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Electron Paramagnetic Resonance Studies of Ion Pairs. Structures and Equilibria in Alkali Metal Naphthalenide and Anthracenide

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Abstract: Epr studies of ion pairs in alkali metal naphthalenide and anthracenide in various ethereal solvents are reported. The classification of different types of ion pairs are based on the temperature dependence of the alkali metal splitting and the line-width dependence on the magnetic quantum number of alkali metal nuclei. The evidence for the existence of rapid equilibria between two different tight ion pairs are given for sodium naphthalenide and anthracenide. The perturbation of the proton hyperfine splittings by the counterions was studied in detail for anthracenides. The implication of such studies for the structural elucidation of ion pairs is discussed. The alkali metal splittings observed in these systems are briefly discussed.

Since the pioneering work of Adam and Weissman¹ and Atherton and Weissman,² there have been a number of epr investigations on the ion pairs of hydrocarbon negative ions with alkali metal ions.³⁻⁹ It is, however, only recently that the detailed nature of the structural and equilibrium properties of these systems began to be understood. In the previous papers, epr studies of the ion-pair equilibria between loose and tight ion pairs in sodium anthracenide, sodium 2,6-dibutyl-naphthalenide, and sodium naphthalenide were described.^{10,11} The

existence of two different classes of ion pairs, loose ion pair and tight ion pair, and the rapid equilibrium among them seem to be now well established from the work by Hogen-Esch, Smid, Szwarc, and their coworkers^{12,13} and our previous work.^{10,11}

Our preliminary studies, however, indicated that the nature of tight ion pair strongly depends on the nature of counterion and solvent. The classification of ion pairs into two classes, loose and tight ion pairs, was found to be too crude to describe the microscopic properties of some ion pairs, and finer distinction in tight ion pairs was necessary.¹¹ Accordingly, we have carried out more systematic studies of the tight ion pairs with all the alkali metal ions. Our present investigations clearly show the existence of rapid equilibrium between two different tight ion pairs in several systems. Here we describe the nature of tight ion pairs together with more general description of the ion pairs in general.

In the preliminary work we noted a systematic correlation between the perturbation to the proton hyper-

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(2) N. M. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961).

(3) H. Nishiguchi, Y. Nakai, K. Nakamura, I. Ishizu, Y. Deguchi, and H. Takaki, *Mol. Phys.*, **9**, 153 (1965).

(4) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

(5) E. de Boer, *Rec. Trav. Chim.*, **84**, 609 (1965).

(6) M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Japan*, **37**, 1651 (1964).

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

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

(9) A detailed review of the field was given by Symons. Most of the data obtained before 1966 are summarized in this review: M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967).

(10) (a) N. Hirota and R. Kreilick, *J. Am. Chem. Soc.*, **88**, 614 (1966); (b) A. H. Crowley, N. Hirota, and R. Kreilick, *J. Chem. Phys.*, **46**, 4815 (1967).

(11) 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).

(12) (a) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); (b) *ibid.*, **88**, 307 (1966).

(13) (a) C. Carvajal, J. K. Toelle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965); (b) R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965); (c) P. Chang, R. V. Slates, and M. Szwarc, *ibid.*, **70**, 3180 (1966).

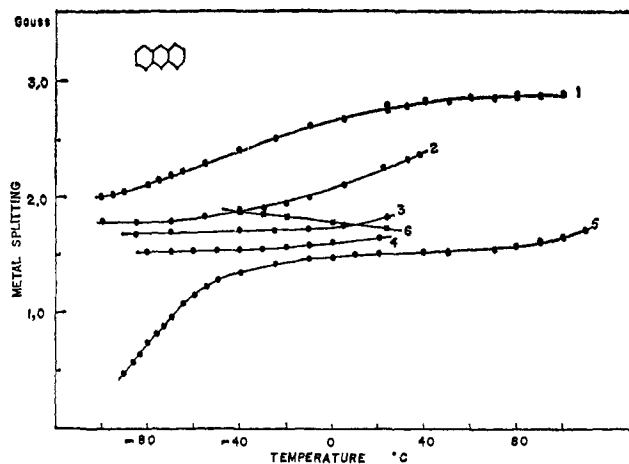


Figure 1. Temperature dependence of alkali metal splittings of tight ion pairs in various solvents. Sodium anthracenide (●): (1) DEE, (2) DEE (0.95) + MTHF (0.05), (3) DEE (0.80) + MTHF (0.20), (4) DEE (0.51) + MTHF (0.49), (5) MTHF. Lithium anthracenide (■): (6) DEE.

