the entropy due to reaction path multiplicity equals $R \ln 6$ or 3.6 eu.[7] If two paths predominate, this contribution to the entropy equals $R \ln 4$ or 2.8 eu. If one path is of an appreciably lower energy than the other two, $\Delta S^{\ddagger} \simeq R \ln 2 \simeq$ 1.4 eu. Since the experimentally determined entropy, 0.45 ± 0.35 eu, is believed to be reliable, the results suggest that one pathway predominates. This derivation is valid only if the principal factor contributing to $\Delta S^{\ddagger}$ is the reaction degeneracy.

Experimental Section

A Varian 100 MHz NMR spectrometer equipped with a specially constructed low-temperature NMR probe was used for all spectra.[5] This probe allowed determination of the temperature to ±0.1°.

Computer program DNMR3 was obtained from Quantum Chemistry Program Exchange[8] and adapted[9] to the CDC 6400 computer at the University of California, Berkeley. Computed spectra were visually compared with experimental spectra to obtain the best fit.[3c] Each experimental spectrum was also compared with computed spectra with rates higher and lower than the "best fit" calculated rate spectrum. Those that could be visually distinguished from the match with the "best fit" spectrum were assumed to represent the limit of error for each rate. These error limits are likely overestimations of the actual error in comparing computed and experimental spectra.

Preparation of NMR Sample. The sample was prepared on a vacuum line using dried degassed vinyl chloride, TMS, and 1,4-oxathiane which were transferred from the drying agents into the NMR tube. Drying agents were as follows: vinyl chloride, phosphorous pentoxide; TMS and 1,4-oxathiane, calcium hydride. The quantities of each solvent and the compound being transferred into the NMR tube were measured by a prior condensation into a calibrated tube (accuracy ±5%) on one arm of a T-tube followed by condensation into the NMR tube which was attached to the other arm of the T-tube. After transferring both solvents and the oxathiane, the NMR tube was degassed again and sealed with a torch. In all measurements, the amounts of the components were as follows: 60 μl of 1,4-oxathiane, 55 μl of TMS, and 350 μl of vinyl chloride.

1,4-Oxathiane was obtained from Aldrich Chemical Company and revealed only one peak by gas chromatography on a 10 ft × 0.25 in. FFAP on Chromsorb W column at 60°.

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(6) We thank Professor L. E. Friedrich of the University of Rochester for this weighted least-squares program.

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(9) We would like to thank Mr. John Vinson for his help in adapting the program to the CDC 6400 computer at the University of California, Berkeley.

Solvent Effects on Reactions of Sodium Naphthalene with Hexyl Fluoride

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Abstract: Among the ethers 1,2-dimethoxyethane, tetrahydrofuran, and 2-methyltetrahydrofuran, solvent effects on the rates of reactions of sodium naphthalene with hexyl fluoride are very small. Addition of tetraglyme, dicyclohexyl-18-crown-6, or 18-crown-6 gives a somewhat larger effect so that the total spread in second-order rate constants through these media is about 10. Increased cation solvating capacity of the medium slows the reactions. No curvature was detected in Arrhenius plots. These solvent effects trend in the opposite direction from those reported for similar reactions of alkyl chlorides, bromides, and iodides. The data suggest that negative charge delocalization characterizes the transition states for alkyl chlorides, bromides, and iodides, but that the negative charge in the transition state for a reaction of an alkyl fluoride is slightly localized relative to that of the naphthalene radical anion.

Alkyl fluorides, chlorides, bromides, and iodides react with alkali naphthalenes through initial, rate-determining dissociative electron transfer steps (eq 1).[1] Unlike the others, the alkyl fluoride reactions are slow enough to monitor with conventional "slow reaction" techniques. Garst and Barton found a substantial metal ion effect on the rates of reactions of 5-hexenyl fluoride with alkali naphthalenes in DME. The second-order rate constant for the reaction of lithium naphthalene is 10^4 times that for potassium naphthalene, with sodium naphthalene intermediate. As a working hypothesis, it was proposed that negative charge is more concentrated or localized in the activated complexes than in naphthalene radical anion. This hypothesis was the basis of the prediction that solvents of better cation solvating ability would slow the reaction.[1]

$$RX + MC_{10}H_8 \rightarrow R\cdot + MF + C_{10}H_8 \qquad (1)$$

Table I. Second-Order Rate Constants for Reactions of Sodium Naphthalene with Hexyl Fluoride at 25.0°

