in THF were derived from conductivities as in our previous work,[29] using a value $\Lambda_0 = 85$ for all of the fluorenes. This value is consistent with previous studies.[27] Given the uncertainties in K_0, the estimated error in the K_d values is on the order of 25% although the relative values are probably more precise. It should be noted that at low concentrations some corrections in the extinction coefficients were necessary to account for the free ion absorbances. It was assumed that the free ions and SSIP's have similar extinction coefficients and $\lambda_{\max}$'s; therefore, for **1** and **2**, the shift to free ions leads to an increase in the solvent separated ion pair (SSIP) absorbance with respect to the contact ion pair (CIP). For **3** and **4**, a single absorbance was seen at the SSIP wavelength because these fluorenes exist solely as SSIP's. The extinction coefficients for **1** and **2** were corrected so as to reflect the observed ratios in the short (CIP) and long (SSIP + free ion) wavelength absorbances.[29]

The dissociation constants, K_0's and free ion fractions (f_{FI}) for the lithium salts are given in Table I. It can be seen immediately that free ions are sufficiently abundant in dilute solutions to play important roles in the kinetic acidities. The two fluorenyllithiums that exist as SSIP's in THF, **3** and **4**, have similar dissociation constants, but the two that form mixtures of SSIP's and CIP's, **1** and **2**, have considerably lower K_d's. The relationship between the relative K_d and SSIP fraction is clearly seen in Figure 1. This figure shows that fluorenyllithium itself, which also gives a mixture with measureable amounts of both SSIP's and CIP's, also fits this correlation. The correlation and its slope of about unity imply that the majority of the specific cation–anion interactions are realized in the ion pair equilibria (SSIP $\rightleftarrows$ CIP); consequently, the SSIP's of these 9-substituted fluorenes are all equally dissociable. The independence of structure on the dissociation constants of SSIP's has been observed for other fluorenyllithium derivatives in THF.[29] The dissociation constant for triphenylmethyllithium in THF (23.4×10^{-6} M) is considerably larger than those of the fluorenyllithiums, probably because of steric interactions with the propeller-shaped anion that increases the effective ion pair distance.

Given the dissociation constants, the next step is to consider how the free ion fraction (f_{FI}) changes as the deprotonation reaction proceeds. Since TPMLi is sufficiently basic to fully deprotonate all of the fluorenes, only the forward reaction needs to be considered:

$$\text{TPM–Li} + \text{R–H} \rightleftarrows \text{TPM–H} + \text{R–Li} \qquad (1)$$

In ethereal solvents, several studies have examined reactions involving mixtures of ion pairs and free ions, but generally in situations where the product salt is relatively insoluble or undissociable (halide or enolate salts); therefore, the contributions of the product salt to the free ion equilibria are negligible.[23-25] However, in our case, the calculation of the free ion fraction is complicated because the K_d's of the product and reactant lithium salts are of the same order of magnitude. Chan and Smid[26] encountered this problem in their deprotonation studies, but they simply assumed that this effect would be small at early reaction times. With the appropriate K_d's, however, the concentration of free triphenylmethyl anion may be determined analytically at all reaction times. Since the dissociation equilibrium expressions are coupled through the concentration of free Li^+, the equations must be solved simultaneously. The details of the solution are given in Appendix A. The result is a third-order equation and a complicated but straightforward solution. In short, the free ion fraction of the base, f_{FI}(TPMLi), is related to the concentration of the free lithium cation. If a less dissociable salt is formed as the reaction proceeds, the concentration of free Li^+ will decrease and f_{FI}(TPMLi) will increase.

$$f_{\text{FI}}(\text{TPMLi}) = [\text{TPM}^-]/([\text{TPM}^-] + [\text{TPMLi}]) = 1/(1 + K_d[\text{Li}^+]) \qquad (2)$$

