is shifted off of the hemistructural position toward C, for example,[52] the C–B bond in CBA would be shorter (and stronger) than the C–B bond in CBC. This decrease in length for C–B would come at the expense of the B–A bond in CBA which would be longer (and weaker) than in ABA. The total bond length, C–B plus B–A, would be constant. The situation is somewhat analogous to Johnston's[51] proposal concerning the conservation of bond order in transition states of atom-transfer reactions, where the bond order of one bond may be greater than $^1/_2$, while the bond order of the other is less than $^1/_2$. The total bond order is always conserved at unity. The speculation that Johnston's empirical principle of bond-order conservation may have its origins in a partial breakdown of the hemistructural relationship is currently under examination.

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Proton-Transfer Reactions between 9-Alkylfluorene and (9-Alkylfluorenyl)lithium in Ether

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Abstract: The rates of proton-transfer reactions between 9-substituted fluorenes and 9-substituted fluorenyllithium have been examined in ether at 25 and 71 °C. A high primary isotope effect ($k^H/k^D = 9.5$) and substantial secondary kinetic (1.11 ± 0.04) and equilibrium (1.19 ± 0.04) isotope effects are observed for fluorene. Surprisingly, intermolecular steric effects seem to play only a minor role in spite of the fact that the alkyl groups are located directly at the carbon involved in the proton transfer. The barriers for the endergonic cross reactions (i.e., those involving different alkyl groups in the anion and hydrocarbon) are half of the sum of the barriers for the two corresponding identity reactions (i.e., those involving the same alkyl groups in the anion and hydrocarbon). This leads to Brønsted slopes which vary from 0.7 for reactions of fluorenyl anion to 1.8 for reactions of 9-(*tert*-butyl)fluorenyl anion. The rates of the identity and cross reactions give approximate linear correlations with each other and with ΔpK and are dominated by an effect which correlates with σ^*. The substituent effect correlated by σ^* is inconsistent with a classical field or repulsive steric effect and may originate from solvation effects. The thermodynamic and kinetic relationships between the identity and cross reactions show that the transition states for the cross reactions are only responding to half of the substituent effect on the identity reactions and that the substituent effect on the equilibria appears absent from the cross-reaction transition states. The results can be consistent with Marcus' theory only if the substituent effect on the equilibria appears in steps separate from proton transfer. The results suggest that changes in solvation and proton transfer occur as discrete kinetic steps.

Introduction

Interaction of Alkyl Groups with Charged Centers. The question of how alkyl groups interact with anionic and cationic centers is one which has occupied organic chemists for decades.[2-10] While many anomalous phenomena in organic chemistry can be treated in terms of two competing effects, the description of alkyl substituent effects has "required" at least half a dozen. These include polarizability, hybridization, the field effect, the inductive effect, hyperconjugation, and steric hindrance. As a further complication, the relative substituent effects of alkyl groups often show inversions in going from one solvent to another[6,7] and to the gas phase,[3-5] and reversals of kinetic and thermodynamic effects have been reported.[8] The results of the present investigation are of interest since it has proved possible to measure the alkyl substituent effect on the rates of identity reactions (where no thermodynamic contribution occurs since $\Delta pK = 0$) and to obtain a kinetic substituent effect free of any thermodynamic component due to a change in $\Delta G°$ of the reaction.

The Question of Aggregation of Fluorenyllithium Derivatives in Ether. Since the kinetic and equilibrium measurements have been carried out at relatively high concentration (0.2–0.4 M) in a relatively nonpolar solvent (ether), it is important to determine whether aggregation is exerting a significant influence on the rates and p*K*'s. Concentration effects are known to be important for

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the rates of carbanion reactions in Me_2SO[11,12] and in THF,[18] and it has been suggested that at higher concentrations (i.e., 0.3 M), the rate-limiting step is not proton transfer but dissociation of higher aggregates to kinetically active units.[13a]

However, there are several indications that aggregation is not significantly affecting the calculated rate constants and the pK's. The high primary isotope effect ($k_H/k_D = 9.5$) and secondary kinetic and equilibrium isotope effects (1.11 and 1.19) for the reaction between fluorene and fluorenyl anion show that the rate-limiting step involves proton transfer.[13] In addition, the relative pK's of the 9-alkylfluorenes in ether are comparable to those measured in cyclohexylamine[14] and in aqueous Me_2SO[15] and are also independent of temperature (25–71 °C). Furthermore, a method of calculating the rate constants is used that does not require a value of K_{eq}, and it is shown that the ratio of the forward and reverse rate constants is equal to K_{eq} within experimental error. Consequently, any deviations from a second-order reversible kinetic expression must be such that the forward and reverse rate constants are incorrect by the same common factor. This factor may be different for each reaction, but for a given pair of 9-substituents it must be independent of which substituent is in the anion. This places some strong constraints on the role of aggregation in affecting the kinetics of proton transfer.

Colligative property measurements indicate that lithium salts of delocalized anions can be monomeric in ethereal solvents. For example, Waack and West[16] have reported that benzyllithium in THF is monomeric over the concentration range 0.04–0.6 M. On the basis of isopiestic molecular weights, Kronzer and Sandel have concluded that (α-methylnaphthyl)- and (β-methylnaphthyl)-lithiums are monomeric in ether.[17a] Charge delocalization in the anion is frequently associated with increased cation–solvent interactions (compared to alkyl- or vinyllithiums),[16,25] which in turn reduces the tendency to form higher aggregates.[16] Consequently, lithium salts of delocalized anions are often monomeric, whereas alkyl-,[16c] aryl-,[16c] or vinyllithiums[17b] usually associate into higher aggregates. The extent of delocalization also appears to be important in affecting the tendency to aggregate. The degree of charge separation is considerably less for allyl anion than for benzyl or α- and β-methylnaphthyl anions, and it has been reported that allyllithium is aggregated in both THF and ether.[17bc] Since the 9-alkylfluorenyl anions are highly delocalized,[25] their isopiestic behavior should resemble that of the α- and β-methylnaphthyl anions, and it would be surprising to find a significant degree of association for (9-alkylfluorenyl)lithiums in ether.

These considerations suggest that aggregation is not significantly perturbing the calculated rate constants and that the kinetics are those of second-order reversible reactions. While the present study cannot clarify the nature of the concentration dependences in other systems[11,18] or rule out similar occurrences[18] at low anion concentrations in ether, there is little doubt that the relative rates and relative pK's reported here are valid indicators of kinetic and equilibrium acidities under the reported conditions.

Results

Equilibrium Measurements. Equilibrium concentrations of the two anions and two hydrocarbons were used to compute the equilibrium constant for the reaction

$$AR^- + AR'H \rightleftharpoons ARH + AR'^-$$

where AR^- and AR'^- are fluorenyl anion derivatives and AR'H and ARH are the substituted fluorenes (R = H, R' = alkyl or R = Me, Et, *i*-Pr, *t*-Bu, R' = alkyl). K_{eq} is given by the expression $K_{eq} = [ARH][AR'^-]/[AR^-][AR'H]$ and is not statistically corrected. The results of the equilibrium measurements are included in Table I.

Table I. Relative Equilibrium Acidities of 9-Alkylfluorenes

run	AR'H[a]	ARH[a]	temp, °C	K_{eq}[b]	ΔpK[c]
JAB-I-146	AMeH	← AHH	25	1.0 ± 0.1	
JAB-II-250	AMeH	→ AHH	25	1.0 ± 0.1	
JAB-II-265	AMeH	→ AHH	25	1.0 ± 0.1	0.00
JAB-III-180	AEtH	→ AHH	25	0.22	
JAB-III-216	AEtH	→ AHH	25	0.28	0.60
JAB-III-89	A-*i*-PrH	← AHH	25	0.061	
JAB-III-104	A-*i*-PrH	← AHH	25	0.049	
JAB-III-109	A-*i*-PrH	→ AHH	25	0.053	1.28
JAB-III-57	A-*t*-BuH	← AHH	25	0.0094	2.03
JAB-II-155	A_DMeH	→ AMeH	25	0.8	
JAB-II-148	A-*i*-PrH	→ A_DMeH	25	0.06	1.32
JAB-III-170	A_D-*t*-BuH	→ AMeH	25	0.010	1.90
JAB-III-14	A_D-*i*-PrH	→ A-i-PrH	25	0.8	
JAB-III-188	A_D-*t*-BuH	→ AEtH	25	0.041	1.89
JAB-III-85	A-*t*-BuH	← AHH	71	0.012	1.92
JAB-III-174	A_D-*t*-BuH	→ AHH	71	0.012	2.02
JAB-III-184	A_D-*t*-BuH	→ AMeH	71	0.020	1.8
JAB-III-200	A_D-*t*-BuH	→ AMeH	71	0.021	1.8
DFM-II-51	AHD	→ AHH	25	0.41 ± 0.04	
DFM-II-57	AHD	→ AHH	25	0.43 ± 0.04	
DFM-IV-20	A_DHH	→ AHH	25	0.81 ± 0.06	

[a] AR'H and ARH represent the appropriate molecules in the equilibrium, $AR^- + AR'H \rightleftharpoons ARH + AR'^-$. The arrow indicates the direction from which equilibrium was approached experimentally. [b] K_{eq} is calculated on the basis of the equilibrium in footnote *a*. [c] ΔpK is calculated to represent the pK_{eq} of the equilibrium in footnote *a* where ARH is 9-methylfluorene and AR' is another 9-alkylfluorene. On the basis of runs JAB-III-14 and JAB-II-155, it has been assumed that eight aryl deuteriums in AR'H lower K_{eq} by a factor of 0.8. ΔpK calculated as above is automatically given on a per hydrogen basis for the 9-alkylfluorenes. When K_{eq} for fluorene itself is statistically corrected, ΔpK is 0.30.

Since the reactions in Table I are not "instantaneous", it is important to be certain that equilibrium has in fact been achieved. To establish this point, we approached equilibrium from both sides of the reaction for several of the examples (AMeH/AHH; A-*i*-PrH/AHH; A-*t*-BuH/AHH (71 °C)). Furthermore, it was established for all of the runs that the anion concentration (i.e., AR^- or AR'^-) was no longer changing when the measurements were carried out.

The reproducibility of the K_{eq} values provides the best measure of the precision attainable with this technique. Several cross-checks are available, and the agreement is excellent. For example, the pK of A-*i*-PrH relative to AMeH is 1.28 or 1.32 when the isopropyl derivative is paired with either fluorene or A_DMeH. The pK of A-*t*-BuH relative to AMeH is 2.03, 1.90, or 1.99 when the *tert*-butyl derivative is paired with fluorene, AMeH, or AEtH. The excellent reproducibility and the agreement of the cross-checks suggest that differences in pK greater than about 0.1–0.2 pK unit are probably significant.