Expt	$[\mathrm{RF}]_0$,[a] M	$[\mathrm{NaC_{10}H_8}]_0$,[b] M	k, M^{-1} sec^{-1}
	In MeTHF		
8	0.156	0.019	3.7×10^{-4}
12	0.176	0.016	3.4×10^{-4}
13	0.177	0.024	3.0×10^{-4}
			Av: 3.4×10^{-4}
	In DME		
4	0.0428	0.015	2.3×10^{-4}
6	0.172	0.016	2.4×10^{-4}
11	0.158	0.018	2.7×10^{-4}
14	0.193	0.034	2.1×10^{-4}
57 (25.2°)	0.0424	0.00071	2.5×10^{-4}
59 (25.2°)	0.0417	0.00083	2.9×10^{-4}
98 (7650 Å)[c]	0.131	0.024	2.4×10^{-4}
			Av: 2.5×10^{-4}
	In THF		
5	0.086	0.037	2.0×10^{-4}
7	0.165	0.026	2.2×10^{-4}
10	0.213	0.032	2.0×10^{-4}
15	0.173	0.024	1.8×10^{-4}
63 (25.2°)	0.0436	0.00076	1.9×10^{-4}
66 (25.2°)	0.0374	0.0010	1.8×10^{-4}
69 (25.2°)	0.0419	0.00043	2.2×10^{-4}
70 (25.2°)	0.0445	0.00074	1.7×10^{-4}
72 (25.2°)	0.0483	0.00017	1.9×10^{-4}
79 (25.2°)	0.144	0.018 (0.087)[d]	1.7×10^{-4}
80 (25.2°)	0.132	0.018 (1.1)[d]	1.6×10^{-4}
96 (25.8°, 7650 Å)[c]	0.0872	0.00061	1.7×10^{-4}
97 (25.8°, 7650 Å)[c]	0.0578	0.000085	1.5×10^{-4}
			Av: 1.9×10^{-4}
	In THF–Tetraglyme		
77 (25.2°)	0.148 (0.040)[e]	0.028	1.4×10^{-4}
78 (25.2°)	0.133 (0.040)[e]	0.022	1.0×10^{-4}
99 (7650 Å)[c]	0.115 (0.112)[e]	0.024	1.2×10^{-4}
			Av: 1.2×10^{-4}
	In THF–Dicyclohexyl-18-crown-6		
73 (25.2°)	0.053 (0.0040)[f]	0.00063	3.9×10^{-5}
74 (25.2°)	0.071 (0.0350)[f]	0.00067	3.5×10^{-5}
75 (25.2°)	0.209 (0.0470)[f]	0.025	3.0×10^{-5}
76 (25.2°)	0.201 (0.0440)[f]	0.028	3.2×10^{-5}
			Av: 3.4×10^{-5}
	In DME–Dicyclohexyl-18-crown-6		
25 (26.0°)	0.074 (0.0376)[f]	0.020	6.6×10^{-5}
27 (26.0°)	0.130 (0.0380)[f]	0.018	4.7×10^{-5}
28 (26.0°)	0.134 (0.0404)[f]	0.034	3.9×10^{-5}
94 (25.8°, 7650 Å)[c]	0.202 (0.0410)[f]	0.018	3.8×10^{-5}
			Av: 4.7×10^{-5}
	In DME–18-Crown-6		
88 (25.8°)	0.088 (0.0538)[g]	0.027	4.8×10^{-5}
89 (25.8°)	0.086 (0.0580)[g]	0.015	4.9×10^{-5}
90 (25.8°, 7650 Å)[c]	0.103 (0.0625)[g]	0.016	4.5×10^{-5}
91 (25.8°, 7650 Å)[c]	0.098 (0.0521)[g]	0.025	4.0×10^{-5}
			Av: 4.5×10^{-5}

[a] Initial concentration of hexyl fluoride. [b] Initial concentration of sodium naphthalene. [c] Sodium naphthalene monitored at 7650 Å instead of 8200 Å. [d] Molar concentration of naphthalene (excess over that converted to sodium naphthalene). [e] Molar concentration of tetraglyme. [f] Molar concentration of dicyclohexyl-18-crown-6. [g] Molar concentration of 18-crown-6.