For fluorenes **3** and **4**, f_{FI}(TPMLi) increases slightly over the course of the reaction (about 10–15%) because their product lithium salts have K_d's about half as large as triphenylmethyllithium. The situation is similar for fluorenes **1** and **2**, but the increase in f_{FI}(TPMLi) is much more significant because the dissociation constants of their lithium salts are about an order of magnitude smaller than that of triphenylmethyllithium. For example, if a 10^{-4} M solution of TPMLi is allowed to react with fluorene **2**, at 10% reaction the f_{FI} for TPMLi is 0.39, but at 90% reaction it has increased to 0.64. Assuming that free ions are more

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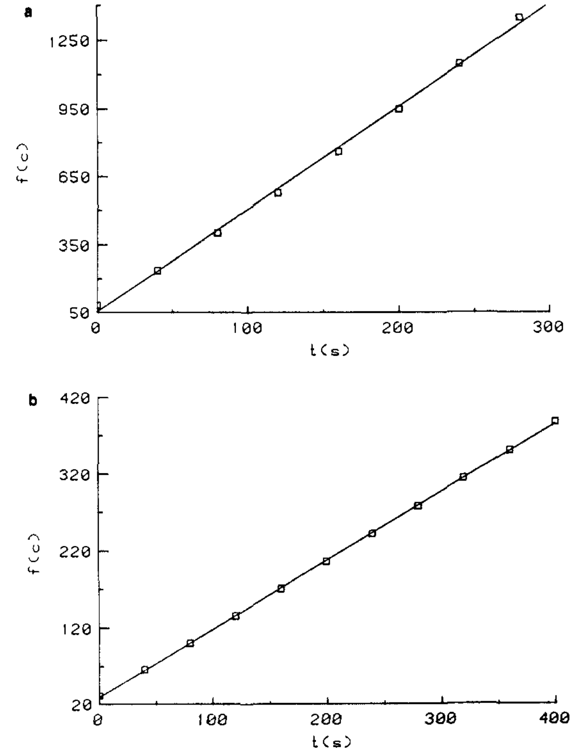

Figure 2. (a) Second-order kinetic plot for the reaction of triphenylmethyllithium with 9-*n*-butylfluorene (**4**) at 25 °C in THF. (b) Second-order kinetic plot for the reaction of triphenylmethyllithium with 9-(2-methoxyethyl)fluorene (**1**) at 25 °C in THF. In the plot, $f(c)$ refers to $[1/(B_0 - S_0)] \ln \{B_tS_0/[B_0(S_0 - B_0 + B_t)]\}$ where B_0 and S_0 are initial base and substrate concentrations and B_t is the base concentration at time t.

reactive, the observed second-order rate constants (first order in substrate and total TPMLi concentrations) will appear to increase somewhat for fluorenes **3** and **4** and considerably for fluorenes **1** and **2** as the reactions proceed. The importance of free ions in the deprotonation reactions is evident in the second-order kinetic plots obtained by monitoring the decrease in TPMLi absorbance. With fluorenes **1** and **2**, distinct curvature is seen in the kinetic plots (Figure 2a). The deviations indicate an increase in rate at lower concentrations and are consistent with an increase in the free triphenylmethyl anion fraction as the reaction proceeds. Therefore, free ion deprotonations are important in these systems and the curved plots can be explained without implicating aggregation. Since free ion–ion pair and monomer–dimer equilibria have similar concentration dependencies (two particles going to one), in the past, curved kinetic plots may have been mistakenly used as evidence of organolithium aggregation. Of course, this explanation applies only to salts with high K_d's (salts of highly delocalized carbanions). The importance of free ions is less visible in kinetic plots for **3** and **4** because their f_{FI}(TPMLi)'s change less through the runs; however, slight curvature is perceptible (Figure 2b).