Finally, it should be noted that the effect of changing the temperature from 25 to 71 °C is relatively small (e.g., pK_{rel} for A-*t*-BuH: 25 °C, 1.90–2.03; 71 °C, 1.92–2.02). Furthermore, fluorene and 9-methylfluorene appear to have the same relative pK's at 25 °C as at 71 °C. Consequently, it would appear that factors which might be sensitive to temperature (e.g., ion pairing, aggregation) are not particularly important in contributing to differences in pK_{rel}.[25,26]

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Table II. Comparison of k_1/k_2 with K_{eq}

reaction	runs	$k_1{}^a$	$k_2{}^a$	k_1/k_2	$k_{eq}{}^b$	std dev[d]
AMe^- + AHH (25 °C)	JAB-1-146 JAB-11-265 JAB-11-250	$(7.91 \pm 0.34) \times 10^{-6}$	$(7.15 \pm 0.30) \times 10^{-6}$	1.11	1.0 ± 0.1	0.0049
AH^- + AEtH (25 °C)	JAB-111-180 JAB-111-216	$(2.70 \pm 0.36) \times 10^{-6}$	$(1.19 \pm 0.30) \times 10^{-5}$	0.23	0.25 ± 0.03	0.011
A-*i*-Pr^- + AHH (25 °C)	DFM-V-112 JAB-I11-104 JAB-111-089	$(1.94 \pm 0.06) \times 10^{-5}$	$(1.12 \pm 0.14) \times 10^{-6}$	15.9	18.2 ± 3	0.011
AH^- + A-*t*-BuH (25 °C)	DFM-V-053 JAB-1-080 JAB-11-093 JAB-111-057	$(2.59 \pm 0.68) \times 10^{-7}$	$(2.77 \pm 0.10) \times 10^{-5}$	0.0094	0.0094	0.012
AMe^- + A_D-*t*-BuH (71 °C)	JAB-111-184 JAB-111-200	$(1.36 \pm 0.28) \times 10^{-6}$	$(6.62 \pm 0.02) \times 10^{-5}$	0.021	0.021	0.0035
AH^- + ADD[c]	DFM-111-30 JAB-1-16-3	$(5.08 \pm 0.21) \times 10^{-6}$	$(1.82 \pm 0.36) \times 10^{-5}$	0.28		0.0097
AD^- + AHH[c]	DFM-49 JAB-24 JAB-23	$(4.45 \pm 0.12) \times 10^{-5}$	$(2.40 \pm 0.22) \times 10^{-5}$	1.85		0.0104

[a] $M^{-1}\ s^{-1}$: not statistically corrected. The computed standard deviations are calculated[27] by assuming normal error propagation of experimental quantities into A of eq 3 and ignoring the fact that the errors associated with A are not completely independent. Rate constants are calculated by using data from all kinetic runs for the appropriate reaction. [b] From Table I. [c] The effective primary isotope effect (k_H/k_D) is given by $(4.45 \times 10^{-5}/5.08 \times 10^{-6})/1.19 = 7.3$ when the runs are combined together. If each run is treated individually, the average value of k_H/k_D is 6.5. [d] Standard deviations for calculated concentrations.

Table III. Rate Constants for Proton Transfer from Fluorene and Substituted Fluorenes

	reaction[a]							
sample	AR'H	ARH	$10^9 k_1$,[a,b] $M^{-1}\ s^{-1}$	$10^9 k_2$,[a,b] $M^{-1}\ s^{-1}$	no. of points	temp, °C	std dev[c]	K_{eq}
JAB-1-146	AMeH	←AHH	8930 ± 400	8930 ± 500	10	25	0.0036	1.0[d]
JAB-11-250	AMeH	→AHH	4620 ± 700	4620 ± 500	13	25	0.0066	1.0[d]
JAB-11-265	AMeH	→AHH	8790 ± 700	8790 ± 500	15	25	0.0094	1.0[d]
JAB-111-180	AEtH	→AHH	1630 ± 200	6500 ± 500	14	25	0.0031	0.25
JAB-111-216	AEtH	→AHH	4670 ± 400	18500 ± 1500	12	25	0.0044	0.25
JAB-111-89	A-*i*-PrH	←AHH	856 ± 75	15800 ± 800	15	25	0.0087	1/18.5
JAB-111-104	A-*i*-PrH	←AHH	971 ± 6	18000 ± 500	16	25	0.0046	1/18.5
JAB-11-80	A-*t*-BuH	←AHH	297 ± 10	27100 ± 700	11	25	0.0087	1/91.0
JAB-11-93	A-*t*-BuH	←AHH	506 ± 14	46000 ± 1300	11	25	0.0095	1/91.0
JAB-111-57	A-*t*-BuH	←AHH	199	18100	13	25	0.0064	1/91.0
DFM-V-053	A-*t*-BuH	→AHH	299 ± 0	23000 ± 0	5	25	0.0021	0.013
JAB-11-155	A_DMeH	→AMeH	2930 ± 200	3660 ± 200	13	25	0.0033	0.8
JAB-1-218	A-*i*-PrH	←AMeH	136	2520	15	25	0.0048	1/18.5
JAB-11-148	A-*i*-PrH	→A_DMeH	359	5980	12	25	0.0051	0.060
JAB-11-205	A_Dt-BuH	←AMeH	43.9 ± 2	4000 ± 200	15	25	0.0290	1/91.0
JAB-11-221	A_Dt-BuH	←AMeH	67.7 ± 2	6160 ± 200	12	25	0.0184	1/91.0
JAB-111-170	A_Dt-BuH	→AMeH	42.6 ± 12	3870 ± 1100	10	25	0.0022	0.011
JAB-111-61	At-BuH	←AMeH	31.3 ± 4	2850 ± 300	13	25	0.0066	1/91.0
JAB-111-188	A_Dt-BuH	→AEtH	7.33 ± 3	167 ± 70	7	25	0.0013	0.044
JAB-111-14	A_Di-PrH	→A-*i*-PrH	42.7 ± 2	53.4 ± 3	24	25	0.0047	0.8
JAB-11-242	A_Dt-BuH	←A-*i*-PrH	4.48	22	10	25	0.0098	1/4.9
JAB-111-85	A*t*-BuH	←AHH	2900 ± 130	243000 ± 12000	13	71	0.0049	1/84.0
JAB-111-174	A_D-*t*-BuH	→AHH	836 ± 600	69600 ± 40000	14	71	0.0026	0.012
JAB-111-184	A_D-*t*-BuH	→AMeH	1680	84000	6	71		0.02
JAB-111-200	A_D-*t*-BuH	→AMeH	1630 ± 500	81600 ± 23000	8	71	0.0039	0.02
JAB-111-128	A_D-*t*-BuH	←A-*i*-PrH	89.6	439	10	71		1/4.9
JAB-111-76	A_D-*t*-BuH	→A-*t*-BuH	23.4 ± 2	29.2 ± 2	17	71	0.0039	0.8

[a] AR'H and ARH represent the appropriate concentrations in the equilibrium, $AR^- + AR'H\ (k_1) \rightleftharpoons ARH + AR'^-\ (k_2)$. The arrow indicates the direction from which equilibrium was approached experimentally. [b] The values for k_1 and k_2 have been calculated separately for each run by using the constraint $k_1/k_2 = K_{eq}$. See text for discussion of error limits. In Table II, k_1 and k_2 have been calculated by using data for all runs *without* the constraint. [c] Standard deviations for calculated concentrations (in M). [d] See footnote c, Table I.

fluorenes were calculated in the same manner as for the other compounds. For measurements involving (9-deuteriofluorenyl)lithium, K_{eq} was calculated from the expression $K_{eq} = [AHH][AD^-]/[AH^-][ADH]$. The fraction of deuterium in the hydrocarbon was calculated from the total amount present and the fraction in the anion. The hydrocarbon deuterium was assumed to be randomly distributed among the species AHH, AHD, and ADD, and this assumption was verified experimentally.

The calculated rate constants are presented in Tables II, III, and V. Kinetic plots for two runs are illustrated in Figures 1 and 2, and the detailed kinetic analysis for obtaining these rate constants is given in the Experimental Section.

Discussion

I. The Relative pK's of Fluorene and 9-Alkylfluorenes. The values of ΔpK from Table I are equivalent to pK's for the fluorenes relative to 9-methylfluorene and are listed in Table IV for comparison with relative equilibrium acidities measured in other solvent systems.[14,15] The observed differences are minor and can be largely rationalized in terms of variations in cation solvation and ion pairing.[25] The present results are complementary to those previously reported,[14,15] since the concentrations (of a given anion) required for this NMR technique vary from 0.4 to 5×10^{-2} M. The earlier measurements used an indicator technique and spanned

Table IV. Acidity of 9-Alkylfluorenes in Various Solvents

	ΔpK				
compd	CsCHA/ CHA[14]	LiCHA/ CHA[14]	Me_4N^+-^-OH Me_2SO/ H_2O[15]	Me_2SO (48a,c)	Li/Et_2O
H	0.41	−0.05	0.30	0.6	0.30
Me	0.00	0.00	0.00	0.00	0.00
Et	0.27	0.36	0.42	0.30	0.60
i-Pr	0.87	1.15	0.90	0.90	1.30
t-Bu	1.90	2.22	1.61	2.00	1.97
benzyl	−1.06		−0.60		

Table V. Log k_1 vs. ΔpK for Fluorenes

R^-	R'H	k_1[a]	$-\log k_1$	ΔpK	temp, °C
H	H	1.93×10^{-5}	4.714	0.00	25
	Me	7.15×10^{-6}	5.146	−0.30	
	Et	2.70×10^{-6}	5.569	0.30	
	i-Pr	1.12×10^{-6}	5.951	1.0	
	t-Bu	2.59×10^{-7}	6.587	1.67	
Me	H	3.95×10^{-6}	5.403	0.30	25
	Me	3.30×10^{-6}	5.482	0.00	
	Et		5.982[b]	0.60	
	i-Pr	3.21×10^{-7}	6.493	1.30	
	t-Bu	5.09×10^{-8}	7.293	1.97	
Et	H	5.95×10^{-6}	5.225	−0.30	25
	Me		5.387[c]	−0.60	
	Et		6.292[d]	0.00	
	i-Pr		6.869[e]	0.70	
	t-Bu	8.20×10^{-9}	8.086	1.37	
i-Pr	H	9.70×10^{-6}	5.013	−1.00	25
	Me	6.69×10^{-6}	5.175	−1.30	
	Et		6.150[f]	−0.70	
	i-Pr	4.81×10^{-8}	7.318	0.00	
	t-Bu	5.01×10^{-9}	8.300	0.67	
t-Bu	H	1.39×10^{-5}	4.859	−1.67	25
	Me	3.85×10^{-6}	5.415	−1.97	
	Et	1.49×10^{-7}	6.826	−1.37	
	i-Pr	1.97×10^{-8}	7.706	−0.67	
	t-Bu		9.00[g]	0.00	
t-Bu	H	1.22×10^{-4}	3.915	−1.67	71
	Me	5.92×10^{-5}	4.228	−1.97	
	Et		5.239[h]	−1.37	
	i-Pr	3.93×10^{-7}	6.406	−0.67	
	t-Bu	2.63×10^{-8}	7.580	0.00	

[a] k_1 statistically corrected. Values for k_1 are taken from Table 11 where available. Other values are from Table 111 and are averages. Reactions with A_DRH or A_DR^- are corrected for the secondary kinetic isotope effect. When A_DRH is a reactant, k_1 in Table 111 is multiplied by $1/(0.8)^{1/2}$, and when A_DR^- is a reactant, k_1 in Table 111 is multiplied by $(0.8)^{1/2}$. [b] Interpolation from Brønsted plot of AMe^- reactions at 25 °C. [c] Interpolation from Brønsted plot of AMeH reactions at 25 °C. [d] Interpolation from the points for A-*t*-Bu^-/AEtH and AMe^-/AEtH at 25 °C. [e] Interpolation from Brønsted plot of A-*i*-PrH reactions at 25 °C. [f] Interpolation from Brønsted plot of A-*i*-Pr^- reactions at 25 °C. [g] Interpolation from Brønsted plot of A-*t*-Bu^- reactions at 25 and 71 °C. [h] Interpolation from Brønsted plot of A-*t*-Bu^- reactions at 71 °C.

a concentration range of 10^{-2}–10^{-4} M.[14] The close agreement of the two techniques suggests that possible aggregation of the fluorenyl salts in ether is not influencing the values of ΔpK. The effect of hydrogen and 9-alkyl substituents on the acidity of fluorene[14] and the similar 9,9-dimethyl-9,10-dihydroanthracene[30] and 5*H*-dibenzo[*a*,*d*]cyclohepta-1,3-diene[30] has been discussed previously, and the relevant points will be brought up in connection with the rate measurements.

