

metal splittings have been made. Atherton and Weissman discussed the admixing of S orbitals of alkali metal ions with  $\pi$  orbitals of anion because of the nonorthogonality of the molecular and atomic orbitals.<sup>2</sup> Aono and Ohashi calculated the splitting of the sodium naphthalenide by admixing the charge-transferred excited state  $\psi_1 = \psi(\text{ArNa})$  with the ground state  $\psi_0 = \psi(\text{Ar}^-\text{Na}^+)$ .<sup>18</sup> They obtained a splitting of the order of  $\sim 0.7$ – $0.8$  G for sodium naphthalenide. This value is, however, much smaller than the observed maximum value of 2.15 G and the extrapolated maximum value of 2.5 G for the tight ion pair in sodium naphthalenide in DEE at high temperatures.

It was first suggested by de Boer<sup>5</sup> that the alkali metal splitting by spin polarization mechanism could be nega-

tive. Particularly in the ion pairs with large positive ions, spin polarization terms may be important owing to the higher polarizability of the ions of larger atomic number. If this is the case, the signs of spin density may be negative in the systems such as cesium anthracenide. However, more detailed experimental studies of alkali metal splittings together with careful theoretical analysis are clearly needed in order to understand the mechanism of producing alkali metal splitting and the nature of the bonding in ion pairs.

**Acknowledgment.** I thank Robert Carraway and William Schook for their assistance in obtaining some of the epr spectra. The financial support from the National Science Foundation (Grant GP-5040) is greatly appreciated.

## Electron Paramagnetic Resonance Studies of Ion Pairs. Kinetics of the Interconversion between Different Ion Pairs and the Rapid Electron-Transfer Reaction between Anion and Neutral Molecule

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**Abstract:** Kinetics of the interconversion between a tight ion pair and a loose ion pair were studied in detail. The rate constants, activation energies, and the entropy of activation for interconversion of ion pairs are determined for sodium naphthalenides in the mixtures of tetrahydrofuran and diethyl ether. The equilibrium properties of the same system are also discussed. The rates of electron-transfer reactions between radical anions and neutral molecules were studied in a variety of naphthalenide systems. The rates are discussed in terms of the ion-pair equilibria, described in the first part of the paper, and the connection between the ion-pair structure. Activation energies and preexponential factors for electron-transfer reactions were determined for many naphthalenide systems.

In the accompanying paper<sup>1a</sup> the structures of the ion pairs of hydrocarbon radical ions and the equilibria among different ion pairs are discussed. In this article two problems of kinetic interest are discussed. They are (1) the rates of interconversion between different ion pairs and (2) the rates of electron-transfer reactions.<sup>1b</sup> The rates of interconversion between two different ion pairs often fall in the range which can be conveniently measured from the line-width broadening in the epr spectra.<sup>2</sup> We describe the determination of the rates, activation energies, and entropies of activation for the interconversion between loose and tight ion pairs in sodium naphthalenides in several ethereal solvents.

Since Ward and Weissman measured the rates of rapid electron-transfer reactions in naphthalenide-naphthalene systems,<sup>3</sup> the measurements of a number of

electron-transfer reaction rates have been reported. The reported rates range from  $\sim 10^9$  to  $\sim 10^6$   $M^{-1} \text{sec}^{-1}$ , and the reported activation energies range from 1 to 18 kcal.<sup>3-11</sup> Although the role of ion-pair formation in determining the rate of electron transfer has been noted for some time,<sup>5,12</sup> there have been no detailed studies reported on the relationships between the reaction rates and the ion-pair structures. In 1962 Zandstra and Weissman<sup>5</sup> noted that the rate of the electron-transfer reaction in sodium naphthalenide-naphthalene in THF increases with decrease of temperature, showing an ap-

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(5) P. J. Zandstra and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4408 (1962).

(6) M. T. Jones and S. I. Weissman, *ibid.*, **84**, 4269 (1962).

(7) W. L. Reynolds, *J. Phys. Chem.*, **67**, 2866 (1963).

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(9) T. Layloff, T. Miller, R. N. Adams, H. Fök, A. Horsfield, and W. Proctor, *Nature*, **205**, 382 (1965).

(10) R. Chang and C. S. Johnson, Jr., *J. Am. Chem. Soc.*, **88**, 2338 (1966).

(11) G. L. Malinosky and W. H. Bruning, *ibid.*, **89**, 5063 (1967).

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(1) (a) N. Hirota, *J. Am. Chem. Soc.*, **90**, 3603 (1968). (b) The preliminary results of this work were reported at the ESR Symposium at the Michigan State University, Aug 1-3, 1966: N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967).

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(3) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957).

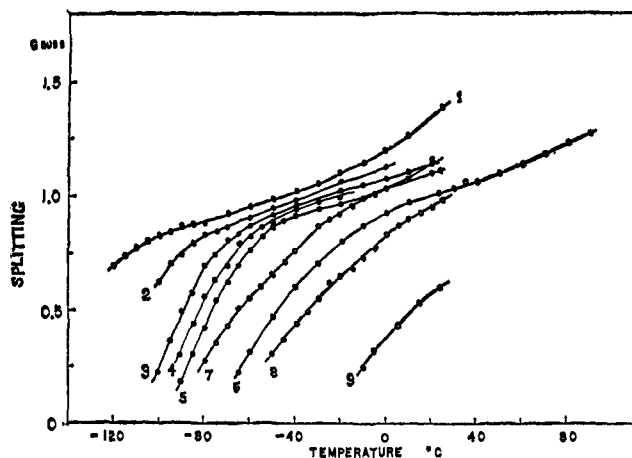


Figure 1. Temperature dependence of sodium splittings in various solvents: (1) DEE (0.93) + THF (0.07); (2) DEE (0.82) + THF (0.18); (3) DEE (0.71) + THF (0.29); (4) DEE (0.54) + THF (0.46); (5) DEE (0.44) + THF (0.56); (6) THF; (7) DEE (0.95) + DME (0.05); (8) DEE (0.85) + DME (0.15); (9) THF (0.56) + DME (0.44). Numbers in parentheses after solvent are mole fractions.