To obtain kinetic acidities, the observed rates must be dissected to give free ion (k_{FI}) and ion pair (k_{IP}) rates. The two rates may be obtained by analyzing the following equation in a manner that goes back to the days of Acree:[30]

$$k_{obsd} = f_{FI}k_{FI} + f_{IP}k_{IP} \qquad (3)$$

Rearrangement with substitution gives

$$k_{obsd} = f_{FI}(k_{FI} - k_{IP}) + k_{IP} \qquad (4)$$

where the slope of k_{obsd} versus f_{FI} gives the difference in rates and the intercept is the ion pair rate. By starting runs with a variety of TPMLi concentrations, a number of (f_{FI}, k_{obsd}) combinations may be obtained. These terms change as the reactions proceed, but initial slopes (tangent at early points in the run) may be used, and the f_{FI} is solved by using the appropriate concentrations. Since the curvature in these plots is relatively small, this approach introduces little error. To develop a wide range of starting TPMLi concentrations, kinetic cells with 1 and 0.1 cm path lengths were used to give concentration ranges of at least tenfold. A typical plot of k_{obsd} versus f_{FI} is given in Figure 3. There is some scatter, but it is consistent with the expected errors (about 10% in the observed rates).

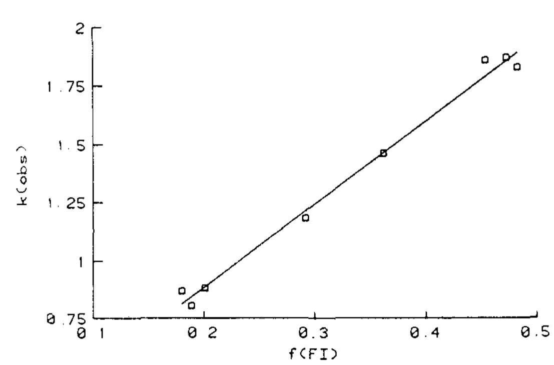

Figure 3. Plot of observed rate (k_{obsd}) versus calculated free ion fraction (f_{FI}) for the reaction of triphenylmethyllithium with 9-*n*-butylfluorene (**4**) at 25 °C in THF.

Table II. Second-Order Rate Constants for Deprotonations by Triphenylmethyllithium in THF at 25 °C[a]

	k_{FI} (M^{-1} s^{-1})	k_{IP} (M^{-1} s^{-1})	k_{FI}/k_{IP}
1	14.6	1.3	11.2
2	4.9	0.93	5.3
3	28.5	5.0	5.7
4	3.7	0.17	21.8

[a] Estimated errors in rates are about ±20–25%.

The free ion and ion pair rates of deprotonation are presented in Table II along with the k_{FI}/k_{IP} ratios. The reactivity ratios, k_{FI}/k_{IP}, vary from about 5 for fluorene **2** to 22 for **4**. These results are in good accord with kinetic studies in DME and THF by Solov'yanov and co-workers.[23-25] For lithium salts of delocalized carbanions (generally SSIP's), they find k_{FI}/k_{IP} ratios of about 3 to 100 in a number of alkylation reactions using substrates such as carbonyls and alkyl halides. These Russian workers also have studied the THF reaction of TPMLi with methyl iodide and found a k_{FI}/k_{IP} ratio of about 3:1.[24] The relative invariance of the k_{FI}/k_{IP} ratios over this wide range of reactions indicates that the lithium plays only a minor nonspecific role in the reactions of SSIP's. It is important to note that in the concentration ranges employed in our kinetic studies, the f_{FI} varies from about 0.2 to 0.5; therefore, free ions may account for from 50 to 95% of the deprotonations. *Free ions can indeed be important in reactions of delocalized carbanions in dilute THF solution.* Since the free ion reactions tend to dominate in these systems, the derived k_{FI}'s are generally more accurate than the k_{IP}'s.