We report the results of our study of the solvent effect, among ethers, on the rates of reactions of sodium naphthalene with hexyl fluoride.[2]

Experimental Section

The general procedures were identical with those of Garst and Barton.[1] Only an outline of these procedures and descriptions of significant modifications will be given here.

Hexyl fluoride (Eastman Organic Chemicals) was distilled on a Nester-Faust annular Teflon still. The material used (bp 91°) was >99% pure by chromatographic assay on a $\frac{1}{8}$ in. × 20 ft 35% polyphenyl ether on Chromosorb W column. Tetraglyme (Eastman Organic Chemicals) was distilled from sodium and then from sodium benzophenone ketyl just prior to use [bp 130° (6 Torr)]. Dicyclohexyl-18-crown-6 was obtained commercially and 18-crown-6 was a gift from R. Hautala and T. Mayer. The latter was distilled [bp 133° (0.3 Torr)] from sodium benzophenone ketyl just before use. Crown ethers and tetraglyme were added to sodium naphthalene solutions through a breakseal.

Kinetic runs employed a large excess of hexyl fluoride in most cases, and the data were computed as pseudo-first-order. First-order plots were linear for at least 1 half-life and usually for several. In view of the formation of an insoluble salt, deviations at long reaction times were to be anticipated. Variations in initial concentrations of reactants did not affect the second-order rate constants. For most experiments, sodium naphthalene was monitored by its absorption at 8200 Å. Toward the end of the work, the Cary Model 14 used in this work became excessively noisy at 8200 Å so, for some experiments, sodium naphthalene was monitored at 7650 Å. The same rate constants were obtained by each method. Since the reactions are first order in sodium naphthalene and pseudo-first-order overall, the extinction coefficient of sodium naphthalene does not enter the calculation of rate constants. Estimates of the initial concentrations of sodium naphthalene used 2500 as the extinction coefficient at 8200 Å and 2250 at 7650 Å.[3] All reactions were conducted in baths regulated to ±0.05°.

To circumvent the "killing" of sodium naphthalene by impurities in the hexyl fluoride, observed by Garst and Barton,[1] the following procedure was used in expt 63, 66, 69, 70, 72, 96, and 97. A serum cap was attached to the end of a tube containing a constriction, then a breakseal. The volume between the serum cap and breakseal was evacuated through a hypodermic needle, and hexyl fluoride and dry nitrogen were introduced. Sodium naphthalene in THF was added dropwise from a gas-tight syringe until a light-green color persisted. The solution was frozen and evacuated and the serum cap removed by sealing off at the constriction. The arm of the tube opposite the one containing the solution was then sealed onto a reaction vessel and evacuated. The preparation of sodium naphthalene in the vessel was carried out as usual,[1] at which point the breakseal was crushed and the alkyl fluoride evaporated into the frozen sodium naphthalene solution. The breakseal was cut away, the contents of the vessel warmed, and the kinetic run carried out as usual. In expt 97, the concentration of hexyl fluoride after complete reaction was determined by VPC in order to ensure that the method effected quantitative transfer; 99% of the hexyl fluoride initially taken was found. The rate constants from these experiments agree with those from similar experiments without the pretreatment of the hexyl fluoride with sodium naphthalene.

Experiments at 6° employed a double jacketed cell. The outer jacket was evacuated and 6° water was circulated through the inner jacket.

Results

The results are summarized in Tables I and II and in Figure 1. The reactions are first order in each reagent, and the concentration of naphthalene has no influence on the rate (expt 79 and 80). In the cases of added tetraglyme and crown ethers, excesses over the sodium naphthalene were used, and these appear to be sufficient to complex all the sodium naphthalene since variations in the concentrations of tetraglyme in THF and of dicyclohexyl-18-crown-6 in DME had no effects on the rate constants.

There is some scatter in the data, but no trends toward curvature are indicated in the Arrhenius plots (Figure 1).