II. Rate–Equilibrium Relationship for Substituted Fluorenes. In Figure 3, log k_1 is plotted against log K_{rel} for the reactions involving proton transfer from the hydrocarbon to the bases AH^-, AMe^-, A-*i*-Pr^-, and A-*t*-Bu^- at 25 °C and to the base A-*t*-Bu^-, at 71 °C. The appropriate data are listed in Table V. While $\Delta G°_{obsd}$ for all of the reactions is within ±2.8 kcal/mol, it is found that the Brønsted plots are linear, and the slopes are considerably different from the value of 0.5 that would be anticipated[31] for nearly thermoneutral reactions. The slopes increase progressively as the 9-substituent on the fluorenyl anion becomes bulkier: 9-H, 0.71 ± 0.05; 9-Me, 0.90 ± 0.06; 9-Et, 1.31 ± 0.11; 9-*i*-Pr, 1.59 ± 0.03; 9-*t*-Bu, 1.76 ± 0.11 (25 °C); 9-*t*-Bu, 1.70 ± 0.01 (71 °C). All but two of these values are outside the "normal" range for α_{exptl} ($0 \leq \alpha_{exptl} \leq 1$).[31] Examples of this type of "deviant" behavior have been reported previously,[13,32,33] but the value of 1.7 for the reactions of A-*t*-Bu^- is one of the largest known. Since the substituents are located at the same carbon from which the proton

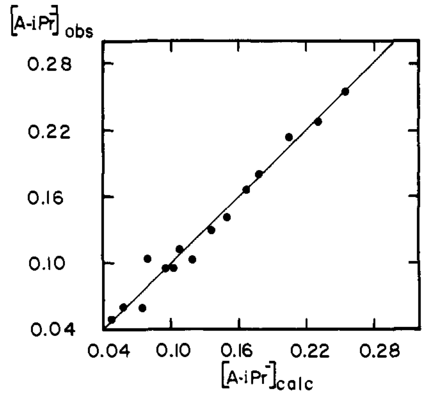

Figure 1. Plot of $[A]_{obsd}$ vs. $[A]_{calcd}$ for run JAB-I-218, A-*i*-Pr^- + AMeH ⇌ AMe^- + A-*i*-PrH. $[A]_{calcd}$ is obtained from the best least-squares fit of the data to eq 8 using the constraint K_{eq} = 1/18.5.

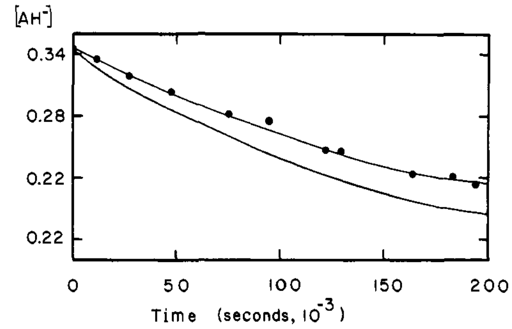

Figure 2. Concentration of fluorenyl anion vs. time in the reacting system: AH^- + ADD ⇌ AHD + AD^- and AH^- + AHD ⇌ AHH + AD^-. The observed values for $[AH^-]$ are plotted as closed circles. The upper line is the best least-squares fit to eq 9 and 10 and gives a primary isotope effect, P_H = 9.5 ± 0.3. The lower line gives $[AH^-]$ calculated for the correct kinetic expression but uses the best value for P_H (6.5) which can be obtained by ignoring the secondary reaction 9a (run DFM-III-30).

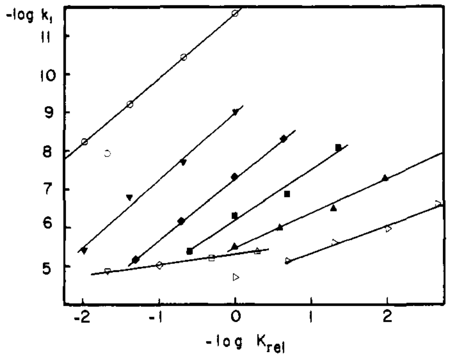

Figure 3. −log k_1 + C vs. −log K_{rel} + D for proton abstraction from fluorene and 9-alkylfluorenes by substituted fluorenyl anions (*C* and *D* = 0 for reactions at 25 °C, *C* = 4 and *D* = 0 for reactions at 71 °C, and *C* = 0 and *D* = 1 for reactions of fluorenyl anions at 25 °C): ▶, AH^- + A–R, 25 °C; ▲, AMe^- + A–R, 25 °C; ■, AEt^- + A–R, 25 °C; ◆, A-*i*-Pr^- + AR, 25°; ▼, A-*i*-Bu^- + AR, 25 °C. Open symbols refer to same reactions where AR = AH: ○, A-*t*-Bu^- + AR, 71 °C.

is transferred and the increase in α_{exptl} parallels the increase in steric bulk of the 9-substituent, it is tempting to attribute the "deviant" Brønsted behavior to a steric interaction which is present in the transition state but absent in the reactants or products.[13,32,33]

Other factors which might indicate a steric effect are the different rates of the identity reactions which progressively decrease in the order Me > Et > *i*-Pr > *t*-Bu. A simple model of a proton-transfer reaction suggests that for an identity reaction where $\Delta G° = 0$, the effect of changing a substituent in both the reactants and products would simply cancel. An additional steric effect between opposing alkyl groups, for example, might then account for the decrease in rate as progressively bulkier substituents are substituted at the 9-positions.

III. Comparison of Steric and Polar Effects. The first indication that a repulsive steric effect is not the only important factor comes in the observation from Figure 3 that the Brønsted plots for the cross reactions give linear correlations with ΔpK. This suggests that if an intermolecular repulsive steric effect were important for the transition states of the cross reactions, then a similar effect should be operating to influence the relative stabilities of the various 9-alkylfluorenyl anions. However, it has been shown that for 9-alkylfluorenes, the two most important factors affecting ΔpK are a dominant "polar" effect (as measured by σ^*)[14a] and a smaller steric effect.[14b] This was shown previously by the linear correlation (including a 9-benzyl substituent) of ΔpK (in CsCHA/CHA) with σ^*, where only the *tert*-butyl substituent gave a significant deviation, suggesting that a slight steric factor is operating to increase the pK of 9-(*tert*-butyl)fluorene relative to 9-methylfluorene.[14] Quantitatively, the steric effect can be shown to be small since the pK's in CHA fit the equation $pK_R = pK_{Me} + (P\sigma^*) + (SE_s)$, where E_s is Taft's steric parameter.[9,10,36] The least-squares values for P and S are -4.61 ± 0.24 and -0.260 ± 0.15, and the standard deviation of the fit is 0.17 pK unit. The relative importance of the "polar" and steric contributions can be seen in the ratio of P/S ($\simeq 18$); the steric effect accounts for only about one-fourth of the total pK difference between 9-methylfluorene and 9-(*tert*-butyl)fluorene. The pK's of 9-alkylfluorenes in ether also show a small steric effect: $P = -6.38 \pm 0.28$; $S = -0.037 \pm 0.057$. Thus, the substituent effects on ΔpK can be quantitatively divided into a dominant "polar" effect and a smaller steric effect.

For the identity reactions ($AR^- + ARH \rightleftharpoons ARH + AR^-$), $-\log k_1^{R,R}/k_1^{Me,Me}$ increases monotonically as R is successively replaced by bulkier alkyl groups. These differences are given in Table V, illustrated in Figure 3, and can be fit to the equation $-\log k_1^{R,R}/k_1^{Me,Me} = (P_I\sigma^*) + (S_IE_s)$. The least-squares estimates of P_I and S_I are $P_I = -7.58 \pm 0.02$ and $S_I = -0.732 \pm 0.004$. The "polar" contribution still outweighs the steric part, and the relative contributions of the "polar" effect and steric effect are comparable to those found for ΔpK. If steric hindrance between alkyl groups is the major force affecting the relative rates and ΔpK, then one would be forced to the conclusion that σ^* actually correlates repulsive steric effects. However, σ^* was originally defined to minimize or eliminate steric effects altogether, and this has been confirmed by correlations with reactions where steric effects are largely absent.[9] DeTar has also provided good evidence that E_s is a measure of alkyl steric effects.[36]

IV. Alkyl Substituent Effect. Comparison of Identity and Cross Reactions. The rate constants for the reactions of AH^- with the various alkylfluorenes (i.e., k_1^{HR}) can be fit to the equation $-\log k_1^{HR}/k_1^{HH} = (P_H\sigma^*) + (S_HE_s)$. The least-squares estimates of P_H and S_H are -3.80 ± 0.2 and -0.173 ± 0.04, respectively. It is interesting that the σ^* coefficient for the AH^- reactions is close to half of the σ^* coefficient for ΔpK of the cross reactions: the ratio P_H/P is 0.59 ± 0.06, and the "classical" interpretation suggests that the "polar" portion of the *equilibrium substituent effect* is half as developed in the transition state as in the products. It should also be noted that $P_H/P_I = 0.50 \pm 0.03$, and one could just as effectively argue that the *identity substituent effect* is half as developed as in the transition states of the cross reactions. Since the cross-reaction substituent perturbations involve changing half as many alkyl groups as in the corresponding identity reactions, this would seem equally plausible.

Table VI. Summary of Alkyl Substituent Effects on the Rates of Identity and Cross Reactions

	AMeH	AEtH	A-*i*-PrH	A-*t*-BuH
AMe^-	*0.000*[a]	*0.500* (0.405)	*1.011* (0.918)	*1.811* (1.759)
AEt^-		*0.810*[a]	*1.387* (1.323)	*2.604* (2.164)
A-*i*-Pr$^-$			*1.836*[a]	*2.818* (2.677)
A-*t*-Bu$^-$				*3.518*[a]
AH^-	*5.146*[b,c] (5.098)	*5.569*[b] (5.503)	*5.951*[b] (6.016)	*6.587*[b] (6.857)

[a] Italic figure equals $-\log k_1^{R,R'}/k_1^{Me,Me}$ from Table V. Figure in parentheses equals $^1/_2(-\log k_1^{R,R}/k_1^{Me,Me} - \log k_1^{R',R'}/k_1^{Me,Me})$. [b] Italic figure equals $-\log k_1^{HR'}$ from Table V. Figure in parentheses equals $^1/_2(-\log k_1^{HH} - \log k_1^{R'R'})$. [c] The difference in ΔpK between AMeH and AHH is essentially equal to $-\log 2$ which is the statistical factor. When the statistical factor is ignored, AHH and AMeH have identical equilibrium acidities, so that the reaction $AH^- + AMeH\ (k_1) \rightleftharpoons AHH + AMe^-\ (k_2)$ is thermoneutral. When the statistical factor for k_2 is ignored, $-\log k_2$ becomes $5.403 - 0.301 = 5.102$ which can be compared with 5.098. However, data are not sufficiently accurate to decide whether the relationship in Table VI holds better with or without the statistical factor.

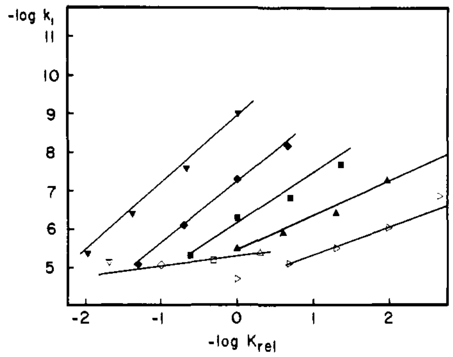

Figure 4. $-\log k_1 + C$ vs. $-\log K_{rel} + D$. $-\log k_1$ for the endergonic reactions is calculated by averaging the identity barriers (e.g., eq 4), while $-\log k_1$ for the exergonic reactions is obtained by subtracting $\delta\Delta pK$ from this average (e.g., eq 5). All other symbols are the same as in Figure 3.