parent negative activation energy. Furthermore, they observed abnormally high activation energies and large preexponential factors for the electron-transfer reactions in several systems. One of the present authors (N. H.) previously proposed that these peculiarities probably arise from the existence of rapid ion-pair equilibria in these systems.<sup>1</sup>

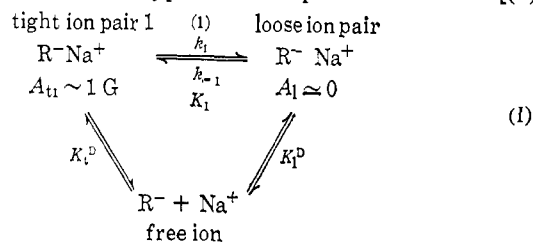
Since the properties of the ion-pair equilibria in the naphthalenides are now better understood, as described in the first part of the paper, it was thought that the data on the electron-transfer reactions should be explained logically on the basis of these data on the ion-pair equilibria, assuming the ion-pair equilibria model is correct. Furthermore, more details of the structural and equilibrium properties of the ion pairs of radical anions are now known. In view of the new structural and equilibrium information, we felt that more systematic studies of the electron-transfer reaction rates could be profitable in obtaining the information concerning the relationship between the reaction rates and the ion-pair structures. Accordingly, we have undertaken more detailed studies on electron-transfer reactions in naphthalene-naphthalenide systems with various alkali metal ions and in various solvents. Although only naphthalene-naphthalenide systems were studied here, the results described in this paper are probably common in many radical-ion systems.

### Experimental Section

All the preparations of samples and the epr measurements are the same as described in the accompanying paper. The rates of rapid electron-transfer reactions were determined from the increase in line widths after the addition of known amounts of naphthalene to the solutions of radical ions according to the procedures already described previously.<sup>8-11</sup> The slow exchange limits were used for all cases except for sodium naphthalenide in mixtures of DME and THF. The calculations of the rate constants are made according to the procedures already described elsewhere.<sup>4,5,7</sup> In the case of sodium naphthalenide in a mixture of DME and THF, a fast exchange limit was used according to the procedures previously described by Chang and Johnson.<sup>10</sup> The solvents used in this work are 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), 2,5-dimethyltetrahydrofuran (DMTHF), and diethyl ether (DEE).

### Results and Discussions

**1. Intensities and Line Widths in Sodium Naphthalenide.** The data on the magnitudes and the line widths of sodium splittings are interpreted in terms of the following equilibrium scheme (eq 1), which is discussed in more detail in the accompanying paper.<sup>1a</sup> The classification of the types of ion pairs into three [(a)



loose ion pair, (b) tight ion pair (1), and (c) tight ion pair (2)] is made according to their respective degrees of solvation as discussed in the accompanying paper. In this paper we are mainly concerned with process 1, the equilibrium between tight ion pair (1) and loose ion pair. Over all the temperature ranges the epr spectra can be treated well in the limit of rapid exchange. Then the observed sodium splittings are given by

$$A_{\text{Na}} = \frac{A_{t1} + K_1 A_l}{1 + K_1} \quad (1)$$

if two equilibrium processes 1 and 2 are well separated. Here  $K_1$  is the equilibrium constant for process 1. The analysis of the ion-pair equilibria was made by this scheme for sodium naphthalenides in THF and the mixtures of THF and DEE. The temperature dependence of the sodium splittings in various mixtures is given in Figure 1, and the results of the analysis are summarized in Table I. Contrary to the case of sodium anthracenide in MTHF,<sup>2</sup> sodium splittings are always temperature dependent. Possibly the separation of the two equilibrium processes 1 and 2 is not complete and both equilibria coexist at some temperatures or the structure of the tight ion pairs is gradually changing. This causes some uncertainties in the estimate of  $A_{t1}$  and, consequently, the thermodynamic quantities calculated from the eq 1. Nevertheless, the plots of  $\log K_1$  vs.  $1/T$  give fairly good straight lines over relatively wide temperature ranges. We believe that the uncertainties in  $\Delta H^\circ$  and  $\Delta S^\circ$  thus determined do not exceed 15%. The magnitudes of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the present systems are very similar to the values already reported for the similar systems, such as sodium anthracenide and sodium 2,6-dibutyl-naphthalenide.<sup>2</sup> Thus the natures of the ion-pair equilibria in the present systems are qualitatively quite analogous to those reported previously, and it is likely that the similar ion-pair equilibria exist in many other systems.  $A_{t1}$  also appears to change gradually as the mixing ratio of THF and DEE is changed. This may be due to the gradual changes of the solvation spheres in the tight ion pair (1) or the gradual structural changes of the tight ion pair with the change of solvent.

As has been discussed previously, the line width of each hyperfine line  $1/T_2$  in case of rapid interconversion is given by<sup>1,2,13</sup>

$$\frac{1}{T_2} = \frac{P_1}{T_{21}} + \frac{P_{t1}}{T_{2t1}} + P_1^2 P_{t1}^2 (W_1 - W_{t1})^2 \tau_{t1} (1 + K_1) \quad (2)$$

(13) N. Hirota and R. Kreilick, *J. Am. Chem. Soc.*, **88**, 614 (1966).