Comparing the rates for the individual fluorenes, both the free ion and ion pair rates give similar orders of reactivity, **3** > **1** > **2** > **4**, with a range from fastest to slowest of about an order of magnitude. Obviously, hetero-substitution increases the deprotonation rates significantly. The most interesting analysis is to compare the rates with the pK_a's via Brønsted plots.[15-17] First, consider the ion pair rates. The question is whether precoordination of the pendant group heteroatom to the lithium cation of the incoming base is responsible for accelerating the rate. Since the oxygen and nitrogen substituted fluorenes, **1** and **2**, form internally chelated salts,[1] they are the most likely to use their pendant groups for coordination in the deprotonation step. Precoordination is not expected with fluorenes **3** and **4** because their pendant groups do not lead to internal chelation. If precoordination is important, there should be a correlation between the ion pair rates (k_{IP}) and the contact ion pair (CIP) pK's because these pK's take into account the effects of pendant group coor-

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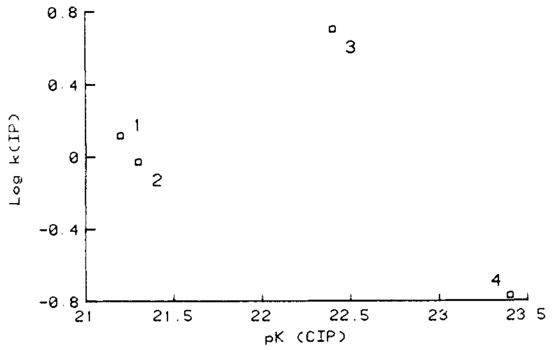

Figure 4. Brønsted plot of ion pair rate (k_{IP}) versus $pK_{Li/THF}$(CIP).

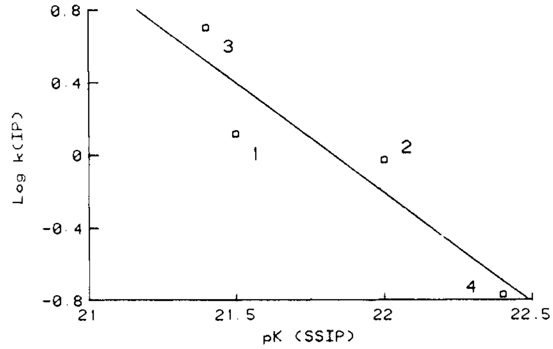

Figure 5. Brønsted plot of ion pair rate (k_{IP}) versus $pK_{Li/THF}$(SSIP).

Table III. Summary of Brønsted Correlations[a]

correlation	α	r^2
k_{IP} vs. $pK_{Li/THF}$(SSIP)[b]	1.23	0.872
k_{FI} vs. $pK_{Li/THF}$(FI)[c]	0.82	0.996

[a] Attempted correlations between k_{IP} and $pK_{Li/THF}$(CIP) give r^2 values less than 0.25, see Figure 4. [b] See Figure 5. [c] See Figure 6.

Table IV. Relative Rate–pK_a Relationships[a,b]

	log $K_{Li/THF}$(SSIP)	log k_{IP}
1	0.9	0.88
2	0.4	0.74
3	1.0	1.47
4	0.0	0.00

[a] In THF at 25 °C. Deprotonation rates with triphenylmethyllithium as the base. [b] Relative to **4**, log $K_{Li/THF}$(SSIP) = −22.36 and log k_{IP} = −0.77.

Table V. Free Ion and Solvent-Separated Ion Pair pK's in THF at 25 °C

	pK_{THF}(FI)[a]	$pK_{Li/THF}$(SSIP)[b]
1	21.6	21.5
2	22.1	22.0
3	21.2	21.3
4	22.3	22.3
fluorene	22.9	22.9

[a] Relative to fluorene, $pK_{Li/THF}$(FI) = 22.9 and $K_d = 6.9 \times 10^{-6}$ M. For details of free ion pK's, see ref 29. [b] Solvent-separated ion pair pK. See previous paper[1] for determination.