V. Alkyl Substituent Effect. Identity Reactions, Cross Reactions, and Marcus' Rate Theory. It is interesting to note that $-\log k_1^{RR'}$ for the thermopositive cross reactions is very close to the arithmetic mean of $-\log k_1^{RR}$ and $-\log k_1^{R'R'}$, even when extreme differences in alkyl groups are involved (e.g., H or Me vs. *t*-Bu). The quantitative results are given in Table VI, are illustrated in Figure 4, and demonstrate that the substituent effects on the endergonic cross reactions can be accounted for by averaging the substituent effects on the identity reactions.

This behavior is theoretically puzzling since traditional models of substituent effects (Hammond's postulate,[31,34] the Bell–Evans–Polanyi principle,[34c] Marcus' rate theory[31,35]) suggest that about half of the thermodynamic substituent effect should influence both endergonic and exergonic reactions.

Averaging the identity barriers may account for the barrier of a hypothetical, thermoneutral cross reaction (i.e., the "intrinsic" barrier $\Delta G_0{}^{\ddagger}{}_{RR'}$)[31c,37]

$$\Delta G_0{}^{\ddagger}{}_{RR'} = \tfrac{1}{2}(\Delta G_0{}^{\ddagger}{}_{RR} + \Delta G_0{}^{\ddagger}{}_{R'R'}) \tag{1}$$

but one would also expect some thermodynamic contribution to the barriers for those reactions where $\Delta G°$ is different from zero. According to Marcus' theory, this contribution is given by $^1/_2\Delta G°$

so that the overall barrier for an uphill cross reaction is

$$\Delta G^{\ddagger}_{\text{for}} = \Delta G_0{}^{\ddagger}{}_{\text{RR'}} + \tfrac{1}{2}\Delta G^{\circ} \tag{2}$$

For the corresponding reverse reaction

$$\Delta G^{\ddagger}_{\text{rev}} = \Delta G_0{}^{\ddagger}{}_{\text{RR'}} - \tfrac{1}{2}\Delta G^{\circ} \tag{3}$$

The present results do not follow this pattern. The thermodynamic term, $^1/_2\Delta G^{\circ}$, is missing for the uphill direction so that

$$\Delta G^{\ddagger}_{\text{for}} = \Delta G_0{}^{\ddagger}{}_{\text{RR'}} \tag{4}$$

while microscopic reversibility requires that

$$\Delta G^{\ddagger}_{\text{rev}} = \Delta G_0{}^{\ddagger}{}_{\text{RR'}} - \Delta G^{\circ} \tag{5}$$

The points shown in Figure 4 are calculated from eq 4 (uphill reactions) or from eq 5 (downhill reactions). The Brønsted slopes and overall pattern for the points are reproduced surprisingly well. The essential point is that the thermodynamic substituent effect appears to be absent in the endergonic direction, while the exergonic reactions respond to the full thermodynamic substituent effect.

The high primary and secondary isotope effects indicate substantial C–H bond breaking (i.e., at least some "product-like" character) in the transition state. Consequently it is difficult to see why the equilibrium substituent effect is important only for the downhill direction and not for the uphill direction. A change in substituent from R to R′ raises the energy of the products (relative to reactants), but none of this equilibrium substituent effect carries over to the transition state. It is instructive to note that eq 2 is equivalent to an energy additivity relationship between the total energies of the three transition states $[\text{R–H–R}]^-$, $[\text{R–H–R'}]^-$, and $[\text{R'–H–R'}]^-$.[31c] It can be shown[31c] that the observed anomaly, in the form of eq 4 and 5, is equivalent to the energy of $[\text{R–H–R'}]^-$ deviating from the mean energies of $[\text{R–H–R}]^-$ and $[\text{R'–H–R'}]^-$ by $-^1/_2\Delta G^{\circ}$ (note that eq 4 and 5 result by subtracting $^1/_2\Delta G^{\circ}$ from eq 2 and 3). In effect, the transition states for the cross reactions are stabilized (relative to reactants) by an extra $^1/_2\Delta G^{\circ}$ which is not anticipated on the basis of Marcus' rate theory.[35,37,38]

The traditional route around this problem has been to invoke some unexpected interaction which is present in the transition state but absent in the separated reactants and products. We could try this approach by considering that the free energy of $[\text{R–H–R'}]^-$ is smaller than the average free energy of $[\text{R–H–R}]^-$ and $[\text{R'–H–R'}]^-$ by $^1/_2\Delta G^{\circ}$. If the changes in the identity barriers are due in part to differences in steric repulsions between alkyl groups, it is easy to see that the free energy of $[\text{R–H–R'}]^-$ could be less than the average free energy of $[\text{R–H–R}]^-$ and $[\text{R'–H–R'}]^-$. However, it is not so easy to see why a repulsive steric effect between opposing molecules should be related to the relative p*K*'s of the various fluorenes. There is no obvious way a repulsive steric effect could either account for the magnitude of the deviation $(=-^1/_2\Delta G^{\circ})$ or explain why this would be the first repulsive steric effect to correlate with σ^*.[39] Similar arguments apply to a repulsive steric effect which is partially or completely relieved by an increased distance between the 9- and 9′-carbons in the transition state.

Alternatively, the suggestion could be made that the extra interaction is a field or inductive effect and arises because of charge polarization to the 9-position in the transition state of the identity reaction so that the charge density is higher in the transition state than in the equilibrium anion. However, this seems unlikely since it is not clear how this could lead to a discrepancy of $-^1/_2\Delta G^{\circ}$.

The central problem that must be overcome in attributing the unusual substituent effects on the cross reactions to a nonadditive transition-state interaction between the two fluorenyl fragments is to account for how transition-state interactions between two molecules could be related to the thermodynamics of the reactions. How such an interaction could always be equal to $-^1/_2\Delta G^{\circ}$ is difficult to account for in terms of steric effects, field (inductive) effects, or resonance effects.

An alternative is to consider the possibility that the thermodynamics of the proton-transfer step may not be the same as the thermodynamics of the overall reaction. There are several possible scenarios to consider,[43] but the simplest one has a thermoneutral proton-transfer step for both identity and cross reactions. If the differences in ΔG° are developed in a step subsequent to proton transfer, then the free energy difference between the transition state and reactants will not include any thermodynamic contribution. However, changes in the "intrinsic" barrier $(\Delta G_0{}^{\ddagger}{}_{\text{RR'}})$ would still be important, and the overall barrier $(\Delta G^{\ddagger}_{\text{for}})$ would be the average of the two identity barriers (i.e., eq 4). The barrier for the reverse direction would be smaller than the barrier for the forward direction by ΔG° since the free energy of the products is higher (by ΔG°) than the free energy of the reactants. The reverse barrier would be described by eq 5. The overall result is that the thermodynamic substituent effect is absent in one direction of the reaction, while the barrier for the other direction responds to the full thermodynamic substituent effect.

It is hard to imagine how a normal inductive, field, steric, or resonance effect could be important for the equilibrium anion yet be virtually absent from the transition state. A solvent effect, however, could fit this role, since it is quite plausible that proton transfer and solvent reorientation could occur nonsynchronously in discrete steps.[39] The present results suggest that the substituent interactions responsible for the changes in Δp*K* occur in step(s) separate from proton transfer and that these interactions may be associated with solvent effects. The only remaining question is to account for how σ^* could correlate solvation changes.

VI. Alkyl Substituent Effect. What does σ^* Correlate? We can approach the problem of how σ^* could correlate solvent effects by posing the question: "what properties of alkyl groups ($-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, $-C(CH_3)_3$) bear a linear relationship to the number of methyl groups attached to a central carbon?" Two such properties immediately come to mind: molar volume and polarizability.[45] That molar volume might be an additive property is obvious, and this is borne out by the observation that the molar volume of molecules such as $X{-}CH_3$, $X{-}CH_2CH_3$, $X{-}CH(CH_3)_2$, and $X{-}C(CH_3)_3$ increase linearly along the sequence where X is a relatively large group such as phenyl or *n*-hexyl. For example, the increase in molar volume between succeeding pairs in the above sequence is 16.052 mL/mol (Me, Et), 16.178 (Et, *i*-Pr), and 16.61 (*i*-Pr, *t*-Bu) for X = *n*-Hx.[40]

Polarizability has frequently been approximated as an additive property,[41] and Brown has shown that the dispersion energy calculated from the interaction of Me, Et, *i*-Pr, or *t*-Bu groups interacting with a neighboring phenyl is essentially a linear function of the number of methyl groups present (0–3).[41] Consequently, any property of alkyl groups directly related to molar volume, polarizability, or dispersion energy might give a linear relationship with σ^*.[46]

In the gas-phase protonation of amines, Aue[3] has found that the effect of additional methyl groups at the α-carbon is approximately additive, and the increase in relative stability of the ammonium ion as more methyl groups are added is consistent with a stabilization mechanism based on polarizability.[3] A similar explanation has been previously suggested to account for the gas-phase basicity order of alkoxides.[4] Interestingly, Arnett and McIver[5] have pointed out that the deprotonation energies of about 20 alcohols in Me_2SO correlate rather well with Taft's σ^* values and that this correlation is largely determined by changes in solvation energies. Since the solution order appears to be dependent on solvational factors and the gas-phase order depends upon the polarizability of the substituent and both the solution reactions and gas-phase reactions give at least rough correlations with σ^*, it appears that both the solvent effect and the polarizability effect are approximately additive functions of the number of methyl groups.

The ability of alkyl groups to stabilize ions in the gas phase by polarizability has been compared to "internal" solvation,[4] and it may be that this is more than just simple analogy. If "external" solvation depends significantly on the polarizability of the solvent, the effect of substituting larger alkyl groups near an ionic center will be to exclude solvent from the volume occupied by the larger group, serving to reduce the dispersion interaction with the solvent and to increase the interaction with the substituent. The net effect of this competition between "internal" and "external" solvation will depend on the relative polarizabilities of the substituent and the solvent that it displaces and result in a substituent effect that is dependent on the volume of the substituent. If the solvation mechanism is primarily polarization and can be treated by a solvent continuum model, the effect of successively replacing alkyl groups along the series Me, Et, *i*-Pr, *t*-Bu would be to change the polarizability of a certain volume of space from that of the solvent to that of the added methyl group. The molar volumes of Me, Et, *i*-Pr, and *t*-Bu change by a constant increment between successive pairs, and if the volumes of space defined by the three methyls of the *tert*-butyl group are equidistant from the reaction center for Me, Et, *i*-Pr, and *t*-Bu and if the change in polarizability from one substituent to the next is also a constant increment, the net substituent effect should change by a constant increment and correlate with σ^*. Such assumptions appear to be not unreasonable in view of the gas-phase results[3-5] and the solution correlations with σ^*.[5]

A competition between "internal" solvation and "external" solvation is essentially the same as the Schubert–Sweeney hypothesis[2] and is attractive since it neatly accounts for the reversals in the substituent orders on going from the gas phase to most solutions,[4] the reversion to the gas-phase order in less nucleophilic and polarizable solvents,[6,7] and the inverse correlation[42] between the alkyl inductive parameter, σ^*, and the alkyl resonance parameter, σ_R. More importantly, it provides a reasonable explanation of how a solvent effect could correlate with σ^* and suggests that, in some cases, both the inductive (or field) effect and resonance (or hyperconjugation) effect of alkyl groups may, in large part, reflect a balance between "internal" and "external" solvation. This balance is probably not the entire picture,[46,47] and additional work will be necessary to further refine the nature of the alkyl substituent effect. In particular, the long standing assumption that σ^* correlates a single interaction mechanism (i.e., the "polar" effect) may require modification in the case of alkyl substituents. Previous work on alkyl substituent effects provides further emphasis of this point.[2-7,48]

Conclusions

The fundamental problem posed by the present data is that the barriers of the endergonic cross reactions are entirely accounted for by the mean of the barriers for the two corresponding identity reactions, and no additional contribution associated with the change in $\Delta G°$ is necessary. Since proton transfer is rate limiting and substantial primary and secondary isotope effects are observed, it is surprising that little or none of the thermodynamic substituent effect on ΔpK carries over to the cross-reaction transition state. The lack of a thermodynamic substituent effect could be accounted for if the change in $\Delta G°$ for the overall reaction is not associated with the proton-transfer step per se. This would be highly uncharacteristic of a field, inductive, resonance, or repulsive steric effect, but it could be consistent with certain kinds of solvent effects. If $\delta\Delta G°$ depends on solvational differences between the various (9-alkylfluorenyl)lithium ion pairs, it is conceivable that proton transfer could be complete before the solvational change is initiated.[49] In such a case, the factors associated with the solvent change (and $\delta\Delta G°$) need not appear at the transition state for the proton-transfer step. Additional work will be necessary to sort out the precise role of solvation and ion pairing in the proton-transfer process.