Table I

A. Thermodynamic and Kinetic Data for Interconversion of Loose and Tight Ion Pairs of Sodium Naphthalenide									
System	$K_1$ (-70°)	$-H_1^\circ$ , kcal	$\Delta S_1^\circ$ , eu	$k_1$ , sec <sup>-1</sup> (-70°)	$\Delta H_1^\ddagger$ , kcal	$\Delta S_1^\ddagger$ , eu	$k_{-1}$ , sec <sup>-1</sup> (-70°)	$\Delta H_{-1}^\ddagger$ , kcal	$\Delta S_{-1}^\ddagger$ , eu
THF	4.8	-5.6	-24	...	...	...	...	...	..
THF (0.56) +	0.55	-6.0	-31	$8 \times 10^7$	4.0	-2.0	$1.5 \times 10^8$	9.3	26
DEE (0.44) THF (0.46) +	0.36	-6.0	-33	$1.3 \times 10^8$	3.7	-2.5	$2.8 \times 10^8$	10.3	32
DEE (0.54) THF (0.29) +	0.15	-6.7	-34	$9 \times 10^7$	4.3	-0.2	$4.1 \times 10^8$	10.3	32
DEE (0.71) THF (0.18) +	0.06	-5.2	-31	$6 \times 10^7$	3.8	-3.5	$8 \times 10^8$	8.8	26
DEE (0.82) THF (0.07) +	0.02	-3.4	-24	...	...	...	...	...	..
DEE (0.93) DME (0.05) +	1.55	-4.9	-23	$2.3 \times 10^7$	2.6	-12	$1.5 \times 10^7$	7.0	10
DEE (0.95)									
B. Thermodynamic Data for the Dissociation of Sodium Naphthalenide in THF									
System	$K_1$ (-35°)	$K_1^D$ , (-35°) M	$k_1^D$ , (-35°) M	$\Delta H_1^\circ$ , kcal	$\Delta H_1^\ddagger$ , kcal	$\Delta S_1^\circ$ , eu	$\Delta S_1^\ddagger$ , eu		
THF	0.62	$6.4 \times 10^{-6}$	$1.0 \times 10^{-5}$	-9.2	-3.7	-62	-38		

where  $P_1$  and  $P_{t1}$  are the fraction of the loose and tight ion pairs, and  $\tau_{t1}$  is the lifetime of the tight ion pair.  $1/T_{2l}$  and  $1/T_{2t1}$  are the line width of each species in the absence of interconversion. Since proton hyperfine splittings and  $g$  values vary depending on the ion-pair structures, differences in hyperfine frequencies,  $W_1 - W_{t1}$  are expected to be different for each hyperfine line. Thus, if the ion-pair equilibrium is contributing to the line width significantly, each hyperfine component must have a different line width and depends partic-

sodium naphthalenide in mixtures of THF and DEE can be explained primarily from eq 2, if the correct frequency difference,  $W_1 - W_{t1}$ , is used for each hyperfine component. Since eq 2 is employed to obtain the kinetic information, it is necessary to test its validity.

In order to use eq 2 correctly, we first have to obtain an accurate value of  $W_1 - W_{t1}$  for each hyperfine component. In order to do this, the superposed spectra of sodium naphthalenide in THF and in mixtures of

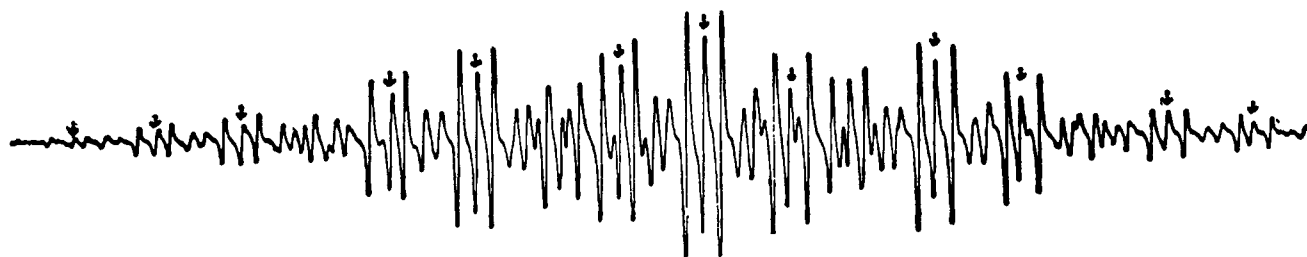


Figure 2. Superimposed epr spectra: sodium naphthalenide in THF and sodium naphthalenide in THF (0.24) + DEE (0.76). Arrows indicate the peaks due to sodium naphthalenide in THF.

ularly on the magnetic quantum number of alkali metal nucleus ( $M_z^M$ ). Such a dependence of the line width on the magnetic quantum number of alkali metal nucleus ( $M_z^M$ ) has been noted by several groups.<sup>1,2,13-15</sup> Although it is agreed that the ion-pair equilibrium is primarily responsible for the line-width variation and the main contribution to  $1/T_2$  comes from  $(M_z^M)^2$  term, slightly different interpretations were given by different authors to the complete analysis of the line-width variations of the entire spectrum.<sup>1,14,15</sup> Therefore it seems appropriate to clarify the nature of the line broadening more precisely. We thought that the line-width variation of the entire spectrum in

THF (0.24) and DEE (0.76) were taken by placing two sample tubings in the cavity at one time. An example of the superposed spectrum is shown in Figure 2.

According to the general theory of relaxation by Freed and Fraenkel<sup>16</sup> and McLachlan,<sup>17</sup>  $1/T_2$  for the  $i$ th line is given by

$$\left(\frac{1}{T_2}\right)_i = a + \sum_{\nu} b_{\nu} M_{\nu}(i) + \sum_{\nu} c_{\nu} M_{\nu}^2(i) + \sum_{\nu \neq \mu} d_{\nu\mu} M_{\nu}(i) M_{\mu}(i) \quad (3)$$

were the  $M_{\nu}(i)$ 's are the resultant nuclear spin quantum numbers for the group of equivalent nuclei corre-

(14) N. M. Atherton, *Chem. Commun.*, 254 (1966).

(15) P. B. Ayscough and P. F. Sargent, *J. Chem. Soc., B*, 900 (1966).

(16) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

(17) A. D. McLachlan, *Proc. Roy. Soc. (London)*, **A280**, 271 (1964).

sponding to the  $i$ th line. If, however,  $i/T_{2i}$  for each hyperfine component is approximately equal in the absence of interconversion process, and the contribution by the interconversion process described by eq 2 is much larger than the contribution from line broadening due to the anisotropy of hyperfine splittings and  $g$  tensor, all the hyperfine lines should fit the equation

$$\left(\frac{1}{T_2}\right)_i = A + B(W_1^i - W_{t1}^i)^2 \quad (4)$$

with appropriate constant parameters  $A$  and  $B$  at one temperature. Here the superscripts represent the  $i$ th hyperfine component.