Discussion

These Are Ion Pair Reactions. The lack of drift of the second-order rate constants with initial concentration of so-

Table II. Effects of Temperature on Rates of Reactions of Sodium Naphthalene with Hexyl Fluoride

Temp, °C	10^4k^a	No. expt[b]
	In MeTHF	
25.0	3.4	3
35.0	7.0	4
46.0	17	3
	$\Delta H^\ddagger = 14 \pm 1$ kcal/mol[c]	
	$\Delta S^\ddagger = -28 \pm 3$ cal mol^{-1} °K^{-1} [c]	
	In THF	
6.0	0.24	2
25.0	2.0	4
25.2	1.8	7
25.8	1.6	2
35.0	3.6	2
46.0	9.2	2
	$\Delta H^\ddagger = 15 \pm 1$ kcal/mol[c]	
	$\Delta S^\ddagger = -25 \pm 2$ cal mol^{-1} °K^{-1} [c]	
	In DME	
25.0	2.4	5
25.2	2.7	2
35.0	5.0	2
46.0	13	2
	$\Delta H^\ddagger = 13 \pm 1$ kcal/mol[c]	
	$\Delta S^\ddagger = -28 \pm 3$ cal mol^{-1} °K^{-1} [c]	
	In DME–Dicyclohexyl-18-crown-6[d]	
26.0	0.47	4
35.0	1.1	2
45.0	4.2	3
	$\Delta H^\ddagger = 21 \pm 2$ kcal/mol[c]	
	$\Delta S^\ddagger = -7 \pm 5$ cal mol^{-1} °K^{-1} [c]	

[a] Average of indicated number of experiments in M^{-1} sec^{-1}. [b] Number of experiments. [c] The thermodynamic parameters and standard deviations are from linear least-squares analyses of the individual data points (not the averages) summarized in this table. The entropies of activation correspond to a 1 M reference state. [d] Concentration of dicyclohexyl-18-crown-6 is 0.04 M.

dium naphthalene implies that we are dealing with reactions of the same ionic aggregate throughout the concentration range 10^{-2} to 10^{-4} M in sodium naphthalene. While one might have suspected the possible incursion of higher aggregates at the higher concentrations, it is unlikely that there are not significant numbers of ion pairs in the solutions of lower concentrations.[4] Thus, we must be dealing with ion pairs throughout the concentration range.

The Activated Complexes Contain One Molecule Each of Sodium Naphthalene and Hexyl Fluoride. The second-order kinetics rule out the possibility that sodium naphthalene disproportionates to naphthalene and disodium naphthalene, which then reacts with hexyl fluoride. Similarly, the possibility that sodium naphthalene reversibly transfers an electron to hexyl fluoride, which decomposes in a slow step (eq 2) is eliminated by the lack of dependence of the rate on the naphthalene concentration. The stoichiometry of the rate-determining step is accurately given by eq 1. If $RF\cdot^-$ is an intermediate in this step, it is not reversibly formed.

$$NaC_{10}H_8 + RF \rightleftarrows Na^+(RF\cdot^-) + C_{10}H_8 \rightarrow R\cdot \text{ etc.} \qquad (2)$$

Previous Hypothesis: Activated Complex Anions Have Higher Cation Affinities than Naphthalene Radical Anion. The "cation affinity" of an anion is measured by $\Delta G°$ for the dissociation, in the gas phase, of an ion pair including the anion and a reference cation.[5] Anions of higher cation affinity will form ion pairs with reference cations which are less dissociated, at equilibrium, than those containing anions of lower cation affinities. Anions of higher cation affinity will, in general, have more concentrated, localized, or sterically accessible sites of negative charge.