The identity barriers may be associated with solvent ion-pair interactions[43,50] and/or with the barrier to proton transfer, but the present data allow us to do little more than speculate on the possible details. Further work will be necessary to determine the applicability of Marcus' rate theory to these ion-pair proton-transfer reactions, but an important prediction of Marcus's rate theory is that the *proton-transfer step alone* for all of the reactions between substituted and unsubstituted fluorenyl anions and fluorenes must be essentially thermoneutral in spite of the fact that the *overall* ΔpK varies over a range of 4 units. Another important, but less fundamental, implication is that the alkyl "polar" effect correlated by σ^* may often represent a solvent effect.

The secondary role played by steric effects is another surprising aspect of these reactions. The fact that the barriers of the endergonic cross reactions can be related in an additive manner to the barriers of the identity reactions is totally unexpected when it is considered that the alkyl substituents are located at the same carbons involved in the proton transfer. These results provide one of the first examples of a proton-transfer reaction where changes in substituents produce changes in the intrinsic barrier.[43] In effect, every point in Figure 3 is a one point Brønsted "plot" each with its own intrinsic barrier.[31,35,37,38]

Experimental[19a,b]

Preparation of Materials. Fluorene (Matheson, Coleman & Bell) was recrystallized three times from 95% ethanol and sublimed (mp 115–116 °C (lit.[20] mp 116–117 °C).

Fluorene-*9,9-d*$_2$ was prepared by treating fluorene in ether solution with butyllithium in hexane, followed by quenching with excess D_2O, to give a mixture of dideuterated and monodeuterated fluorene in 90% yield. The process was repeated to give the dideuterated species which was shown by NMR to contain 95% deuterium at the 9-position.

Fluorene-*9-d* was prepared by delivering a solution of fluorenyllithium in THF into a rapidly stirred mixture of excess deuterioacetic acid in THF. The deuterated fluorene obtained by this technique was 98–100% monodeuterated at the 9-position as determined by NMR and mass spectrometry.

9-Methylfluorene and 9-Isopropylfluorene were prepared by the addition of either methyl iodide or isopropyl bromide to a solution of fluorenyllithium in ether. Yields of 9-methylfluorene, mp 45.5–46.5 °C (lit.[21] mp 46–47 °C), ranged from 40–60%, while isopropylfluorene, mp 54–55 °C (lit.[21] mp 55 °C), was produced in 74% yield.

9-(*tert*-Butyl)fluorene was prepared by the procedure of Anet and Bavin.[22] Fluorene-9-carboxylic acid, obtained by treating benzilic acid with aluminum chloride in benzene,[23] was esterified, and the methyl ester was alkylated at the 9-position with *tert*-butyl bromide.[22a] The 9-*tert*-butyl derivative of the methyl ester was hydrolyzed and decarboxylated to give, after recrystallization from methanol and sublimation, 9-(*tert*-butyl)fluorene, mp 99.5–101 °C (lit.[22a] mp 101.5 °C).

9-Ethylfluorene was prepared by reaction of fluorenone and ethylmagnesium bromide in ether[24] followed by catalytic hydrogenation (10% Pd on charcoal in ethanol acidified with a few drops of 70% $HClO_4$) of the resulting 9-ethylfluoren-9-ol. The product was distilled at 86–88 °C at reduced pressure, producing a clear liquid distillate, n^{22}_D 1.6224 (lit.[21] n^{20}_D 1.6120, n^{24}_D 1.6182). Microanalysis gave 92.68% C and 7.30% H (calculated for $C_{15}H_{14}$: 92.74% C, 7.26% H).

9-Alkylfluorene-*1,2,3,4,5,6,7,8-d*$_8$ was prepared from the undeuterated analogue by aluminum bromide catalyzed deuterium exchange with DCl. The appropriate compound was dissolved in CS_2, and DCl (generated from the reaction between benzoyl chloride and D_2O) was bubbled through the solution. A small amount of freshly sublimed aluminum tribromide was added to the reaction mixture, and the reaction was allowed to proceed for 2–6 h. Following workup of the crude mixture by ether/water extraction, the crude product was recrystallized from methanol. The procedure was repeated 2–3 times yielding a compound with a total aromatic deuterium content (by NMR) of 96–99%. When the procedure was applied to 9-isopropylfluorene, an impurity was produced which was difficult to remove. Consequently, 9-isopropylfluorene-d_8 was prepared by alkylation of fluorene-d_8. The melting points and aromatic deuterium content were found to be: fluorene-d_8, 114.5–115 °C, 99%; 9-methylfluorene-d_8, 46–47 °C, 95%; 9-isopropylfluorene-d_8, 54–55 °C, 99%; 9-(*tert*-butyl)fluorene-d_8, 102.5–103 °C, 95%.

Preparation of Kinetic Reaction Mixtures. Samples were prepared in a flask containing three compartments and one attached NMR tube. With this arrangement, introduction of solvent, selective mixing of components, and the sealing off of the NMR tube could be accomplished under vacuum.

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(19) (a) D. F. McMillen, Thesis, Stanford University, 1967. (b) J. A. Bryson, Thesis, Stanford University, 1971. (c) C. Capelos and B. H. J. Belski, "Kinetic Systems", Wiley-Interscience, New York, 1972.

(20) F. A. Askew, *J. Chem. Soc.*, **512** (1935).

(21) K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970).

(22) (a) F. A. L. Anet and P. M. F. Bavin, *Can. J. Chem.*, **34**, 991 (1956). (b) P. M. G. Bavin, *Anal. Chem.*, **32**, 554 (1960).

(23) H. J. Richter, *Org. Synth.*, **33**, 37.

(24) C. L. Arcus and E. A. Lucken, *J. Chem. Soc.*, 1634 (1955).

The procedure will be illustrated by description of the preparation of a sample initially containing fluorenyllithium and 9-methylfluorene. Weighed amounts of fluorene and 9-methylfluorene were each placed in separate compartments. The appropriate amount of *n*-butyllithium in hexane was injected by syringe into the third compartment. The contents of the flask were then degassed by successive cycles of freezing with liquid N_2, evacuation of the flask under vacuum ($\sim 1\ \mu$m), and thawing.

After the flask was degassed, the hexane was removed from the *n*-butyllithium (Foote Mineral Co., 1.6 M) by vacuum transfer, followed by the vacuum transfer of an appropriate quantity of ether which had been dried over lithium aluminum hydride and degassed. A slightly lower channel between the arms of the flask containing fluorene and *n*-butyllithium permitted mixing of these two components without introducing 9-methylfluorene into the solution.

After sufficient time (up to 4 h) had been allowed for the production of anion, the anion and hydrocarbon components were mixed. A portion of the sample was introduced into the NMR tube, and after the contents of *both* the tube and the flask were frozen, the apparatus was evacuated and the NMR tube was sealed off and removed. The contents of the tube were kept frozen until the first NMR measurement was made. Samples prepared in this manner showed no signs of decomposition over periods of time up to 3 years.

The samples were maintained in one of two temperature baths which were kept at either 25.0 ± 0.2 °C or 71.0 ± 0.5 °C.[44] The total volume of solution was found by measuring the volume of liquid left behind in the apparatus and by determining the volume of material in the NMR tube. Although freezing the NMR tube and the reaction flask prevents vacuum transfer of liquid between the flask and the NMR tube, solvent vapor is free to condense into both the flask and the tube. Since small quantities of vapor frequently condensed into the NMR tube during the process of freezing the sample, the volume of solution in the NMR tube was determined before and after freezing. Consequently, the concentrations of anion and hydrocarbon in the NMR tube could be determined from the initial weights of the two hydrocarbons, the volume of material remaining in the apparatus, and the volume of liquid in the NMR tube after correction for dilution during the freezing process.

Determination of Time-Dependent Concentrations. It was found that the 60-MHz NMR spectrum of a mixture of fluorenyl hydrocarbons and the lithium salts was a simple superposition of the spectra of the components. Furthermore, it was found that the resonance frequency of the 4,5 protons of fluorenyllithium or 9-(alkylfluorenyl)lithium occurred at lowest field and did not overlap with the resonance frequency of other aromatic protons in either the hydrocarbons or the lithium salts. Since the signals corresponding to the 4,5 protons of fluorenyllithium and (9-alkylfluorenyl)lithium occur at very similar frequencies, it was possible to determine the fraction of anion in a mixture of fluorene, 9-alkylfluorene, and the respective anions by comparing the integrated area for the entire aromatic region. During the course of a kinetic run, the fraction of anion is time independent. A comparison of the integrated area of the 4,5 protons in the anionic material to the integrated area of the 9 proton in fluorenyllithium gives the ratio of total anion to anion which is fluorenyllithium. This quantity is time dependent. In the case of 9-(*tert*-butylfluorenyl)lithium, the signals for the 1,8 protons overlap the signals of the 4,5 protons when observed at 60 MHz, making it necessary to correct for this overlap in all reactions with 9-(*tert*-butyl)fluorene. From the initial weights of the two hydrocarbons, the volume of solution, the fraction of material which is anionic, and the ratio of fluorenyllithium to total anion, it is possible to compute the concentration of each hydrocarbon and its corresponding anion as a function of time. This technique was also suitable for computing the time-dependent concentration of AH^- in runs which used $AH^- + ADD$ or $AD^- + AHH$ as starting materials.

Since it is impossible to distinguish different alkylfluorenyl anions by examining only the aromatic region of the 60-MHz NMR spectrum, a modified procedure had to be employed for runs involving two alkylfluorenes. The method selected was to deuterate the aryl positions of one of the alkylfluorenes. In this case, the comparison of the area of the 4,5 signals to the area of the total aromatic signal gives the ratio of anion-containing aromatic hydrogens to the sum of anion and hydrocarbon-containing aromatic hydrogens. This ratio is time dependent. Consider a mixture of 9-methylfluorene-*1,2,3,4,5,6,7,8-d*$_8$ (A_DMeH) and (9-isopropylfluorenyl)lithium (A-*i*-Pr$^-$).

$$\underset{A}{\text{A-}i\text{-Pr}^-} + \underset{B}{\text{A}_\text{D}\text{MeH}} \rightleftharpoons \underset{C}{\text{A-}i\text{-PrH}} + \underset{D}{\text{A}_\text{D}\text{Me}^-}$$

When the reaction was followed from left to right (i.e., deuterated hydrocarbon as reactant), a less than stoichiometric amount of *n*-butyllithium was used in the sample preparation, ensuring that both A and C would be present at time zero. If the sample is prepared carefully, there is no D present at time zero, and all of the anion is anion A. Integration of the 4,5-proton signal and the total aromatic signal gives the fraction of material with aryl protons which is the anion. From this fraction at time zero and at time *t* and from the initial weights of the two hydrocarbons and the volume of solution, it is possible to compute the concentration of each hydrocarbon and its corresponding anion as a function of time.