In the limit of rapid exchange, each hyperfine line is expected to be Lorentzian, and the intensity of each line is inversely proportional to the square of the line width. Thus

$$I_i \propto \frac{1}{\{A + B(W_1^i - W_{t1}^i)^2\}^2} \quad (5)$$

where  $W_1^i - W_{t1}^i$  can be measured from the superposed spectrum if the structures of ion pairs are not much different in two different solvents. This is expected because DEE is a much poorer solvating solvent than THF and THF would solvate preferably toward  $\text{Na}^+$

Table II. Comparison between Measured and Calculated Intensities of the Epr Spectrum of Sodium Naphthalenide

Peak ( $M_z^{\text{H}\alpha}$ , $M_z^{\text{H}\beta}$ )	$M_z$	Binomial intensity	Inten- sity <sup>a</sup> (measd), $A_m$	Inten- sity <sup>b</sup> (calcd), $A_o$	$\frac{A_m - A_o}{A_o}$
(2, 1)	-2	4	5.0	4.8	+0.040
	-1	4	15.2	15.0	+0.013
	+1	4	18.0	17.4	+0.034
(2, 0)	+2	4	6.0	6.1	-0.016
	-2	6	7.4	7.2	+0.028
	-1	6	23.5	22.9	+0.026
	+1	6	25.5	24.6	+0.037
(1, 1)	+2	6	8.1	8.3	-0.024
	-2	16	?	20.1	...
	-1	16	60.2	59.2	+0.017
(1, 0)	+1	16	68.6	68.1	+0.007
	+2	16	21.5	21.5	0.000
	-2	24	30.4	30.7	-0.010
(0, 0)	-1	24	93.0	92.0	+0.011
	+1	24	98.5	97.2	+0.013
	+2	24	33.5	33.3	+0.006
	-2	36	47.0	48.2	-0.025
(-1, 0)	-1	36	?	...	...
	+1	36	?	...	...
	+2	36	46.2	48.4	-0.045
	-2	24	33.0	33.1	-0.003
(-1, -1)	-1	24	95.5	97.1	-0.016
	+1	24	93.0	94.4	-0.015
	+2	24	30.5	29.5	-0.033
	-2	16	23.0	23.8	-0.034
(-2, 0)	-1	16	66.8	67.8	-0.015
	+1	16	58.5	57.0	+0.026
	+2	16	...	...	...
	-2	6	8.0	7.9	+0.011
(-2, -1)	-1	6	23.5	24.1	-0.025
	+1	6	22.5	23.0	-0.022
	+2	6	7.5	7.5	0.000
	-2	4	6.0	6.1	-0.016
	-1	4	16.5	17.3	-0.046
	+1	4	14.6	15.3	-0.046
	+2	4	4.7	4.9	-0.042

<sup>a</sup> THF (0.24) + DEE (0.76) (at  $-90^\circ$ ). <sup>b</sup> Intensities are given in arbitrary units.

ion in the loose ion pair. The comparison between the observed intensities among various peaks, and the ones predicted from eq 5 with constants,  $A$  and  $B$ , is given in Table II. It is clearly seen that the fits between the experimental values and the predicted ones are reasonably good for all lines. A slight systematic deviation, however, was noticeable. This probably arises from the fact that  $A$  cannot be exactly constant for all hyperfine lines as the general relaxation theory predicts. However, this deviation seems to be relatively small compared to the contribution from the rapid ion-pair equilibrium.

**2. Estimate of Rate Constants and Thermodynamic Quantities for the Interconversion.** Since eq 2 describes the observed line-width variation reasonably well, the rates of interconversion were determined using a formula which directly follows from eq 2.

$$k_1 = 2.03 \times 10^7 P_1^2 P_{t1}^2 (1 + K_1) \frac{\Delta H_{\pm 3/2}^2 - \Delta H_{\pm 1/2}^2}{\delta H_{\pm 3/2} - \delta H_{\pm 1/2}} \text{sec}^{-1} \quad (6)$$

Here  $\delta H$ 's are the line widths of the hyperfine lines measured in gauss, and  $\Delta H$ 's are the differences in the hyperfine frequencies between two ion pairs measured in gauss. Subscripts refer to the corresponding magnetic quantum number of sodium nucleus. Usually  $k_1$  was determined for two pairs of lines  $+3/2 - +1/2$  and  $-3/2 - -1/2$ , and the averages were taken.  $k_{-1}$  were obtained from  $k_{-1} = k_1/K_1$ .  $k_1$  and  $k_{-1}$  vs.  $1/T$  are given in Figures 3 and 4. The calculated activation energies, the preexponential factors, and the entropies of activation are given in Table I. The activation energies for the  $k_1$  process is  $\sim 4-5$  kcal, and the preexponential factors were approximately  $10^{11}-10^{12}$   $\text{sec}^{-1}$ .  $\Delta S_1^\ddagger$ 's are found to be small and the degree of solvation does not seem to change much at the transition state. On the contrary, the preexponential factors for the  $k_{-1}$  process are  $\sim 10^{17}$   $\text{sec}^{-1}$  and  $\Delta S_{-1}^\ddagger \sim 30$  eu. Since  $\Delta S_1^\circ$  for the change from tight ion pair to loose ion pair is  $\sim -30$  eu and  $\Delta S_1^\ddagger \sim 0$ , the value of  $\Delta S_{-1}^\ddagger \sim 30$  eu is reasonable. Thus the transition state for the interconversion process must be close to the tight ion pair (1) in THF-DEE mixtures.

**3. Thermodynamic Quantities for Dissociation.** Although we did not make any detailed studies of the dissociation processes of ion pairs into free ions, we often noted peaks due to free ions at lower temperatures. Szwarc and his coworkers made detailed measurements of the conductivity of the solution of radical ions and estimated the dissociation constants of ion pairs.<sup>18</sup> However, in their measurements the distinction between loose and tight ion pairs was not made clear in analyzing the data. Since the equilibrium constants for the equilibrium between loose and tight ion pairs are now known, one can obtain the separate dissociation constants for tight and loose ion pairs.