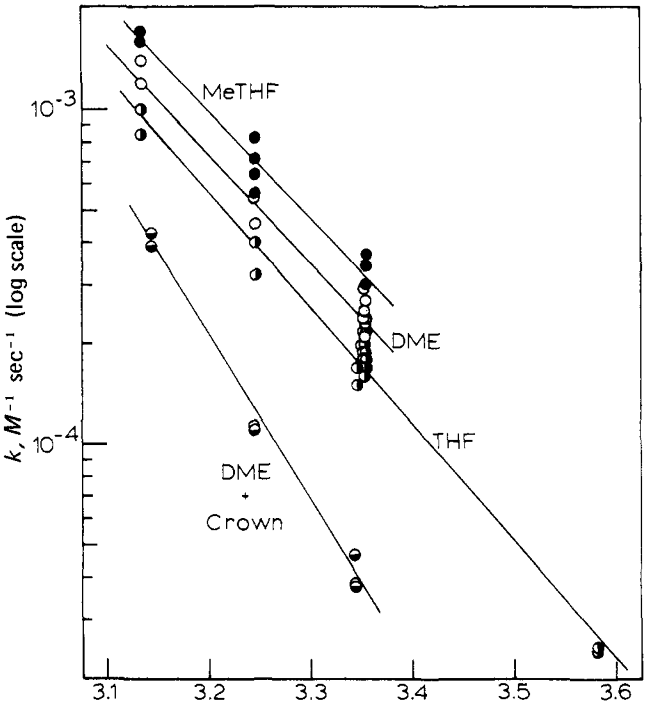

Figure 1. Arrhenius plots for reactions of sodium naphthalene with hexyl fluoride in 2-methyltetrahydrofuran (●), 1,2-dimethoxyethane (○), tetrahydrofuran (◑), and 1,2-dimethoxyethane + dicyclohexyl-18-crown-6 (⊖).

The energies, relative to dissociated ions, of gas phase ion pairs containing anions of higher cation affinity are more affected by changes in cation radius than the energies of ion pairs containing anions of lower cation affinity. Thus, if activated complex anions have a higher cation affinity than reactant anions, a change in cation from sodium to lithium will accelerate the gas phase ion pair reaction by lowering the transition state energy relative to that of the reactant state.

The essence of the hypothesis of Garst and Barton[1] is that the reactions of alkali naphthalenes with primary alkyl fluorides fall into the category just described, and that the gas phase effects still dominate in solution.

Prediction from Hypothesis: Better Cation Solvating Media Will Slow the Reactions. In solution things are less simple. For organoalkali ion pairs in ethers, it may be presumed that specific cation–solvent interactions dominate solvation.[5,6] However, the nature of the anion can have a profound influence on cation solvation in an ion pair. Anions of higher cation affinity will encumber the solvation of associated cations more than anions of lower cation affinity.[5] Thus, solvation free energies for ion pairs containing anions of lower cation affinities will be larger than those for ion pairs containing anions of higher cation affinities, and the solvation energy difference will be more pronounced in media of better cation solvating capacities. Consequently, if activated complex ion pairs contain anions of higher cation affinity than reactant ion pairs, as prescribed in the hypothesis of Garst and Barton, better cation solvating media will slow the reaction by decreasing reactant standard free energy relative to that of the transition state.

The solvent effect should be more definitive of the relative cation affinities of the reactant and activated complex anions than the metal ion effect, which can be reversed in direction, in principle, by moving to a more or less polar solvent.[5,7]

Broadly, but Weakly, the Prediction Is Realized. The

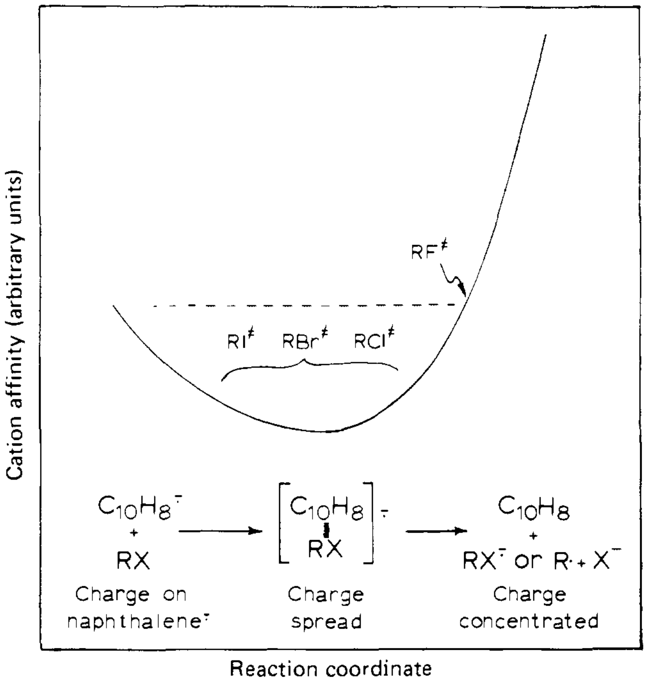

Figure 2. Schematic representation of the variation of cation affinity with progress along the reaction coordinate in a collision leading to reaction of a naphthalene radical anion with an alkyl halide molecule (eq 3). Relative locations of transition states for different halogens are indicated, the assumption being that the transition states for different halogens are indicated, the assumption being that the transition states come earlier along the reaction coordinate for the more exothermic or less endothermic reactions. The indicated transition state locations permit a general rationalization of available data.

