Interscience, New York, N.Y., 1965.
(9) R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968).
(10) The spin densities and negative charge densities on the aromatic carbon atoms in **2**$\cdot^-$ and **3**$\cdot^-$ are of the same magnitude at least according to simple theory in these species since the naphthalene moieties present are alternant π systems.
(11) In **2** (and presumably also **2**$\cdot^-$), consideration of a molecular model suggests that this molecule has a $C_2C_3C_b$ (C_b = bridgehead carbon atom) angle of approximately 110° rather than the strain free value of 120° for sp^2-hybridized carbon atoms. A similar model of **3** suggests that the $C_2C_3C_b$ angle in this molecule is approximately 116°.
(12) The magnitudes of the hfsc's of a "free" radical anion can vary with solvent due to perturbations of the spin densities by different solvent interactions. Such variations, at least for aromatic hydrocarbon radical anions, are usually quite small ($<\sim$0.1 G). The appreciable variations (up to $\sim$0.5 G) found in the present study are best viewed as resulting from shifts in the position of a rapid equilibrium of ion pairs and/or a free ion.
(13) See N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967), for a discussion of such equilibria.
(14) Cf. E. DeBoer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964).
(15) M. Iwaizumi and J. R. Bolton, *J. Magn. Reson.*, **2**, 278 (1970), and references cited therein.
(16) R. D. Rieke and S. E. Bales, *Tetrahedron Lett.*, 2439 (1972).
(17) Polarization of spin density and hence negative charge density toward ring A, which is closer to the counterion, would result in a decrease in the distance between the positive counterion and the average center of negative charge. Some polarization of spin density in this direction may give a more favorable electrostatic arrangement of the charges, and, to the extent that it is more favorable, would occur. Polarization in the opposite direction toward ring B on the other hand would always represent a less favorable electrostatic arrangement of the charges (since the distance between the positive counterion and the average center of negative charge would be increased) and hence should not occur.
(18) The theoretical basis for the direction of variations of the hfsc's is developed in the discussion in terms of the changes expected in the hfsc's of **2**$\cdot^-$ and **3**$\cdot^-$ in going from a free radical anion to an ion paired radical anion. The hfsc's actually measured for **2**$\cdot^-$ and **3**$\cdot^-$, however, are believed to be average hfsc's resulting from a rapid equilibrium(a) between two or more types of ions differing in the extent to which they are ion paired. This does not matter for present purposes, however, since the experimentally measured changes in the hfsc's as a result of shifts in the above equilibrium(a) are in the same direction and reflect the changes expected in the hfsc's of **2**$\cdot^-$ and **3**$\cdot^-$ in going from a free radical anion to an ion paired radical anion.
(19) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).
(20) A perturbation of the spin densities at atoms C_9 and C_{10} cannot be detected directly since these carbon atoms do not bear protons. However, the observation that $a_{5,8}$ increases in magnitude to the same extent that $a_{1,4}$ decreases (see later discussion) while all of the other hfsc's remain essentially the same upon more extensive ion pairing strongly indicates that any perturbation of the spin densities at these atoms is at most a small one.
(21) Ion pairing is generally much more extensive in MeTHF than in either THF or DME, since MeTHF has a considerably lower dielectric constant than either THF or DME. Ion pairing is generally less extensive in DME than in THF, which is usually attributed to the fact that DME can act as a bidentate ligand and coordinate more effectively with the counterion than can THF. Both DME and THF have very similar dielectric constants. See A. C. Aten, J. Dieleman, and G. J. Hoijtink, *Discuss. Faraday Soc.*, **29**, 182 (1960).
(22) As a general rule, the extent of ion pairing increases with increasing size of the counterion. Thus the smaller Na$^+$ is less likely to form an ion pair with a radical anion than is the larger K$^+$. See reference cited in ref 21.
(23) See reference cited in ref 21.
(24) I. B. Goldberg and J. R. Bolton, *J. Phys. Chem.*, **74**, 1965 (1970).
(25) The fact that only slight changes in the hfsc's were observed suggests that the shift in the position of this equilibrium with temperature is also very slight and ion pair **7** is always present to only a very small degree. If substantial amounts of **7** were present at equilibrium, one might expect to observe nonequivalence of the vinyl proton hfsc's and/or line width alternation in this radical anion.
(26) This is indicated by the fact that the substituent constants for Me and *i*-Pr are virtually the same. For Me, $\sigma_m = -0.069$ and $\sigma_p = -0.17$. For *i*-Pr, $\sigma_m = -0.068$ and $\sigma_p = -0.15$.
(27) Cf., for example, ref 2b.
(28) For example, a simple Hückel calculation in which $\beta_{2,11}$ (and other resonance integrals for equivalent 1,3-transannular interactions) = 0.25 and in which other resonance integrals were assigned their standard values (i.e., $\beta = 1$ for adjacent interacting AO's and $\beta = 0$ otherwise) afforded a coefficient of -0.049 at each vinyl carbon atom in the LAMO. Smaller (more realistic) values for $\beta_{2,11}$, etc., in this calculation afford even smaller coefficients at these positions for the LAMO.
(29) This expectation follows from the well-known fact that there is an approximate linear correlation between the half-wave reduction potential of a compound and the energy of its lowest antibonding MO, which the odd electron occupies in most radical anions. See the discussion in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N.Y., 1961, Chapter 7.
(30) This expectation follows from the fact that a spin polarization mechanism of spin transfer should not be dependent upon any dihedral angle as is a hyperconjugation mechanism.
(31) H. E. Zimmerman and C. O. Bender, *J. Am. Chem. Soc.*, **92**, 4366 (1970).
(32) Cf., for example, H. E. Zimmerman and J. R. Dodd, *J. Am. Chem. Soc.*, **92**, 6507 (1970).