Suppose that the total dissociation constant is  $K$  and the dissociation constants of loose and tight ion pairs are  $K_1^D$  and  $K_t^D$ , respectively. Using the previous

(18) (a) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966); (b) C. Caravajal, J. K. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

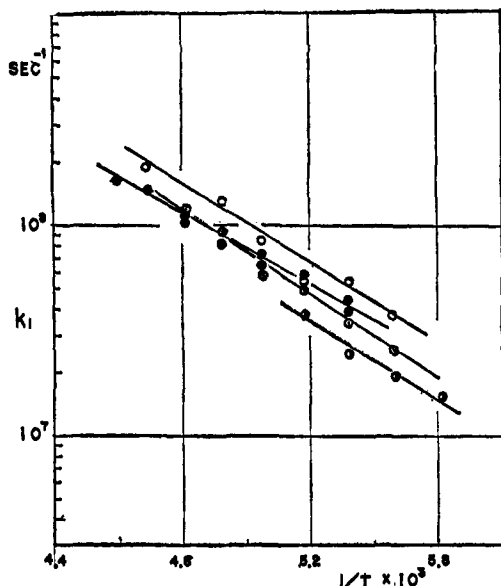


Figure 3. Temperature dependence of  $k_1$  in various solvents: ●, THF (0.56) + DEE (0.44); ○, THF (0.46) + DEE (0.54); ⊙, THF (0.29) + DEE (0.71); ⊕, THF (0.18) + DEE (0.82).

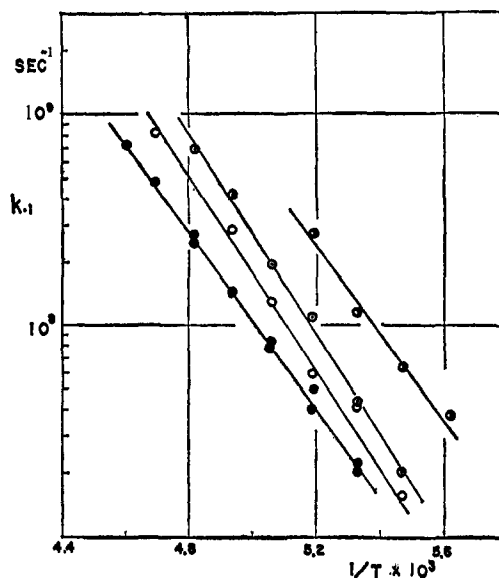


Figure 4. Temperature dependence of  $k_{-1}$  in various solvents: ●, THF (0.56) + DEE (0.44); ○, THF (0.46) + DEE (0.54); ⊙, THF (0.29) + DEE (0.71); ⊕, THF (0.18) + DEE (0.82).

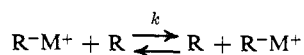
equilibrium scheme,  $K_1^D$  and  $K_t^D$  are given by

$$K_1^D = \frac{K(1 + K_1)}{K_1} \quad (7)$$

$$K_t^D = K(K_1 + 1)$$

Combining our data with Szwarc's data, we obtain separate values of  $K_t^D$  and  $K_1^D$ . Some of these values together with the thermodynamic quantities for each dissociation process are given in Table IB.

**4. The Electron-Transfer Reaction and the Structure of Ion Pairs. Ion-Pair Equilibrium and Electron-Transfer Reaction Rate.** Although there have been a number of studies of electron-transfer reaction rates in hydrocarbon radical anions, there seem to be no detailed studies on the relationship between the ion-pair equilibrium and electron-transfer rates. Since the equilibrium properties of ion-pair equilibria for sodium naphthalenide is well known from the results described in the previous part, details of the electron-transfer reaction were studied in these systems. The reaction is written as



Since the system is ion paired, the electron-transfer reaction is considered to be identical with the ion transfer reaction in the sense that the counterion has to be transferred together with the electron.<sup>19</sup>

The relevant information is shown by the plots of  $\log k$  vs.  $1/T$  for various systems, which are given in Figure 5. As shown in Figure 5, the rates of electron-transfer reactions in sodium naphthalenides in many systems increase at lower temperatures, showing apparent negative activation energies. Such a behavior was previously reported by Zandstra and Weissman in sodium naphthalenide in THF.<sup>5</sup> Our results in THF agree well with their data. If the transfer rates for loose ion pairs are much faster than those for tight ion

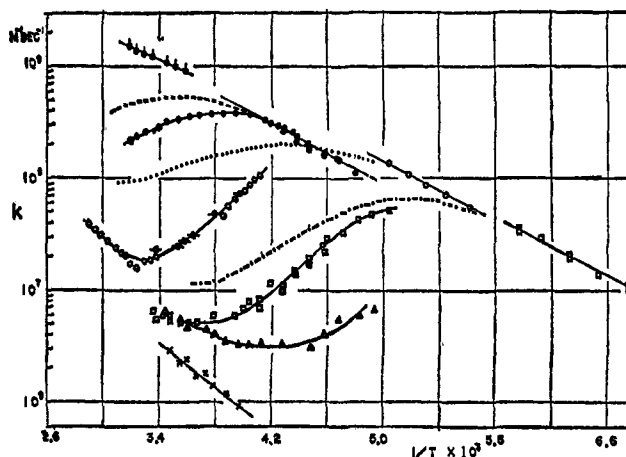


Figure 5. Temperature dependence of the electron-transfer rates of various sodium naphthalenide systems: ●, free ion, THF (0.56) + DME (0.44), rapid exchange; ●, ion pair, THF (0.56) + DME (0.44), rapid exchange; ⊙, ion pair, THF (0.56) + DME (0.44), slow exchange; -●-, THF, measured in this experiment; ○, THF, determined by Zandstra and Weissman; □, THF (0.56) + DEE (0.44); △, THF (0.29) + DEE (0.71); ×, DMTHF; ----, predicted for THF (0.56) + DME (0.44), using eq 8; ·····, predicted for THF using eq 8; -·-·-·, predicted for THF (0.56) + DEE (0.44), using eq 8.