When the reaction was followed from right to left (i.e., protonated hydrocarbon as reactant), a slight excess of *n*-butyllithium was used in order to convert all of the deuterated hydrocarbon to the anion. Since the reaction of *n*-butyllithium with alkylfluorenes is appreciably faster than reaction of (alkylfluorenyl)lithium, the excess portion of *n*-butyllithium will react with some of the protonated hydrocarbon to form the corresponding anion. Integration of the aromatic region at time zero gives the ratio of anion with aryl protons to total material with aryl protons. From this ratio at time zero and time *t* and from the initial concentrations of hydrocarbon and the volume of solution, the concentration of each hydrocarbon and the corresponding anion can be calculated at time *t*.

The concentration of a given anion at the beginning of a run was generally 0.2–0.4 M, which could drop as low as 10^{-2} M at equilibrium. The major source of error is determined by the accuracy of the NMR integrations. To minimize this error, we recorded seven or more integrations each time the sample was observed, and, for equilibrium runs, each sample was observed several times after it reached equilibrium. The deviations of the observed points from the calculated lines (Figures 1 and 2) provide a reasonable estimate of the uncertainties in the time dependent concentrations. For most of the runs, the standard deviation for the concentration data is about 0.002–0.005 M.

Rate Measurements for Proton Transfer from Substituted Fluorenes. Rate constants for the reactions can be determined by fitting the concentration data to the integrated expression[19] for a second-order reversible reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D \quad k_1/k_2 = K_{eq}$$

$$F_1(A_0, B_0, C_0, D_0, K_{eq}, A) = k_1 t \tag{6}$$

$$F_2(A_0, B_0, C_0, D_0, K_{eq}, A) = k_2 t \tag{7}$$

The left-hand side of the equations for k_1 and k_2 is a linear function of time and can be computed from the initial concentrations, the time dependent [A], and K_{eq}. A simple linear least-squares analysis on eq 6 and 7 then gives the rate constants for both the forward and reverse directions.

The first problem with the above procedure is that the errors in the observed values of the left-hand side of eq 6 and 7 are correlated and *not* independent of each other as required in the usual least-squares treatment.[27] Qualitatively, this can be seen by considering that the left-hand side of eq 6 and 7 are computed in terms of K_{eq}, A_0, B_0, C_0, D_0, and A, which in turn are calculated from the initial weights of hydrocarbons, the volume of solution, and various ratios of integrated NMR peak areas at time *t*, time 0, and time ∞. Consequently, each "observed" value of the left-hand side of eq 6 or 7 computed for a different time will contain certain common observations and their associated errors so that the error associated with left-hand side value will not necessarily be independent of the error associated with some other value.

A related problem is the choice of weighting factors. In a complete least-squares treatment error correlation in the dependent variable and nonequal standard deviations of the dependent variables are handled by a proper choice of the weighting matrix.[27] However, the influence of this weighting matrix on the calculated least-squares parameters becomes less important as the fit between the data and the equation becomes closer. For a kinetic run which closely follows a second-order expression, the choice of the weighting matrix may not be particularly important. In order to decide this question for the present example, we used standard formulas[27,28] to construct a weighting matrix on the basis of the error correlation and the error propagation of all measured quantities (e.g., volume of solution, initial weight of hydrocarbons, etc.) into the "observed" values of the left-hand side of equation 6 for a hypothetical kinetic run. This example was deliberately constructed to exaggerate the

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(25) J. R. Murdoch and A. Streitwieser, Jr., *Intra-Sci. Chem. Rep.*, **7**, 45 (1973).

(26) A. Streitwieser, Jr., C. J. Chang, W. B. Hollyhead, and J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 5288 (1972).

(27) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, 1964.

(28) D. DeTar, "Computer Programs for Chemistry", W. A. Benjamin, New York, 1973, pp 1 and 71.

necessity for choosing the proper weighting matrix, and it was found that the effect of the weighting matrix on the log of the computed rate constant was negligible. Consequently, for this particular kinetic system, choice of the weighting matrix is not crucial, and no substantial systematic deviations are introduced into log k_1 because of failure to apply the correct statistical weights to the observations.

The second complicating factor is that while all of the runs yield good second-order plots, there is no guarantee that the runs are uniquely second-order. With a more complicated mechanism the experimental data might still fit a second-order expression over limited concentration ranges but yield rate constants substantially different from those corresponding to the actual proton-transfer reaction. For a true second-order reaction, the rate of the reaction near equilibrium is dependent on K_{eq}, and consequently it should be possible to fit experimental data to a second-order equation and obtain both k_1 and k_2 without knowing K_{eq} or including equilibrium concentration data in the calculation. By comparing the calculated ratio of k_1/k_2 with K_{eq} (measured independently from equilibrium concentration data, one could obtain an additional criterion of judging whether the data uniquely fit a second-order expression. When the ordinary least-squares procedure is used on eq 6 and 7, the ratio k_1/k_2 is automatically constrained to have the value K_{eq}, and consequently this second criterion of a good fit is lost. Since this constraint is unnecessary, it would be desirable to carry out the least-squares procedure without it. A detailed presentation of the treatment has been presented elsewhere,[29] but a brief outline follows.

Values of A at a particular time t can be computed[29] as a function of k_1, k_2, A_0, B_0, C_0, and D_0. Since the initial concentrations, A_0, B_0, C_0, and D_0 are generally known, the two unknowns are k_1 and k_2.

$$A = F_3(k_1, k_2, A_0, B_0, C_0, D_0, t) \qquad (8)^{29}$$

Attempts to apply a normal nonlinear least-squares approach to eq 8 in order to estimate k_1 and k_2 resulted in a total failure to achieve convergence for data obtained from a single kinetic run. For reactions which are "uphill" thermodynamically, it was only possible to follow changes in the concentration of A which amounted to as little as 6–7%. Even in the most favorable cases, the maximum accessible range was only a factor of 2–8. Consequently, it is difficult to find a unique k_1 and k_2 for reactions of this type without imposing some constraint on the system, and for single runs it is sufficient to require that $k_1/k_2 = k_{eq}$.

The problem is that relatively small systematic or random errors in the concentration measurements can exert substantial effects on the calculated rate constants. An example of this can be seen for the reactions of AH^- with AEtH in Table III where the two rate constants for different runs are $(1.63 \pm 0.2) \times 10^{-6}$ and $(4.67 \pm 0.4) \times 10^{-6}$ M^{-1} s^{-1}. In both cases, the least-squares fit to the concentration data gives standard deviations (±0.0031 M and ±0.0044 M, respectively), which are in reasonable agreement with our estimated[28] uncertainties in concentration (~0.005 M). Furthermore, the deviations in concentration for each run show no easily discernible pattern: positive and negative abberations occur throughout the course of a run. When the data for these two runs are combined into one calculation, the value of k_l is $(2.70 \pm 0.4) \times 10^{-6}$ M^{-1} s^{-1} (Table II), and the standard deviation for the calculated concentrations increases to ±0.011 M. Compared with the estimated value of ~0.005 M, this is surprisingly small when the threefold variation in rate constants for the separate runs is considered. In addition, the deviations in concentration fall into a simple pattern: the points from one run are consistently low, while the points from the other run are consistently high. These systematic deviations average out to 5–7% of the measured concentrations and are equivalent to 1–1.5 standard deviation units. That these small concentration errors can translate into substantial errors in rate constants confirms that a single kinetic run (without the equilibrium constraint) does not contain enough information to precisely define either k_1 or k_2. This can be verified by an analysis[29b] of the least-squares matrix[27] and its inverse[27] which shows an unusually high degree of correlation between k_1 and k_2 and a relatively poor definition of k_2. Adding the equilibrium constraint, $k_1/k_2 = k_{eq}$, corrects both of these deficiencies to the point that least-squares convergence on k_1 and k_2 can be obtained, but combining the data from several runs is equally effective. In the case of the reaction AH^- + AEtH, the two runs together define k_1 and k_2 without external constraints, while

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(29) (a) J. R. Murdoch, *Comput. Chem.*, *3*, 125 (1979).

$$A = F_3(k_1, k_2, A_0, B_0, C_0, D_0, t) = \frac{P_3e^{P_1t}(A_0 + P_2) - P_2(A_0 + P_3)}{(A_0 + P_3) - e^{P_1t}(A_0 + P_2)}$$

$$P_1 = k_1(b^2 - 4ac)^{1/2}$$

$$P_2 = [b - (b^2 - 4ac)^{1/2}]/2\mathrm{a}$$

$$P_3 = [b + (b^2 - 4ac)^{1/2}]/2a$$

$$a = (k_2/k_1) - 1$$

$$b = -[B_0 - A_0 + (D_0 + C_0 + 2A_0)(k_2/k_1)]$$

$$c = (k_2/k_1)(C_0 + A_0)(D_0 + A_0)$$

(b) J. R. Murdoch, unpublished work.

(30) A. Streitwieser, Jr., J. R. Murdoch, G. Haefelinger, and C. J. Chang, *J. Am. Chem. Soc.*, **95**, 4248 (1973).

(31) (a) J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 4410 (1972); (b) J. R. Murdoch, *ibid.*, **102**, 0071 (1980); (c) J. R. Murdoch and D. E. Magnoli, *ibid.*, in press. Equation 2 can be derived from this additivity relationship by recognizing that a simple thermodynamic balancing procedure allows one to relate the free energies of the transition states, $[R{-}H{-}R]^-$, $[R{-}H{-}R']^-$, and $[R'{-}H{-}R']^-$, to the two identity barriers and $\Delta G°$. This balancing operation consists of adding two molecules of R'^- to each side of the reaction $R^- + H{-}R \rightleftharpoons RH + {}^-R$, one molecule each of R'^- and R^- to each side of $R^- + H{-}R' \rightleftharpoons RH + {}^-R'$, and two molecules of R^- to each side of $R'^- + H{-}R' \rightleftharpoons R'H + {}^-R'$. When the extra balancing structures are introduced, the free energy of the reactants for one identity reaction and the cross reaction are identical, while the free energy of the reactants for the other identity reaction is higher by $\Delta G°$. If the free energy of $[R{-}H{-}R']^-$ (i.e., $G°_{RR'}$) is the mean of the free energies of $[R{-}H{-}R]^-$ and $[R'{-}H{-}R']^-$, then $G°_{RR'} = {}^1/_2(G°_{RR} + G°_{R'R'}) = {}^1/_2(\Delta G_0{}^\ddagger{}_{RR} + \Delta G_0{}^\ddagger{}_{R'R'} + \Delta G°) = {}^1/_2(\Delta G_0{}^\ddagger{}_{RR} + \Delta G_0{}^\ddagger{}_{R'R'}) + {}^1/_2\Delta G° = \Delta G^\ddagger{}_{RR'}$, which is equivalent to eq 2. (d) J. R. Murdoch, *J. Am. Chem. Soc.*, preceding paper in this issue.

(32) A. J. Kresge, *Chem. Soc. Rev.*, **2**, 475 (1973).

(33) M. H. Davies, B. H. Robinson, and J. R. Keefe, *Annu. Rep. Prog. Chem., Sect. A*, 123 (1973).

(34) (a) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); (b) J. E. Leffler, *Science (Washington, D.C.)*, **117**, 340 (1953); (c) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).

(35) R. A. Marcus, *J. Am. Chem. Soc.*, **91**, 7224 (1969).