Activation Parameters for the Ring Inversion of 1,4-Oxathiane. The Use of Complex Spectral Patterns for Obtaining Reliable Thermodynamic Parameters

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Abstract: The activation parameters for the ring inversion process (chair to twist) of 1,4-oxathiane were found to be $\Delta H^\ddagger = 8.78 \pm 0.7$ kcal/mol, $\Delta S^\ddagger = 0.45 \pm 0.35$ eu, and $\Delta G^\ddagger = 8.69 \pm 0.3$ at 177.2°K by variable temperature NMR. These results are discussed in relation to the use of new methods of computer analysis and more accurate temperature measurement and control. Predictions of entropies of activation, and hence calculation of enthalpies of activation, for ring inversion processes based on reaction path degeneracies are discussed.

Measurement of enthalpies and entropies of activation for the ring inversion process in six-membered rings by NMR methods has not always produced satisfactory results. This arises from difficulties inherent in the NMR methods of determining rate constants. Results reported for the cyclohexane ring inversion (Table I) illustrate the problem. The original results[1a] for this compound ($\Delta G^\ddagger = 10.1$ kcal/mol, determined; $\Delta S^\ddagger = 3.6$ eu,[2] estimated; $\Delta H^\ddagger = 10.8$ kcal/mol,[2] estimated from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$) are in excellent agreement with the most recent results from experimentally derived data[1g] ($\Delta G^\ddagger = 10.22$ kcal/mol, $\Delta S^\ddagger = 2.8$ eu, and $\Delta H^\ddagger = 10.8$ kcal/mol). In the years between these two reports a wide range of enthalpies and entropies of activation ($\Delta H^\ddagger = 9.0$ to 11.5 kcal/mol, $\Delta S^\ddagger = -6.5$ to 4.9 eu) were reported. In contrast, the $\Delta G^\ddagger$ values are relatively invariant. The difficulties in determining accurate enthalpies of activation, even though accurate free energies of activation can be determined, have been discussed elsewhere.[3]

Inaccuracies in the NMR method can be separated into

Table I. Activation Parameters Reported for Ring Inversion in Cyclohexane and Cyclohexane-d_{11}

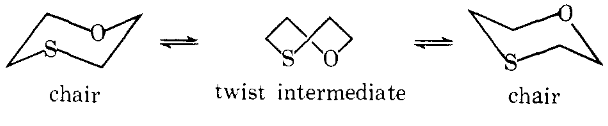
Compd	$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref
C_6H_{12}	10.1	$(10.8)^b$	$(3.6)^b$	1a
C_6H_{12}	10.3	9.0 ± 0.2	−6.5 ± 1.0	1b
C_6H_{12}	10.7	11.5	4.9	1c
C_6HD_{11}	10.3	10.9 ± 0.6	2.9 ± 2.3	1d
C_6HD_{11}	10.2	10.5 ± 0.5	1.4 ± 1.0	1e
C_6H_{12}	10.3	9.1 ± 0.5	−5.8 ± 2.4	1f
C_6HD_{11}	10.3	9.1 ± 0.1	−5.8 ± 0.4	1f
C_6HD_{11}	10.22	10.8	2.8	1g