pairs, and the fraction of loose ion pair increases rapidly at lower temperatures, the transfer rates may increase at lower temperatures. Qualitatively this interpretation seems to agree very well with the observations. The electron-transfer rates start to increase when the sodium splitting starts to decrease sharply. The temperature at which  $d \log k/d(1/T)$  changes the sign increases in the following order: DME (0.44) + THF (0.56) > THF > THF (0.56) + DEE (0.44) > THF (0.29) + DEE (0.71). The numbers in parentheses represent the mole fractions. This is exactly the same order as the decrease of the sodium splitting shown in Figure 1. This certainly confirms the qualitative correctness of our model. Closer inspection of the figure reveals several interesting features on the electron-transfer rates.

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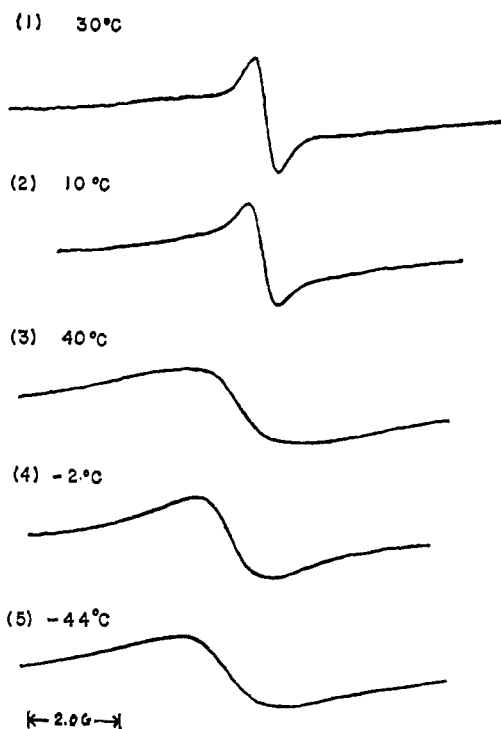


Figure 6. Spectra of sodium naphthalenide in THF (0.56) + DME (0.44) in the rapid exchange limit; 0.867 *M* naphthalene was added. Spectra 1 and 2 were taken at low concentration of naphthalenide. The central peak represents the free-ion spectrum: (1) 30°, (2) 10°. Spectra 3–5 were taken at high concentration of naphthalenide. Spectra represent those of loose ion pairs: (3) 40°, (4) 2°, (5) –44°.

(a) Na splitting in sodium naphthalenide approaches zero at lower temperatures, and only the spectra without Na splittings are obtained at further lower temperatures. The dissociation constants of these ion pairs are about  $10^{-5} M^{-1}$ ,<sup>18</sup> and the spectra are predominantly due to loose ion pairs, if the concentrations of radical anions are kept higher than  $10^{-4} M$ . In certain temperature ranges, the line widths are considerably broader than those for free ions and decrease with the decrease of temperature, although the sodium splittings are not observable. Under this circumstance the sodium splittings are not resolved but clearly contribute to the line width, and the spectrum without sodium splitting is mainly due to a loose ion pair and not a free ion. The electron-transfer reaction between naphthalene and sodium naphthalenide loose ion pair can be studied using these temperature and concentration ranges.  $\log k$  vs.  $1/T$  given by a straight line at the right-hand side of Figure 5 represents plots for such reactions. It is seen that the electron-transfer rates for loose ion pairs in THF and mixtures of THF and DEE have activation energies of  $\sim 3$  kcal, and the rate constants extrapolated to room temperature are  $\sim 10^9 M^{-1} \text{sec}^{-1}$ . These rates and activation energies for loose ion pairs are very close to those for free ions. Thus the loose ion pairs behave almost like a free ion as to the electron-transfer reactions in these systems. These rates and activation energies are very close to those for diffusion-controlled reactions. This statement is further confirmed by the observation in rapid exchange limit in sodium naphthalenide in 50:50 DME and THF mixtures (Figure 6). At higher temperatures the

spectra are clearly the superposed spectra, possibly one from free ion and the other from ion pair undergoing rapid interconversion. By adjusting the concentration one can obtain the spectra for mostly free ion or those of mostly equilibrium mixtures of ion pairs. In the temperature range from 44 to 0°, the line width for the free ion slightly increases with the decrease of temperature, indicating a small activation energy, but the spectrum for the ion pair narrows as the temperature goes down, indicating a negative activation energy. At further lower temperatures, the line width for the ion pair starts to increase, indicating a normal activation energy. The spectrum in this region possibly represents that of the loose pair if the concentration of the radical is relatively high. The electron-transfer rates for separated species are given in Figure 5.

The fact that the rates and activation energies for loose ion pairs are almost the same as those for free ions seems to be noteworthy. As mentioned in the beginning of the section, the electron-transfer reaction for the ion pair is also an ion-transfer reaction, and the sodium ion has to be transferred when the electron is transferred. If the positive ion is very loosely bound in the loose ion pair, the transfer of an electron may take place whenever a negative ion encounters a neutral molecule, regardless of the position of the positive ion. However, if the interaction between the positive and the negative ions is still relatively strong in the loose ion pair, the neutral molecule may have to assume a favorable orientation with respect to the positive and negative ions in order for the electron to be transferred. If this is the case, the transfer rates for loose ion pairs may seem to be slower than for free ions. However, the positive ion is probably moving very rapidly around the negative ion, because they are only loosely bound. If the motion of the positive ion with respect to the negative ion is very fast, the reorganization of the orientation takes place within a very short time and the favorable orientation for the electron transfer may be obtained within the time in which the colliding pair stays close (possibly  $\sim 10^{-10}$  sec). Then the transfer rate will be close to the diffusion-controlled rate.