dination (internal chelation). If the pendant groups play only inductive roles in stabilizing the transition state, there should be a correlation between the rates and the solvent separated ion pair (SSIP) pK's because these pK's neglect coordination to the pendant group. The derivations of $pK_{Li/THF}$(CIP) and $pK_{Li/THF}$(SSIP) are discussed in the previous paper. The Brønsted plots in Figures 4 and 5 indicate that precoordination is not important in these systems. The scatter between log (k_{IP}) and $pK_{Li/THF}$(CIP) shows no significant correlation. In contrast, there is a correlation between log (k_{IP}) and $pK_{Li/THF}$(SSIP) and a reasonable Brønsted α can be derived from the slope (Table III). There is some scatter in Figure 5, but the ion pair rate is clearly dependent on $pK_{Li/THF}$(SSIP) rather than $pK_{Li/THF}$(CIP). Therefore, in the transition state, the pendant group does not coordinate to the lithium cation. In other words, the deprotonation proceeds through a solvent separated rather than a contact ion pair mechanism. This conclusion implies that the first product of proton transfer is the solvent separated fluorenyllithium ion pair, even in those cases where contact ion pairs are important at equilibrium. By the Principle of Microscopic Reversibility, this conclusion also implies that the reverse reaction of these fluorenyllithiums with triphenylmethane must involve the solvent separated ion pair components.

Given the small number of compounds and narrow range of pK's and rates, it is not possible to report a definitive Brønsted α value; however, some important trends may be observed. The slope of the Brønsted plot of log (k_{IP}) versus $pK_{Li/THF}$(SSIP) is about 1.2 (Figure 5), indicating that the effects of the substituents are similar in the transition states and in the products. Although there may be some error in the slope determination, it is clear that there is nearly a 1:1 or larger relationship between the rate enhancements and the pK reductions (Table IV). This is an unusual result because Brønsted slopes (α) are generally between 0 and 1.[18] For example, previous work in this laboratory on proton transfers with benzo-substituted and related fluorene derivatives in CH_3OH gave a Brønsted slope of 0.35.[19] Furthermore, the extent of proton transfer at the transition state often has been related to the magnitude of the α value, but an α value of about 1 implies that proton transfer is nearly complete at the transition state.[18] This is inconsistent with the Hammond postulate which predicts an "early" transition state for an exothermic deprotonation.[31] The key to the anomalous α value is the way the pendant groups stabilize the transition states. These substituents provide stabilization through inductive effects rather than delocalization. The effect of the pendant heteroatom is related to its proximity to the locus of charge. In the transition state, there has been only partial charge transfer to fluorene, but the leaving proton localizes this charge at the 9-position, a position near the pendant heteroatom. In the product, the charge is more fully delocalized; consequently, much of it is far from the substituent. Apparently, in this system the localization of charge in the transition state offsets the greater charge transfer in the product; therefore, the substituent provides similar stabilizations in both the transition state and product. In the study of benzofluorenes cited above, only changes in the π-system were important. Since the location of the charge is not as important when dipolar inductive effects are absent, the extent of proton transfer dominates the determination of α for the benzofluorenes. Brønsted α's of 1 or more have been observed, particularly with nitro-substituted carbon acids.[15,20-22] Both Bordwell[20,21] and Kresge[15] have studied such systems and presented similar transition state–charge localization arguments to explain the anomalous values. *Both the extent of proton transfer and the charge distribution in the transition state are important in determining the Brønsted α value, particularly with dipolar substituents.*

Next, consider the Brønsted relationship between the free ion rate and pK. The pK_{THF}(FI) is the relative free ion pK and is derived from the ion pair pK and the relative dissociation constant

$$pK_{THF}(FI) = pK_{Li/THF} - \log (K_d/K_d^\circ) \qquad (5)$$

where K_d° is the dissociation constant of the reference indicator (fluorenyllithium).[29] The free ion pK's are presented in Table V, and as expected, they parallel the $pK_{Li/THF}$(SSIP)'s. A good correlation between log (k_{FI}) and pK_{THF}(FI) is seen with a slope of about 0.8 (Table III and Figure 6). The better plot is indicative of the higher certainty in the k_{FI}'s with respect to the k_{IP}'s. Again, α is nearly unity and, consequently, the effects of the substituents are nearly the same in the transition state as in the product. The slightly smaller α value may be interpreted as evidence of an earlier transition state for the free ion deprotonation. More importantly, the similar Brønsted correlations for the ion pair and free ion