broad trend of the data conforms to the prediction, but the observed effects are really quite small. For the reaction of sodium naphthalene with hexyl fluoride in MeTHF at 25°, the rate constant is 3.4×10^{-4} M^{-1} sec^{-1}. This is the largest we found, and MeTHF is the solvent of least sodium ion solvating capacity in our study.[8] The rate constant is slightly smaller in DME and THF and slightly smaller yet in THF-tetraglyme. Finally, the rates in DME and THF containing crown ethers, dicyclohexyl-18-crown-6 and 18-crown-6, are the slowest of all, with rate constants ca. 4×10^{-5} M^{-1} sec^{-1}, nearly a factor of 10 smaller than in MeTHF. The media containing crown ethers are those of greatest sodium ion solvating abilities in our study. Thus, the data support the activated complex model proposed earlier, but the magnitude of the observed effects are smaller than those which were hoped for.

Trends in the Thermodynamic Parameters of Activation Are Also Consistent with the Model. In MeTHF, $\Delta H^{\ddagger} = 14$ kcal mol^{-1} and $\Delta S^{\ddagger} = -28$ cal mol^{-1} °K^{-1} while, in DME containing dicyclohexyl-18-crown-6, $\Delta H^{\ddagger} = 21$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7$ cal mol^{-1} °K^{-1}. The rise in both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in going to the medium of better cation solvating ability is consistent with additional desolvation of activation in that medium. The increment in $\Delta H^{\ddagger}$ reflects the energetics of this desolvation difference, and the increment in $\Delta S^{\ddagger}$ reflects the concomitant relaxation of constraints on solvent molecules. These are the expected trends if activated complex anions have a larger cation affinity than naphthalene radical anion.

Data for Reactions of Sodium Naphthalene with Alkyl Chlorides, Bromides, and Iodides Suggest That Activated Complex Anions Have Lower Cation Affinities than Naphthalene Radical Anion. Bockrath and Dorfman have studied the kinetics of reactions of sodium naphthalene with butyl bromide and butyl iodide in THF using pulse radiolysis techniques.[9] The ion pair reaction rate constant at 25° is 5×10^{7} M^{-1} sec^{-1} for the iodide and $<2 \times 10^{5}$ M^{-1} sec^{-1} for the bromide. Free naphthalene radical anions are more reactive than loose ion pairs, which are more reactive than tight ion pairs. This is the opposite of a prediction based on a model in which activated complex anions have larger cation affinities than naphthalene radical anion.

Using stopped flow, Bank and Juckett obtained rate constants of 2×10^{2} and 7×10^{4} M^{-1} sec^{-1} for hexyl chloride and bromide, respectively, in THF at 20°.[10] For the chloride, they specifically examined the solvent effect, finding a rate constant a factor of 5-6 faster in DME than in THF. DME is the better sodium ion solvating medium of this pair,[8] and it is believed that sodium naphthalene exists essentially as solvent-separated ion pairs in DME up to temperatures of about 10° while, in THF, sodium naphthalene is 85-99% tight ion pairs at 20°.[10,11] Bank and Juckett's observations on solvent effects contrast with ours and, like the findings of Bockrath and Dorfman, they suggest that activated complex anions have lower cation affinities than naphthalene radical anion.