(b) At the extreme left hand of the figure,  $d \log k / d(1/T)$  is negative and again shows the normal temperature dependence. From the data for the ion-pair equilibria, the ion pairs are known to be primarily tight ion pairs in these temperature ranges. Thus the  $\log k$  vs.  $1/T$  plots represent those for tight ion pairs. The activation energies are  $\sim 5$  kcal and the frequency factors are  $10^{11} M^{-1} \text{sec}^{-1}$ .

(c) In the intermediate temperature ranges the ion pair is undergoing very rapid interconversion between tight and loose pairs. The observed electron-transfer rate would be given by the weighted average of the rate of each species, if the lifetime of each species is longer than the time in which the reacting molecules stay in the same solvent cage. Then the observed rate is given by

$$k = P_1 k_1 + P_{t1} k_{t1} = P_1 k_1^\circ \exp\left(-\frac{E_{a1}}{RT}\right) + P_{t1} k_{t1}^\circ \exp\left(-\frac{E_{at1}}{RT}\right) \quad (8)$$

Here,  $P_1$ ,  $P_{t1}$ ,  $k_1$ ,  $k_{t1}$ ,  $E_{a1}$ , and  $E_{at1}$  are the fractions, the rates of electron transfer, and the activation energies

for loose and tight ion pairs, respectively.  $P_t$  and  $P_{t1}$  are known from the splitting measurements, and  $E_{at}$  and  $E_{at1}$  can be estimated from the data in the limiting cases. The plots of the predicted  $k$  are given in Figure 6 together with the observed  $k$ . Qualitatively, the observed  $k$  and the predicted  $k$  agree with each other, but they do not agree quantitatively, particularly at the temperatures where  $P_{t1}$  is small. The observed  $k$  is generally smaller than the predicted  $k$ . Of course the extrapolated values for  $k_{t1}$  and  $k_1$  are used in the calculation, and some uncertainties are always involved. However, the deviation seems to be larger than expected from these uncertainties. Although we have no definite explanation for these deviations, we can suggest some possible explanations. First, one would obtain slower rates at higher temperatures, if the loose ion pairs become more tightly bound and  $k_1$  at higher temperatures are considerably smaller than those expected from the extrapolation of low-temperature values. Another possibility is the inability to use eq 8 in the present systems. In the intermediate temperature ranges the major contribution to the over-all rate comes from the contribution due to loose ion pairs. If the lifetime of a loose ion pair becomes very short ( $\sim 10^{-10}$  or less), the loose ion pair may be converted to a tight ion pair before the favorable orientation for electron transfer is obtained. In this case the transfer of electron does not take place in every encounter between a loose ion pair and a neutral molecule. The rate will be slower than that predicted from eq 8. This suggestion is, of course, very speculative, but there seems to be such a possibility.

**Electron-Transfer Rates and the Nature of Counterion and Solvent.** In order to study how the electron-transfer reaction rates correlate with the structures of ion pairs, we have studied the transfer rates in a number of different ion pairs with different alkali metals in different solvents. Such studies were already undertaken in the original studies by Ward and Weissman,<sup>8</sup> but the improved resolution and the sensitivity of the spectrometer make it possible to obtain more detailed information. More recently Chang and Johnson<sup>10</sup> also obtained the rates for free ions and ion pairs in several systems using the rapid exchange limit.

(i) **Loose Ion Pair. Lithium and Sodium Naphthalenide.** As shown in Figure 7, the rates and the activation energies for the loose ion pairs are close to those for diffusion-controlled reactions. However, the rate seems to depend slightly on the counterion and solvent. In THF the rate for Li ion pair is slightly slower than for Na ion pair, and the rate for Na ion pair in DME is slower than that in THF. The loose ion pairs in these systems are probably solvent separated, but the electrostatic interaction between positive and negative ions would be stronger for the Li pair than for the Na pair, and stronger in DME than in THF for the same cation because the solvated positive ion with its solvation shell is probably smaller for Li than for Na and for DME than for THF. These factors seem to affect the rates slightly and the small differences in rates and activation energies appear to be observed.<sup>20</sup>

(20) It should be noted that Szwarc and his coworkers found that the dissociation constant for solvent-separated (solvated) ion pair is larger for sodium naphthalenide in THF than for sodium naphthalenide in DME, indicating the smaller size of solvated ion for DME than for THF; see ref 18.

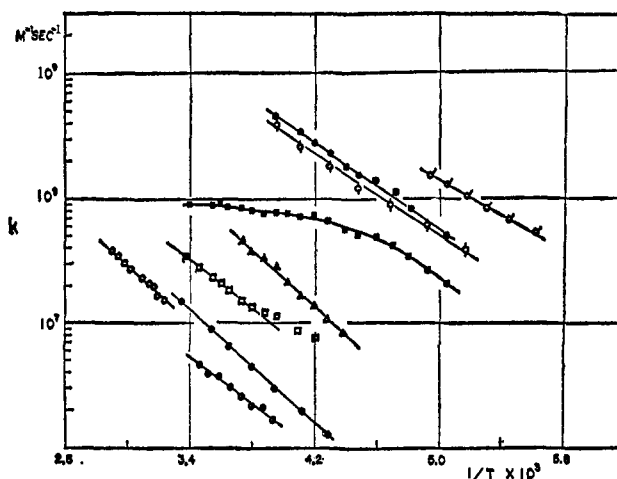


Figure 7. Temperature dependence of the electron-transfer reaction rates for various naphthalenides:  $\circ$ , Na, THF, tight ion pair;  $\bullet$ , Na, THF, loose ion pair;  $\odot$ , Na, DME;  $\ominus$ , Na, DEE;  $\square$ , Na, DMTHF (0.50) + DEE;  $\triangle$ , Li, DME;  $\blacksquare$ , K, DME;  $\square$ , K, THF;  $\blacktriangle$ , Cs, THF.