[a] At ca. −67°. [b] Estimates, see ref 2.

three categories. First, accurate temperature control and measurement in the NMR probe is difficult. Second, interpretation of complex spin-coupled spectra to yield rate constants has not been possible with the simplified equations used to describe line shapes (using the method of line width measurements to obtain rates above and below the coalescence point is extremely prone to introduction of systematic errors and thus use of rate constants determined by this method often led to erroneous activation enthalpies and entropies).[3c] Third, noncomplex spin systems (equilibrium AB $\rightleftharpoons$ BA, etc.) undergo their complete spectral change in a matter of a few degrees. Any systematic errors introduced over such a short temperature range are unlikely to be detected.[3a]

Recently, improvements in the computer programs available to interpret NMR spectra of exchanging systems have become available.[4] Since the type of program now available (DNMR3) allows complex spin spectra to be produced under exchange conditions, rate constants can be determined over a much larger range of temperatures. (In complex spin-coupled systems, coupling in the fast-exchange spectrum disappears first as the temperature is lowered, followed by appearance of the separate nonexchanging spectra of the different nuclei. Finally, fine structure due to coupling begins to appear in the nonexchanging spectrum as the temperature is lowered even further.) This method of analysis has been applied to azacycloheptatrienes and norcaradienes.[3c]

In our laboratory a variable temperature NMR probe capable of maintaining and measuring a temperature to better than ±0.1° has been constructed.[5] This probe, used in conjunction with program DNMR3 on a highly coupled system, should in theory yield accurate rate constants over a large temperature range. These could then be used to determine an accurate enthalpy and entropy of activation for an exchange process. A number of heterocyclic six-membered rings would provide the necessary complex spin system desired (there is, however, a limitation on the complexity of the systems which are analyzable by DNMR3). 1,4-Oxathiane fulfills all of the requirements of a complex spin-coupled system and has the additional advantage of having an almost first-order spectrum at low temperature which is easily analyzable for its static parameters. Additionally, the ring inversion barrier for this six-membered ring has not been reported.



(1)

Results and Discussion

In Figure 1 is shown the 100 MHz ^1H NMR spectrum of 1,4-oxathiane at −111.7°. Peaks labeled A and B arise from the hydrogens on the carbons attached to oxygen while C and D arise from the hydrogens on the carbons next to sulfur. Chemical shifts of the four resonances are listed in Table II as well as the coupling constants obtained by computer simulation (see Figure 1). The large negative J_{AB} and J_{CD} are the respective geminal coupling constants. Since the remaining coupling constants are small except for J_{BC} this coupling is assigned to axial-axial coupling and therefore B and C are respectively the axial proton next to oxygen and the axial proton next to sulfur. Thus, for the protons on the carbon attached to sulfur, the resonance of the axial proton appears downfield from that of the equatorial proton. The reason for this reversal of the normal relative positions of axial and equatorial protons in the cyclohexane system is not known. The observation of this reversal makes the assignment of axial and equatorial position solely on the basis of relative chemical shift more tenuous in other systems.

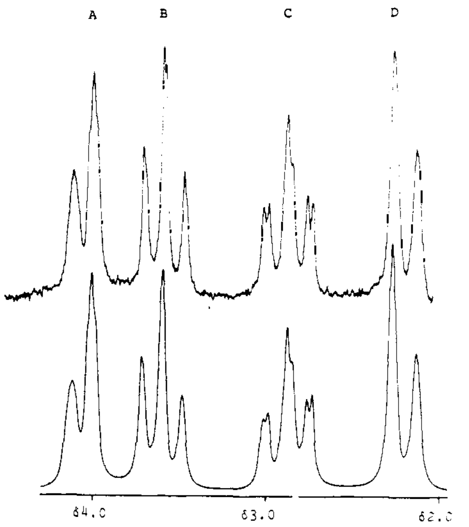


Figure 1. The slow exchange spectrum (100 MHz) of 1,4-oxathiane at −111.7° (upper) (solvent, vinyl chloride; internal standard, TMS) and the calculated spectrum using DNMR3 and the static parameters listed in Table II with T_2 = 0.24 (the apparent relaxation time) and k = 7.5 sec^{-1}. The four different proton resonances are labeled A, B, C, and D as described in the text.