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(31) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

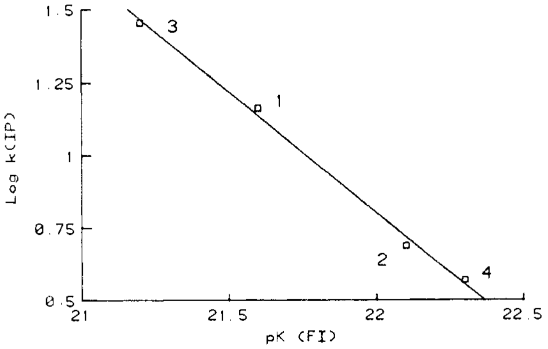

Figure 6. Brønsted plot of free ion rate (k_{FI}) versus pK_{THF}(FI).

deprotonations indicate that the mechanisms are similar and the the lithium plays only a minor role. That is, internal coordination is not important with SSIP's.

Finally, the high reactivity of **3** warrants comment. Since the rates are higher for this sulfur-substituted fluorene than for the corresponding oxygen-substituted fluorene, **1**, it appears that heteroatom polarizability rather than electronegativity is most important in determining the rate of proton transfer. The importance of substituent polarizability has been noted by Bunnett[32] for nucleophilic displacement reactions. Bunnett found that the interaction of polarizable substituents (i.e., I, Br) on the substrate with a thiophenoxide nucleophile leads to dramatic rate increases relative to using methoxide as the nucleophile. In our studies, the joint polarizability of the sulfur and the delocalized carbanions apparently are combining to give **3** a high kinetic acidity. Undoubtedly, the polarizability of sulfur is also responsible for the high equilibrium acidity observed for **3** in the previous study.

Conclusion

This study has shown that although fluorenes with oxygen and nitrogen substituted pendant groups form internally chelated salts in THF, precoordination to the lithium cation of the incoming base is not important in deprotonation by triphenylmethyllithium; however, through inductive effects, pendant group heteroatoms significantly accelerate the rates of deprotonation. Brønsted analysis gives α values of about 1 indicating that the substituents provide similar stabilizations to the transition states and products. These unusually large α values are a result of transition-state charge localization near the pendant group. Finally, although THF has a low dielectric constant, lithium salts of delocalized carbanions have significant free ion fractions in the 10^{-4} to 10^{-5} M range. Kinetic studies indicate that these free ions are about an order of magnitude more reactive than the corresponding ion pairs and at low concentrations may play an important role in such deprotonations.

Experimental Section

General. The synthesis and preparation of the necessary compounds are detailed in the previous paper.[1] Most of the equipment employed in this study is also described in the previous paper. Resistance measurements were completed with an EMI video bridge.

Conductivity Studies. These measurements were carried out in the glovebox. The details of the glovebox arrangement have been presented previously.[29,33] In general, a THF solution of the desired fluorene was equilibrated at 25.00 ± 0.02 °C in a conductivity cell of cell constant 0.1016 equipped with a 1.00-cm optical compartment. The initial resistance (R_0) of the solution was then determined. Triphenylmethyllithium (TPMLi) was added and allowed to fully react and equilibrate at 25.00 °C. The resistance and absorbance of the solution were then measured. Concentrations were derived from Beer's law by using the previously determined extinction coefficients.[1] For fluorenyllithiums **1** and **2**, a molar extinction coefficient of 14 500 was assumed for the isolated ion pairs and free ions (i.e., pure SSIP). Additional TPMLi was added and the sequence was repeated to give at least five points over a concentration range of about 10-fold. Dissociation constants were derived from these data with use of the Fuoss equation as detailed previously.[29]