(36) D. F. DeTar and C. J. Tenpas, *J. Am. Chem. Soc.*, **98**, 7903 (1977).

(37) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

(38) R. A. Marcus, *J. Chem. Phys.*, **42**, 679 (1965).

(39) In the language of Marcus' rate theory, one could express the present substituent effect behavior in terms of a nonadditive intrinsic barrier, where the nonadditivity is equal and opposite in sign to ${}^1/_2\Delta G°$ for each alkyl substituent. The nonadditive term from the intrinsic barrier cancels the ${}^1/_2\Delta G°$ term, resulting in an overall additivity for $\delta\Delta G^\ddagger{}_{RR'}$. The main problem with this explanation is trying to deduce a model for substituent effect behavior which produces the required cancellation. In one approach, $\delta\Delta G_0{}^\ddagger$ for the cross reactions was obtained from the equation $-\delta\Delta G_0{}^\ddagger/2.3RT = 0.262n + 0.05305n^2$ where n is the number of methyls comprising the alkyl substituent ($n = 0$ for Me, $n = 1$ for Et, $n = 2$ for i-Pr, $n = 3$ for t-Bu), and the coefficients were determined from the four identity reactions ($n = 0$ for Me/Me, $n = 2$ for Et/Et, $n = 4$ for i-Pr/i-Pr, $n = 6$ for t-Bu/t-Bu). Since the equation is quadratic, the calculated values of $-\delta\Delta G_0{}^\ddagger/2.3RT$ are somewhat lower than the mean value derived from the corresponding identity reactions, but the differences are close to negligible (0.01–0.07 log unit). The nonadditivity is insufficient to cancel $\delta\Delta pK$. Similar results were found when intrinsic barriers for the cross reactions were generated through geometric mean relationships. In spite of this analysis the present data are probably not sufficiently precise to exclude with complete confidence the possibility that ${}^1/_2\delta\Delta G°$ is cancelled by nonadditivity of the intrinsic barriers. [See D. E. Magnoli and J. R. Murdoch, *J. Am. Chem. Soc.*, **103**, 7465 (1981) for an example of a highly additive alkyl substituent effect at the reaction center of a gas-phase proton transfer between amines.]

(40) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburg, 1953.

(41) T. L. Brown, *J. Am. Chem. Soc.*, **81**, 3232 (1959).

(42) J. March, "Advanced Organic Chemistry", McGraw-Hill Book Co.: New York, 1968; p 243.

(43) The changes in intrinsic barriers measured in this work may include substituent effects on the intrinsic barrier for the proton-transfer step and/or substituent effects on the encounter or work terms[31,37,38] associated with assembling the reactants into a reactive configuration. In the present case, encounter terms would be associated with prior equilibria since proton transfer is rate limiting. The quantities in eq 4 and 5 refer to experimental quantities measured for the overall reaction rather than to quantities appropriate for a single elementary step as in eq 1, 2, and 3. The reader who is interested in pursuing this matter is referred to ref 31.

(44) The critical temperature of ether is 194 °C (467 K). H. E. Stanley, "Introduction to Phase Transitions and Critical Phenomena", Oxford University Press, Oxford, 1971.

(45) σ^* values for alkyl groups form a linear progression: 0.00, −0.100, −0.196, and −0.300 for Me, Et, i-Pr, and t-Bu. Taft's steric parameters for the same substituents are markedly nonlinear: 0.00, −0.075, −0.475, −1.7.

(46) For sufficiently large interactions, the linearity of dispersion energy with σ^* is expected to break down. This point has been discussed previously.[3,4]

this is not possible for the individual runs. That these values for k_1 and k_2 are chemically meaningful is suggested by the fact that k_1/k_2 (=0.23) agrees with K_{eq} (=0.25 ± 0.03) measured independently.

The difficulties with the AH⁻ + AEtH reactions were also encountered to a comparable degree for the reactions A-*i*-Pr⁻ + AHH and AH⁻ + A-*t*-BuH. In both cases, small systematic deviations appeared in the calculated concentrations from one kinetic run to another. However, the remaining runs AMe⁻ + AHH and AMe⁻ + A_D-*t*-BuH (Table II) were much "cleaner". Although the individual runs show substantial variations in rate constants (e.g., a factor of 2 for AMe⁻ + AHH, Table II), there are no substantial *systematic* deviations in calculated concentrations from run to run in the combined least-squares calculation. The standard deviations for the calculated concentrations (0.0049 and 0.0035 M, respectively) compare favorably with the estimated standard deviation (i.e., 0.005 M), and the calculated ratios of k_1/k_2 are in good agreement with K_{eq}.

The variations in rate constants seen in Table III are not due to "poor" kinetic data but from the fact that well-defined rate constants cannot be obtained from *single* kinetic runs over the limited concentration ranges which are experimentally accessible. The problem is not with the data per se but with the traditional least-squares approach for obtaining the rate constants. The results in Table II, and the runs AMe⁻ + AHH and AMe⁻ + A_D-*t*-BuH in particular, show that the data from two or more runs contain the information necessary to define k_1 and k_2 but that a fairly sophisticated treatment[29] is necessary to extract it. The entire matter can be put into proper perspective when we realize that the variations in k_1 seen in Table III produce deviations in log k_1 which are limited to 0.1 − 0.3 log unit. None of the general conclusions of this paper will be substantially affected by this uncertainty. A typical plot of A_{obsd} vs. A_{calcd} for one of the runs is shown in Figure 1. Incidentally, the fact that k_1/k_2 equals K_{eq} may be regarded as an experimental demonstration of microscopic reversibility for an organic reaction in solution.

Primary Deuterium Isotope Effect for Fluorene. The measurement of the primary isotope effect for proton transfer from fluorene to fluorenyllithium is complicated by the presence of two exchangeable positions and the secondary isotope effects which influence subsequent exchange reactions.

When the starting materials consist of AH⁻ and ADD, their rate of disappearance is determined by the rate of reactions 9 and 9a. In the case of a mixture initially containing AD⁻ and AHH, the pertinent reactions are eq 10 and 10a.

$$\mathrm{AH^- + ADD} \underset{k_{\mathrm{D-DH}}}{\overset{2k_{\mathrm{H-DD}}}{\rightleftharpoons}} \mathrm{AHD + AD^-} \tag{9}$$

$$\mathrm{AH^- + AHD} \underset{2k_{\mathrm{D-HH}}}{\overset{k_{\mathrm{H-HD}}}{\rightleftharpoons}} \mathrm{AHH + AD^-} \tag{9a}$$

$$\mathrm{AD^- + AHH} \underset{k_{\mathrm{H-HD}}}{\overset{2k_{\mathrm{D-HH}}}{\rightleftharpoons}} \mathrm{ADH + AH^-} \tag{10}$$

$$\mathrm{AD^- + ADH} \underset{2k_{\mathrm{H-DD}}}{\overset{k_{\mathrm{D-DH}}}{\rightleftharpoons}} \mathrm{ADD + AH^-} \tag{10a}$$

The optimization problem can be described in terms of the two possible secondary isotope effects, the two possible primary isotope effects, and the rate constant $k_{\mathrm{H-HH}}$.

$$\begin{aligned} S_{\mathrm{H}} &= k_{\mathrm{H-HH}}/k_{\mathrm{H-HD}} & S_{\mathrm{D}} &= k_{\mathrm{D-HH}}/k_{\mathrm{H-HH}} \\ P_{\mathrm{H}} &= k_{\mathrm{H-HD}}/k_{\mathrm{H-DD}} & P_{\mathrm{D}} &= k_{\mathrm{D-HH}}/k_{\mathrm{D-DH}} \end{aligned} \tag{11}$$

These four equations may be combined into two additional equations as

$$S_{\mathrm{H}}S_{\mathrm{D}} = k_{\mathrm{D-HH}}/k_{\mathrm{H-HD}} \tag{12}$$

$$\frac{P_{\mathrm{D}}}{P_{\mathrm{H}}} = \frac{k_{\mathrm{D-HH}}}{k_{\mathrm{D-DH}}}\frac{k_{\mathrm{H-DD}}}{k_{\mathrm{H-HD}}} = \frac{1}{2}\frac{[\mathrm{ADH}]_e[\mathrm{AH^-}]_e}{[\mathrm{AD^-}]_e[\mathrm{AHH}]_e}\,\frac{1}{2}\frac{[\mathrm{AD^-}]_e[\mathrm{ADH}]_e}{[\mathrm{ADD}]_e[\mathrm{AH^-}]_e} = \frac{1}{4}\frac{[\mathrm{ADH}]_e^2}{[\mathrm{AHH}]_e[\mathrm{ADD}]_e} \tag{13}$$

The quantity on the right-hand side of eq 13 is equal to unity if H and D are randomly distributed among the various protonated and deuterated fluorenes at equilibrium. Since this assumption has been verified experimentally, eq 13 becomes

$$P_{\mathrm{D}}/P_{\mathrm{H}} = 1$$

and eq 12 can be evaluated from the secondary equilibrium isotope effect reported in Table I.

$$S_{\mathrm{H}}S_{\mathrm{D}} = \frac{k_{\mathrm{D-HH}}}{k_{\mathrm{H-HD}}} = \frac{1}{2}\frac{[\mathrm{AH^-}]_e[\mathrm{ADH}]_e}{[\mathrm{AD^-}]_e[\mathrm{AHH}]_e} = \frac{1}{2K_{eq}} = 1.19$$

The optimization problem can now be reformulated in terms of fitting the variables $k_{\mathrm{H-HH}}$, S_{H}, S_{D}, P_{H}, and P_{D} to values of [AH⁻] vs. time and imposing the two constraints represented by eq 12 and 13. An additional constraint, $S_{\mathrm{H}} = S_{\mathrm{D}}$, was also added for the initial optimization. Details are presented elsewhere.[29]

The complete least-squares analysis was carried out by using data from five kinetic runs and the three constraints mentioned above. Three kinetic runs pertained to reactions 10 and 10a and the remainder were

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(47) The previous treatment of alkyl substituent effects centers on the polarizability of a certain volume of space. A simple interpretation of polarizability is that it measures the capacity of a molecule to distort its electron density distribution in response to the perturbation of an external electric field. In molecular orbital language, the polarizability of a molecule can be described in terms of mixing between vacant and filled orbitals. When two molecules interact, the electric field of each may polarize the other (i.e., vacant and occupied orbitals on the same molecule may mix). In addition, vacant orbitals on one molecule may mix with occupied orbitals on the other (often referred to as charge transfer), and interactions between occupied orbitals (electrostatic or dipole interactions) may also be significant. This description could also be applied to changes in the interactions between two fragments of a single molecule when one of the fragments is structurally altered. An example would be the change in interaction between an alkyl substituent and the fluorenyl moiety when the latter is deprotonated.

A general treatment of substituent effects might be developed by considering the effect of both occupied and vacant orbitals in a specific spatial region and by recognizing that both solvent and substituent may make significant contributions. Such an approach should be capable of treating polarization of the substituent region (e.g., an alkyl group, including any solvent present) and charge transfer between the substituent region and the reaction zone[9] (e.g., fluorenyl group), as well as electrostatic or dipolar interactions between the two regions. A theoretical base on which such a treatment might be organized has been presented.[31d]

(48) Other authors have dealt with electronic effects of alkyl groups or have presented evidence that σ^* may not represent an inductive effect: (a) F. G. Bordwell, G. E. Drucker, and Gregory J. McCollum, *J. Org. Chem.*, **41**, 2786 (1976); (b) F. G. Bordwell and J. E. Bartmess, *ibid.*, **43**, 3101 (1978); (c) F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *ibid.*, **43**, 3095 (1978); (d) F. G. Bordwell and H. E. Fried, *Tetrahedron Lett.*, 1121 (1977); (e) A. J. Mcphee and J. E. Dubois, *ibid.*, 2471 (1976); (f) M. Charton, *J. Am. Chem. Soc.*, **99**, 5687 (1977). (g) M. Charton, *J. Org. Chem.*, **44**, 903 (1979); (h) M. Charton and B. I. Charton, *ibid.*, **44**, 2284 (1979); (i) W. Adcock and T. C. Khor, *ibid.*, **43**, 1272 (1978); (j) A. Pross and L. Radom, *J. Am. Chem. Soc.*, **100**, 6572 (1978); (k) R. W. Taft, M. Taagepera, J. L. M. Abboud, J. F. Wolf, D. J. Defress, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *ibid.*, **100**, 7765 (1978); (l) Delos F. DeTar, *ibid.*, **102**, 7988 (1980).