(ii) **K Ion Pair and the Ion-Pair Equilibrium.** Although no potassium splitting was observed in potassium naphthalenide, the data for electron-transfer reactions indicate that these systems exist as ion pairs. As far as the electron-transfer reaction data indicate, potassium naphthalenide in THF forms relatively tight ion pairs because the transfer rates are much slower than those for free ions. The rate constant is considerably smaller than that for the sodium naphthalenide loose ion pair. The rate for potassium naphthalenide in DME is slightly faster than that for potassium naphthalenide in THF. The temperature dependence of the rate is quite different from other systems and extremely small at temperatures from 24 to  $-30^\circ$ . The plot of  $\log k$  vs.  $1/T$  approaches normal behavior at lower temperatures ( $< -30^\circ$ ), but the rate is slower than for sodium naphthalenide in DME at the same temperatures. The  $\log k$  vs.  $1/T$  plot suggests that the system exists as an equilibrium mixture between different ion pairs. This system, however, does not give any negative activation energy. The change in the fraction between different ion pairs is probably not rapid enough to change the sign of apparent activation energy, but is enough to produce anomalous behavior in the  $\log k$  vs.  $1/T$  plot. This implies that  $\Delta H_1^\circ$  for this system is relatively small. The differences in  $k_t$  and  $k_1$  may also be smaller in this system than in sodium naphthalenide systems.

(iii) **Tight Ion Pairs.** As described in the accompanying paper, some systems exist as equilibrium mixtures of two tight ion pairs. In order to see whether or not the structural difference in tight ion pairs affects the rates of electron-transfer reaction much, we have measured electron-transfer reaction rates in several tight-ion-pair systems of sodium naphthalenide. The rates were found to be not very much different from that for sodium naphthalenide in THF. Sodium naphthalenide in THF at higher temperatures, potassium naphthalenide in THF, and cesium naphthalenide in THF all appear to form tight ion pairs. The rates decrease in the order, Na < K < Cs.

(iv) **The Activation Energies and the Preexponential Factors in Electron-Transfer Reactions.** The acti-

**Table III.** Rate Constants and Activation Energies for Electron-Transfer Reactions. Sodium Naphthalenide + Naphthalene

System	Characterization	Temp, °C	$k \times 10^{-8} M^{-1} \text{sec}^{-1}$	$E_a^a$ , kcal	Log $A^a$
Li, THF	Loose ion pair	-30	2.6	3.6	11.7
Na, DME	Loose ion pair	-30	3.4	3.6	11.8
Na, DME, THF	Loose ion pair	-55	1.7	3.3	11.5
Na, DME, THF	Free ion	24	12	2.5	10.9
Na, THF	Loose ion pair	-70	1.5	3.1	11.2
Na, THF	Equil mixture	-10	0.47	...	...
Na, THF	Tight ion pair	57	0.27	4.6	10.5
Na, THF, DEE	Loose ion pair	-105	0.35	2.9	11.3
Na, DEE	Tight ion pair	10	0.09	5.1	10.9
Na, DMTHF	Tight ion pair	15	0.03	5.1	10.3
K, THF	Tight ion pair (?)	24	0.32	4.2	10.6
K, DME	Equil mixture	24	0.99	...	...
Cs, THF	Tight ion pair	0	0.38	5.1	11.8

<sup>a</sup> Determined from the equation  $k = A \exp(-E_a/RT)$ .

vation energies and the preexponential factors determined for the electron-transfer reactions studied in the present investigations are summarized in Table III. The rates for loose ion pairs at 25° are of the order  $10^9 M^{-1} \text{sec}^{-1}$  and the rates for tight ion pairs range from  $10^8$  to  $5 \times 10^6 M^{-1} \text{sec}^{-1}$ . The activation energies are 2.9–3.6 kcal for loose ion pairs and 4–6 kcal for tight ion pairs. The preexponential factors are  $\sim 10^{10}$ – $10^{12} M^{-1} \text{sec}^{-1}$  for most systems irrespective of the type of ion pair. Neither abnormally high activation energies nor high preexponential factors as reported in the previous work<sup>5</sup> were obtained in the

present systems. The slower rates in the tight-ion-pair systems seem to be primarily due to the higher activation energies. These energies would be required to remove some solvent molecules from the solvation sphere and to reorganize the solvation sphere to form a transition state, in which the positive ions are shared between two organic molecules, and the environment with respect to two organic molecules is symmetric.

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## Hyperfine Splittings from Naturally Occurring Sulfur-33 in Electron Paramagnetic Resonance Spectra

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**Abstract:** The cation radicals of 1,4-dithiin, 1,4-benzodithiin, phenoxathiin, thianthrene, and some substituted thianthrenes have been reinvestigated in the  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  system. Improved resolution has enabled the proton splitting constants to be analyzed in greater detail than previously possible. Naturally occurring sulfur-33 hyperfine splittings have also been detected in all cases. The theory of the <sup>33</sup>S splittings has been considered using the Karplus-Fraenkel formulation. Using spin densities calculated from the McLachlan molecular orbital method, it is found that an equation of the form  $a^S = Q_S^S(\text{C}_2\text{P})\rho_S^\pi$  holds to a good approximation, where  $Q_S^S(\text{C}_2\text{P}) = +33.4 \pm 0.7 \text{ G}$ .

The low natural abundance of sulfur-33 (0.74%) has made measurements of the hyperfine splitting from this nucleus in esr spectra difficult to detect without resorting to enriching procedures.<sup>1</sup> In fact, only recently has it been found possible to measure these hyperfine splittings in organic radicals<sup>2</sup> with a natural abundance of <sup>33</sup>S. The cation radicals of a number of sulfur compounds have been previously studied in 98% sulfuric acid,<sup>3–5</sup> but in some cases only a partial analysis of the

proton hyperfine interactions has been possible owing to incomplete resolution.

Recent work with other methods of producing cation radicals<sup>2,6</sup> indicated that these compounds might yield further information if the radicals were produced differently. The cation radicals of 1,4-dithiin (1), 1,4-benzodithiin (2), thianthrene (3), phenoxathiin (4), and some substituted thianthrenes were therefore reinvestigated using the aluminum chloride-nitromethane system to produce the radicals.<sup>6,7</sup>

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