All the Data Can Be Reconciled with a Model in Which the Transition State Lies Further along the Reaction Coordinate for Electron Transfer to Alkyl Fluorides than to Other Alkyl Halides. Equation 3 represents the gas phase analog of eq 1 for reactions of free anions. For a primary

$$RX + C_{10}H_8\cdot^- \rightarrow R\cdot + X^- + C_{10}H_8 \qquad (3)$$

alkyl fluoride, reaction 3 is endothermic by 30 kcal/mol.[12] The endothermicity persists for primary alkyl chlorides, but it is much smaller, 2 kcal/mol. For primary alkyl bromides and iodides, reaction 3 is exothermic by 5 and 14 kcal/mol, respectively. It is often postulated that, for a series of closely related reactions, the transition state comes later along the reaction coordinate for the more endothermic (or less exothermic) reactions and earlier for the more exothermic (or less endothermic) ones. Let us presume that this is the case for reaction 3 as X (the halogen) is varied.

The positions of the transition states along the reaction coordinate will be modified by association of the ions to ion pairs and by solvation effects (when the ion pairs are immersed in a solvent). These factors will cause even the alkyl fluoride reaction to be exothermic in THF or DME.[1] Let us presume further that the transition state for the alkyl fluoride reaction (eq 1) still lies further along the reaction coordinate than for the other alkyl halides.

Now consider the cation affinity of a collisional complex for reaction 3 as a function of reaction coordinate. Initially, the negative charge will expand and delocalize as the reaction coordinate increases from that representing reactants because the charge is being spread out onto the alkyl halide moiety. At some further point along the reaction coordinate, the negative charge begins to localize and concentrate; finally, it must be localized on the halide ion X^-, a reaction product. Even if $RX\cdot^-$ is taken as an intermediate following the transition state along the reaction coordinate, the same considerations apply since the negative charge must be quite localized in $RX\cdot^-$. Perhaps the extra electron occupies an antibonding C-X orbital in the latter species, if it exists. Figure 2 is a schematic representation of the variation of cation affinity with reaction coordinate for reaction 3.

This rationalizes all the currently available observations. From the relatively small solvent effects on the alkyl fluoride reactions, it is reasonable to conclude that the activated complex anions have only slightly greater cation affinities than naphthalene radical anion. For the other alkyl halides, the transition states come earlier along the reaction coordinate and the activated complex anions have lower cation affinities than naphthalene radical anion. Thus, the solvent effects for ion pair reactions in solution will be in opposite directions for the alkyl fluoride and other alkyl halide reactions, as is observed.

Some Details Are Still Puzzling. Both the rate constants and thermodynamic parameters of activation for the reaction of sodium naphthalene with hexyl fluoride vary only very slightly among MeTHF, THF, and DME. This is especially striking because sodium naphthalene in DME is supposed to tend to exist as solvent-separated ion pairs, while it exists as tight ion pairs in THF at 25°.[14] We conclude that loose and tight ion sodium naphthalene ion pairs must have very similar reactivities toward hexyl fluoride in MeTHF, THF, and DME. It appears to be a coincidence, but it is consistent with the rather small solvent effects we observed over a wide range of cation solvating abilities. As mentioned above, this is consistent with activated complex anions in the hexyl fluoride reactions with only slightly higher cation affinities than naphthalene radical anion.

Both Bockrath and Dorfman[9] and Bank and Juckett[10] found the grotesquely curved Arrhenius plots which are typical when tight and solvent-separated ion pairs differ in reactivity, and a temperature range is covered over which the equilibrium between tight and solvent-separated ion pairs is significantly shifted.[15] Our data show no indications of such curvature, although we are at a disadvantage because it is difficult to cover a wide temperature range for our rather slow reactions. We did some reactions at 6° in THF, in an effort to establish the nature of the plot in that solvent more clearly, and it still is a satisfactory straight line. Of course, if tight and solvent-separated ion pairs had equal reactivities, the Arrhenius plots would be expected to be straight no matter how the temperature affected the distribution between the two types of reactant ion pairs. Thus, the nature of our Arrhenius plots further substantiates the idea that tight and solvent-separated ion pairs have similar reactivities in MeTHF, THF, and DME.