(49) Similar ideas have been used previously in somewhat different contexts: (a) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 3415 (1968); (b) M. M. Kreevoy and D. Konasewich, *Adv. Chem. Phys.*, **21**, 241 (1971); (c) J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 4410 (1972); (d) W. J. Albery, A. N. Campbell-Crawford, and J. S. Curran, *J. Chem. Soc., Perkin Trans. 2*, 2206 (1973); (e) J. L. Kurz and L. C. Kurz, *J. Am. Chem. Soc.*, **94**, 4451 (1972); (f) M. M. Kreevoy and Sea-Wha Oh, *ibid.*, **95**, 4805 (1973); (g) A. I. Hassid, M. M. Kreevoy, and T. M. Laing, *Symp. Faraday Soc.*, **10**, 69 (1975); (h) A. J. Kresge, *Acc. Chem. Res.*, **8**, 354 (1975). (i) A. J. Kresge and W. K. Chwang, *J. Am. Chem. Soc.*, **100**, 1249 (1978).

(50) It is well known that the rates of ion pair proton-transfer reactions can be significantly affected by concentration. For example, the rate constant[11] for the reaction between fluorenyl lithium and fluorene in Me_2SO at 0.3 M (38 °C) is over 10^3 smaller than the rate constant[12] between (4,5-methylenephenonthryl)potassium and 9-methylfluorene in Me_2SO at 5×10^{-4} M in anion (25 °C). Similar concentration effects have been noted by Hogen-Esch and Smid[18] for reactions of fluorenyllithium with 3,4-benzofluorene in THF. An important aspect of their data is that the observed rate "constant" is affected *more* at the *lower* concentrations rather than the higher ones and that addition of a common ion does *not* slow the rate. For example, k_{obsd} is 158 M^{-1} s^{-1} at 1.36×10^{-5} M and steadily decreases as the concentration of anion is raised: k_{obsd} = 29 M^{-1} s^{-1}, 5 M^{-1} s^{-1}, and 2.86 M^{-1} s^{-1} at 10.8×10^{-5}, 61×10^{-5}, and 370×10^{-5} M, respectively. The results suggest that at high anion concentrations (>10^{-2} M) the rate constant may have leveled off.

At the relatively high anion concentrations (10^{-2} to 0.4 M) used in the present study, these concentration effects may not be significant. In any event, the kinetic analysis did not pick up any gross abberations, and the excellent agreement between k_1/k_2 and K_{eq} is reassuring. The large isotope effects, the lack of any substantial temperature effect on the relative rates and p*K*'s, and the isopiestic data reported for similar systems do not support the view that aggregation is perturbing the results.

It may be that the number of solvent molecules coordinated to the cation in these carbanion ion pairs is concentration dependent. Such an effect could conceivably affect the reactivity of the ion pair in the observed direction, but further studies will be necessary to clarify the concentration dependences observed at low concentration in THF.

for reactions 9 and 9a. Since S_H is fixed by this particular set of constraints, only $k_{H\text{-}HH}$ and P_H can vary. The optimized values of $k_{H\text{-}HH}$ and P_H converged to within 0.1%: $k_{H\text{-}HH} = (1.966 \pm 0.7) \times 10^{-5}$ M^{-1} s^{-1} and $P_H = 9.47 \pm 0.3$. The constraint that $S_H = S_D$ was then removed, and the optimization process was continued. The best values for the parameters were $k_{H\text{-}HH} = (1.93 \pm 0.7) \times 10^{-5}$ M^{-1} s^{-1}; $P_H = 9.50 \pm 0.3$; $S_H = 1.07 \pm 0.04$; $S_D = 1.11 \pm 0.04$. The two values for S_H and S_D are nearly equal as anticipated. The next step was to examine the effect of the constraint $S_HS_D = 1.19$ on the computed values of S_H and S_D. The value 1.19 was replaced successively by 1.10 and 1.30, yielding values for S_D of 1.10 and 1.11. Since the constraint on S_HS_D forces S_H to be 0.99 and 1.17, it would appear that S_D is determined by the kinetic data while S_H is sensitive only to the constraint. This is not surprising since S_D contains the term $k_{D\text{-}HH}$ which is determined by the main reaction of (10), while S_H contains the term $k_{H\text{-}HD}$ which is obscured by the strong contribution of reactions 9 and 9a. A careful analysis of this problem suggests that both S_H and S_D might be obtained if additional runs employing AH$^-$ and AHD as starting materials had been employed.

Since data for reactions 9 and 10 should *not* fit a single second-order reversible kinetic expression, these data afford a good opportunity to test whether deviations from a second-order reversible mechanism can be revealed by discrepancies between k_1/k_2 and K_{eq}. The data for reactions 9 and 10 were fitted to eq 8 with no constraint on k_1/k_2 (see Table II). For the reaction AD$^-$ + AHH, the ratio of k_1/k_2 is algebraically identical with $2k_{D\text{-}HH}/k_{H\text{-}HD}$. The value of the latter is $2S_HS_D$ or 2.38, while the computed ratio of k_1/k_2 is only 1.85. The deviation is nearly 25% and is about 2–4 times larger than the estimated standard deviation of $2S_HS_D$ (±0.12–0.24). By contrast, the deviation between k_1/k_2 and K_{eq} for the other examples in Table II range from 0% to 13% and all are within the experimental error of K_{eq}. For the reaction between AH$^-$ + ADD, the secondary reaction is more important, and this is reflected in the high value for $k_{D\text{-}DH}/2k_{H\text{-}DD}$ of 3.57 (Table II) compared with the experimental value of 0.59 (i.e., $S_HS_D/2$).

The rate constants from Table II show that neglecting the secondary reaction results in a substantial error of about 30–45% for the primary isotope effect. If this low value of k_H/k_D (i.e., 6.5–7.3) is substituted for $P_H = 9.50$, the computed concentrations of [AH$^-$] at various times deviate significantly from those calculated by using the correct rate expression and the optimized values of P_H, S_H, and $k_{H\text{-}HH}$. This is shown in Figure 2 for run DFM-III-30.

These examples provide an excellent argument for the earlier suggestion that the agreement between k_1/k_2 and K_{eq} is one necessary criterion for a unique relationship between a set of data and a second-order reversible rate expression. While such agreement cannot prove a second-order mechanism, the present examples are especially satisfying since the same data give an excellent fit to different rate expressions, but the parameters calculated for one of them do not give consistent agreement between k_1/k_2 and K_{eq}.

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Communications to the Editor

Molecular Structure of Dichloro(*endo*-dicyclopentadiene)palladium(II). Unsymmetrically Bound Olefins and the Preferred Site of Nucleophilic Attack

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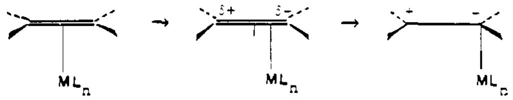
The activation of coordinated olefins toward nucleophilic attack has been a topic of interest for a number of years.[1] While nucleophiles react readily with coordinated olefins, this is not the case for unactivated olefins. The source of activation by the metal center has recently been discussed by Eisenstein and Hoffmann in this journal.[2] They have suggested that the activation results from an unsymmetrically oriented olefin, i.e., one that has laterally "slipped" the metal away from the symmetric η^2–π complex:



In order to test this hypothesis it is necessary to examine a conformationally constrained complex which shows selectivity toward nucleophilic attack to see if this slipping or an analogous distortion is observed and whether the activation of the olefin occurs in the direction predicted. We report here the molecular structure of such a system.

Dichloro(*endo*-dicyclopentadiene)palladium(II) was prepared following the procedure of Chatt.[1b] Recyrstallization by slow evaporation of a CH_2Cl_2 solution of the diene complex yielded golden-yellow platelets suitable for single-crystal X-ray diffraction. Cone axis and zero-layer precession photographs clearly gave the monoclinic space group $P2_1/c$ and least-squares refinement of 12 carefully centered reflections with $2\theta > 35°$ [$\lambda_{\text{Mo}K\alpha} = 0.70926$ Å] resulted in cell dimensions of $a_0 = 11.346$ (7) Å, $b_0 = 7.687$ (4) Å, $c_0 = 17.429$ (6) Å, and $\beta = 138.50$ (2)°. Using the θ–2θ scan method (scan = 1.5 + 0.692tan θ) for the range $3 \leq 2\theta \leq 45°$, 1185 unique reflections with $I > 2\sigma(I)$ were collected on an automated Picker FACS I diffractometer. The dimensions of the crystal used during data collection were ca. 0.3- × 0.4- × 0.1 mm. No correction for absorption was made; μ(Mo Kα) = 23 cm^{-1}.

The structure was solved by the heavy-atom method.[3] From a three-dimensional Patterson map, the position of the palladium was determined, and subsequent electron density maps yielded the positions of all the chlorine, carbon, and hydrogen atoms. The palladium and chlorine atoms were refined with anisotropic temperature factors, and the real and imaginary parts of their anomalous dispersion were considered.[4] Full-matrix least-squares

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(1) (a) Chatt, J.; Valerino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496–2507. (b) *Ibid.* **1957**, 3413–3416. (c) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135–5141. (d) Hines, L. F.; Stille, J. K. *Ibid.* **1972**, *94*, 485–490. (e) Wipke, W. T.; Goeke, G. L. *Ibid.* **1974**, *96*, 4244–4249. (f) Goeke, G. L. Ph.D. Thesis, Princeton University, 1973. (g) De Renzi, A.; Palumbo, R.; Paiaro, G. *J. Am. Chem. Soc.* **1971**, *93*, 880–883. (h) Betts, S. J.; Harris, A.; Haszeldine, R. N.; Parish, R. V. *J. Chem. Soc. Sec. A* **1971**, 3699–3705.

(2) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148–6149. (b) Eisenstein, O.; Hoffmann, R. *Ibid.* **1981**, *103*, 4308–4320.

(3) The crystal structure of the platinum analogue has been published twice. In the first publication the residual was only down to 13% and only three carbon–platinum bond lengths were reported. Baenziger, N. C.; Doyle, J. R.; Richards, G. F.; Carpenter, C. L. "Advances in the Chemistry of Coordination Compounds"; Kirshner, S., Ed.; The MacMillan Co.: New York, 1961; pp 136–137. In the second structure no geometrical parameters were reported due to high standard deviations in bond lengths (±0.15 Å) and angles (±5–6°). Avitabile, G.; Ganis, P.; Lepore, U.; Panunzi, A. *Inorg. Chim. Acta* **1973**, *7*, 329–330.

(4) (a) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w_i(|F_{o_i}| - |F_{c_i}|)^2/\sum w|F_{o_i}|^2]^{1/2}$; $w_i = 1/\sigma^2$, with σ given as per Corfield et al. (Corfield, P.; Doedens, R.; Ibers, J. *Inorg. Chem.* **1967**, *6*, 197–210) using a value of 0.045 as the fudge factor p.

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