Table II. Static Parameters of the Low-Temperature Spectrum of 1,4-Oxathiane Obtained by the Best Fit Computer Simulation of the Observed Spectrum

Chemical shifts[a]	Coupling constants, Hz
ν_A = 405.7	J_{AB} = −11.8
ν_B = 360.0	J_{AC} = 3.2
ν_C = 287.4	J_{AD} = 2.0
ν_D = 220.9	J_{BC} = 11.6
	J_{BD} = 1.4
	J_{CD} = −14.0

[a] In Hz downfield from TMS lock (100 MHz).

Using the spectral parameters listed in Table II a series of spectra were calculated with program DNMR3 and compared with the observed spectra. A few selected experimental and calculated spectra are shown in Figure 2. Rate constants for chair-to-twist intermediate are assumed to be twice those obtained for the chair-to-chair interconversion as obtained from the comparison with the computed spectra. In this treatment it is assumed that the twist intermediates, one of which is shown in eq 1, interconvert rapidly and hence have an equal probability of returning to either chair form. The rate constants for chair-to-twist intermediate are listed in Table III along with the free energy of activation calculated at each temperature.

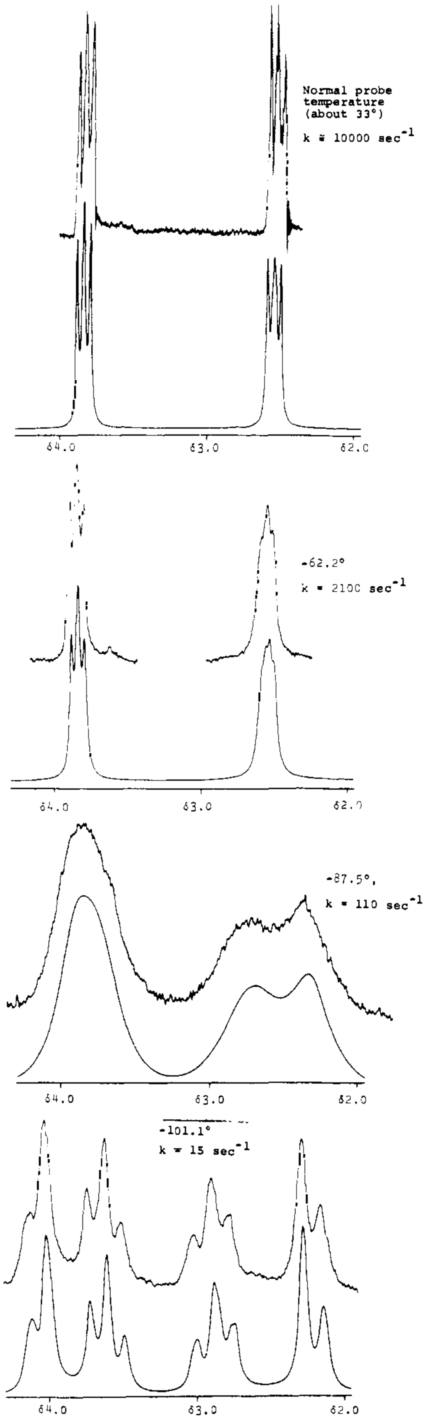
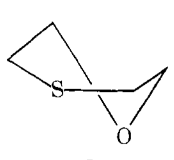


Figure 2. Experimental (upper) and calculated (lower) spectra of 1,4-oxathiane at various temperatures. The chemical shifts and coupling constants used to calculate the spectra with DNMR3 are given in Table II (T_2 = 0.24). Rates calculated by the computer program are for the chair-to-chair interconversion and are half the rate for the chair-to-twist-chair interconversion.

These data which cover a 47° range in temperatures show little deviation from linearity (Figure 3) when plotted with the Eyring equation (using a weighted linear least-squares computer program[6]). Because of the large temperature range over which the data were obtained, the effect of systematic errors in the data is minimized in the calculation of the enthalpy ($\Delta H^{\ddagger}$ = 8.78 ± 0.07 kcal/mol) and entropy ($\Delta S^{\ddagger}$ = 0.45 ± 0.35 eu).

It has been pointed out that translational, rotational, and vibrational contributions to the entropy of activation in ring reversals are probably small.[1a,3a] An estimate of this quantity can be made solely on the basis of reaction path degeneracies for hydrocarbons such as cyclohexane. For compounds containing polar groups differential solvation may occur in the ground and transition states and therefore some uncertainty exists regarding the validity of predicting reaction path degeneracies from observed $\Delta S^{\ddagger}$, and vice versa, in such compounds.