Kinetic Studies. These measurements also were carried out in the glovebox. In a cell equipped with either a 0.1- or 1.0-cm optical compartment (calibrated as detailed previously),[34] a THF solution of triphenylmethyllithium was equilibrated at 25.0 °C to give a steady absorbance at 502 nm (ca. 10^{-3} to 10^{-4} M). A sample of the substrate fluorene was then added, and after sufficient mixing, the absorbance at the λ_{max} of TPMLi (502 nm) was recorded as a function of time (every 10 s). Absorbances were converted to TPMLi concentrations making a correction for the absorbance derived from the product fluorenyllithium. The TPMLi molar extinction coefficient at 502 nm (31 500) was determined by comparison with salts of known extinction coefficient.[33] Comparison of the final fluorenyllithium derivative concentration with the starting TPMLi concentration indicated negligible decomposition.

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Appendix A. Determination of Free Ion Fraction

An expression for the concentrations of free ions when two dissociable salts are present can be derived in the following way from the dissociation equilibria:

$$K_1 = \frac{[\mathrm{Li}^+][\mathrm{R}_1^-]}{[\mathrm{R}_1\mathrm{Li}]};\ K_2 = \frac{[\mathrm{Li}^+][\mathrm{R}_2^-]}{[\mathrm{R}_2\mathrm{Li}]}$$

$$\text{where } [\mathrm{Li}^+] = [\mathrm{R}_1^-] + [\mathrm{R}_2^-]$$

Let $C_1 = [\mathrm{R}_1\mathrm{Li}]^*$ and $C_2 = [\mathrm{R}_2\mathrm{Li}]^*$ (an asterisk indicates the total salt concentrations, ion pair + free ion); then,

$$K_1 = \frac{([\mathrm{R}_1^-] + [\mathrm{R}_2^-])[\mathrm{R}_1^-]}{(C_1 - [\mathrm{R}_1^-])};\ K_2 = \frac{([\mathrm{R}_1^-] + [\mathrm{R}_2^-])[\mathrm{R}_2^-]}{(C_2 - [\mathrm{R}_2^-])}$$

$$\rightarrow \frac{K_1(C_1 - [\mathrm{R}_1^-])}{[\mathrm{R}_1^-]} = \frac{K_2(C_2 - [\mathrm{R}_2^-])}{[\mathrm{R}_2^-]}$$

$$\rightarrow [\mathrm{R}_1^-] = \frac{1}{(1/C_1 - K_2/C_1K_1 + K_2C_2/K_1C_1[\mathrm{R}_2^-])} \quad (1)$$

Substitution into the expression for K_2 followed by rearrangement leads to

$$(K_1 - K_2)[\mathrm{R}_2^-]^3 + (K_1C_1 + K_2(C_2 + K_1 - K_2))[\mathrm{R}_2^-]^2 + (K_2C_2(2K_2 - K_1))[\mathrm{R}_2^-] - C_2^2K_2^2 = 0$$

Letting

$$a = (K_1C_1 + K_2(C_2 + K_1 - K_2))/(K_1 - K_2)$$
$$b = (K_2C_2(2K_2 - K_1))/(K_1 - K_2)$$
$$c = -(C_2^2K_2^2)/(K_1 - K_2)$$

and

$$Q = \frac{3b - a^2}{9};\ R = \frac{9ab - 27c - 2a^3}{54}$$

three solutions may be found; however, two solutions give either $[\mathrm{R}_2^-] < 0$ or $[\mathrm{R}_2^-] > C_2$. The proper solution in this system is

$$[\mathrm{R}_2^-] = 2(-Q)^{1/2}\cos(\theta/3 + 240°) - a/3$$

$$\text{where } \theta = \arccos(R/(-Q^3)^{1/2})$$

$[\mathrm{R}_1^-]$ may be solved for with the relation in eq 1.

Registry No. 1, 57722-05-1; **2**, 57722-08-4; **3**, 113647-97-5; **4**, 3952-42-9; TPMLi, 733-90-4.

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