Another clue to unusual Arrhenius plot behavior would be anomalous values of the derived thermodynamic parameters of activation. However, the values determined from our plots are in no way unusual. The entropies of activation in MeTHF, THF, and DME are all around -27 cal mol^{-1} °K^{-1}, which compares favorably with the -32 cal mol^{-1} °K^{-1} mentioned by Karasawa, Levin, and Szwarc[15] as applying to the conversion of tight to solvent-separated ion pairs for three different sodium salts in THF. Perhaps this is the characteristic $\Delta S°$ for binding an additional solvent molecule in THF. If so, perhaps it is similar for binding an additional molecule of any roughly similar type in THF. In going from reactants to activated complexes, an additional molecule (RF) is bound in the reactions of sodium naphthalene with hexyl fluoride. It makes a satisfying picture to imagine that no solvent molecules are bound or released in going from reactants to activated complexes in these solvents (MeTHF, THF, DME), and that the entropy of activation simply reflects the binding of the sodium naphthalene ion pair and a hexyl fluoride molecule.

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References and Notes

(1) J. F. Garst and F. E. Barton, II, *J. Am. Chem. Soc.*, **96**, 523 (1974); *Tetrahedron Lett.*, 587 (1969).

(2) Presented, in part, at the First Fall Organic Conference, Cape Cod, Mass., Oct 1973.

(3) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **93**, 430 (1971), used 7650 Å with this extinction coefficient. We[1] and others have obtained extinction coefficients of 2500 at 8200 Å; however, some groups and some procedures give slightly higher values, e.g., 3000–3200; see ref 11.

(4) Numerous conductivity studies of alkali hydrocarbon radical anions and related organoalkali compounds in ethers have failed to indicate aggregation higher than ion pairs in 10^{-4} *M* solutions. By analogy with sodium biphenyl, sodium triphenylene, and sodium perylene [P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966)], the ion pair dissociation constant for sodium naphthalene in DME is probably about 5×10^{-6} *M*. Thus, at 10^{-4} *M* sodium naphthalene, 0.8 of the ion pairs would be undissociated. The crown ethers may promote more dissociation but, since we find no concentration effect on the rate constant in THF–dicyclohexyl-18-crown-6, it seems most reasonable to assign all our observed reactivities to ion pairs.

(5) J. F. Garst in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, pp 539–605.

(6) M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes", Interscience, New York, N.Y., 1968.

(7) An example of reversal of metal ion effects is found in anionic styrene polymerizations, where the second-order rate constant for propagation is larger for CS^+ counterion than Li^+ in dioxane, but the reverse in THF: D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).

(8) Many studies indicate that the order of sodium ion solvating capacities at room temperature is MeTHF < THF < DME. See ref 5 and 6 for leading literature citations.

(9) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, 77, 2618 (1973).

(10) S. Bank and D. A. Juckett, *J. Am. Chem. Soc.*, **97**, 567 (1975).

(11) Y. Karasawa, G. Levin, and M. Szwarc, *Proc. R. Soc. London, Ser. A*, **326**, 53 (1971); N. Hirota, R. Carraway, and W. Shook, *J. Am. Chem. Soc.*, **90**, 3611 (1968).

(12) Calculated from bond dissociation energies of typical primary alkyl halides (S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, p 215) and electron affinities of naphthalene [3.5 kcal/mol; W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445, (1966); R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966); W. E. Wentworth and E. Chen, *J. Phys. Chem.*, **71**, 1929 (1967)] and the halogen atoms (tabulated by F. A. Cotton and G. W. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1972, p 57).

(13) $RF\cdot^-$ cannot be reversibly formed, as argued earlier above from the absence of an effect of the concentration of naphthalene on the rate constant. However, it is still possible that a complex $C_{10}H_8RFNa$ in which the anion closely resembles $RF\cdot^-$ could be reversibly formed, and it is possible that the transition state for the dissociative electron transfer could resemble $RF\cdot^-$. Similar remarks apply to the reactions of the other alkyl halides as well.

(14) The very small rate constant difference between DME and THF is actually in the direction opposite from the general trend of our data. Since the rate constant variations among MeTHF, THF, and DME are so small, we do not find this disturbing. It may be a reflection of dielectric constant effects superimposed on the more specific interactions which, we believe, determine the directions of solvent effects when there are large effects on ion pair reactions of this type. The dielectric constant of THF is actually slightly larger than that of DME, ca. 7.4 vs. 7.2. See ref 6.

(15) An early example is provided by T. Shimomura, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 769 (1967). An example in an equilibrium system is given in ref 11 (Karasawa, Levin, and Szwarc).