If dipolar effects are small, the reaction path degeneracy is obtained in the following manner. There are three possible half-chair transition states (plus their mirror images)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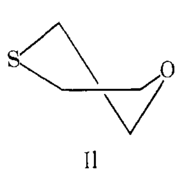
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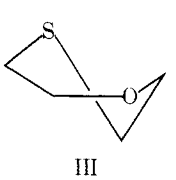
III

and no attempt has been made to estimate their relative energies. If all these transition states are of equal energy, the degeneracy, which includes the mirror images, is six and

Table III. Rate Constants for the Chair-to-Twist Interconversion of 1,4-Oxathiane

k, sec^{-1a}	T, °K^{b}	$\Delta F^{\ddagger}$, kcal/mol
20 ± 5	168.05	8.65
25 ± 5	170.00	8.68
30 ± 5	172.06	8.72
35 ± 5	172.86	8.71
45 ± 4	174.72	8.72
65 ± 5	175.97	8.66
70 ± 5	177.20	8.69
85 ± 10	178.65	8.70
150 ± 10	183.10	8.72
220 ± 20	185.67	8.70
260 ± 20	186.92	8.70
2200 ± 200	203.35	8.64
2600 ± 200	205.99	8.69
3200 ± 200	207.84	8.68
3400 ± 200	209.26	8.72
4200 ± 200	210.94	8.71
4800 ± 300	211.47	8.67
5800 ± 400	212.67	8.65
6200 ± 400	213.75	8.66
7000 ± 600	215.12	8.67

[a] The actual rate constant calculated by DNMR3 is one-half of these values and represents the chair-to-chair interconversion constant. [b] The error for these temperatures is ±0.1°.

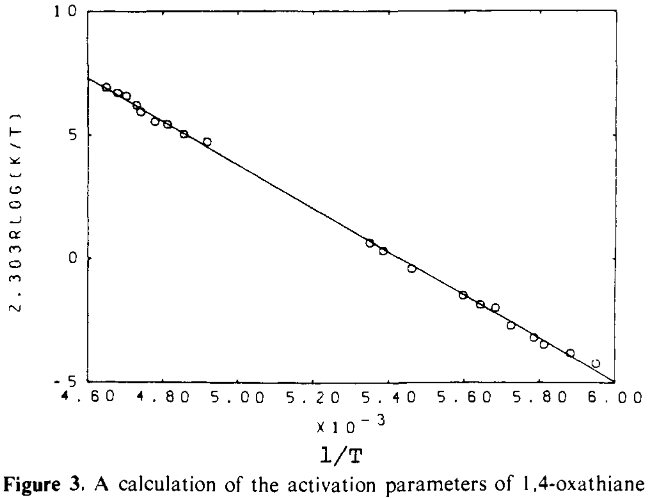

Figure 3. A calculation of the activation parameters of 1,4-oxathiane by a weighted linear least-squares analysis of the rate data in Table III using the Eyring equation.

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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(2) The authors originally estimated quantities to be $\Delta H^\ddagger$ = 11.1 kcal/mol and $\Delta S^\ddagger$ = 4.9 eu based on the assumption of a 12-fold degeneracy of the transition state. However, for the half-chair transition state (degeneracy of six) the values become those given in Table I for ref 1a (see ref 3a).

(3) (a) G. Binsch, *Top. Stereochem.*, **3,** 97 (1968); (b) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88,** 3185 (1966); (c) A. Steigel, J. Sauer, D. A. Kleier, and G. Binsch, *ibid.*, **94,** 2770 (1972).

(4) (a) G. Binsch, *J. Am. Chem. Soc.*, **91,** 1304 (1969); (b) D. A. Kleir and G. Binsch, *ibid.*, **92,** 3787 (1970); *J. Magn. Reson.*, **3,** 146 (1970).

(5) The construction of this variable temperature NMR probe is described in the Ph.D. Thesis of R. A. Neese, University of California, Berkeley, 1971. An equivalent (although of different construction and design) NMR probe has been constructed for Varian's HR 60 instrument: F. R. Jensen, L. A. Smith, C. H. Bushweller, and B. H. Beck, *Rev. Sci. Instrum.*, **43,** 894 (1972).

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

(7) R. K. Harris and N. Sheppard, *J. Mol. Spectrosc.*, **23,** 231 (1967), and references cited therein.

(8) G. Binsch and D. Kleir, Program DNMR3 obtained from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana, 47401.

(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]

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

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