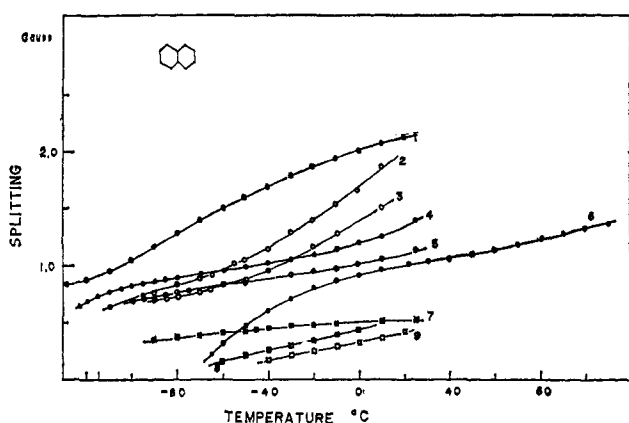


Figure 2. Temperature dependence of alkali metal splittings of tight ion pairs. Sodium naphthalenide, ●, ○, ○: (1) DEE, (2) DEE (0.50) + DMTHF (0.50), (3) DMTHF, (4) DEE (0.93) + THF (0.07), (5) MTHF, (6) THF. Lithium naphthalenide, ■, □, □: (7) DEE, (8) DEE (0.93) + THF (0.07), (9) DEE (0.18) + THF (0.82).

fine splittings by counterions and the magnitudes of the sodium splittings in sodium anthracenide.¹¹ We have extended such investigations to the system with other alkali metal ions. We have also compiled more systematic data on the alkali metal splittings. We thought that detailed studies of the proton and alkali metal splittings would give more detailed information concerning the structure of ion pairs and the nature of binding and interaction in ion pairs. In this paper we only describe the experimental results on these problems, but it is hoped that the detailed theoretical analysis of these data, to be given later, will lead to knowledge of the detailed structures of ion pairs.

The kinetic aspects of ion-pair equilibria and the relationship between the ion-pair structures and the rates of rapid electron-transfer reactions are discussed in the accompanying paper.

Experimental Section

The preparation of radical ions was made according to the standard procedure already described elsewhere.^{14,15} The preparation

(14) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(15) T. R. Tuttle, Thesis, Washington University, 1957.

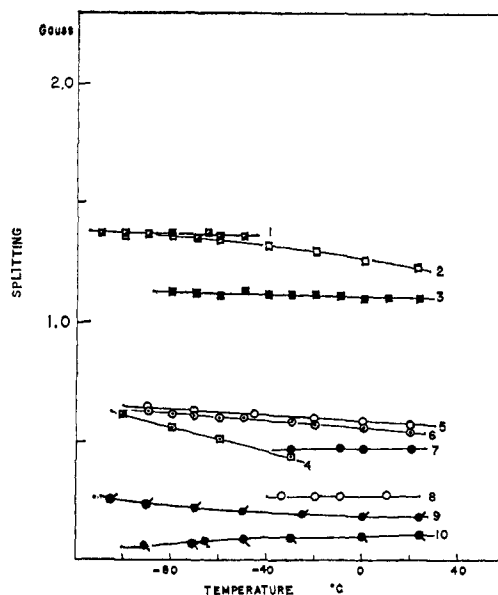


Figure 3. Temperature dependence of alkali metal splittings of tight ion pair potassium, rubidium, and cesium naphthalenide and anthracenide. □, ▤, ■, □, naphthalenide: (1) Cs, DEE (0.51) + MTHF (0.49), (2) Cs, MTHF, (3) Cs, DME, (4) Rb, THF. ○, ●, ⊙, ●, anthracenide: (5) Cs, MTHF, (6) Cs, THF, (7) Cs, DME, (8) Rb, DEE, (9) K, DEE, (10) K, MTHF.

of alkali metal naphthalenides and anthracenides in diethyl ether solution was carried out at lower temperatures (*ca.* -20 to -60°) in order to avoid easy decomposition of the radical anions in this solvent at higher temperatures. All of the epr spectra were taken with a Varian V-4502 spectrometer, equipped with a field dial and a variable-temperature control unit. The estimated accuracy of the temperature measurement is $\pm 2^\circ$.

The chart paper was marked with pips at appropriate intervals, while the spectrometer was being scanned by the field dial. The field strength of the pip position was calibrated by use of a Harvey Wells proton gaussmeter and a Hewlett-Packard frequency counter. All the hyperfine frequencies were determined from the above procedure, except in the case of some naphthalenides. In the latter case, the spectrum was taken together with sodium or potassium naphthalenide in DME or THF whose spectra served as standards.

The usual concentrations of the negative ions are roughly estimated to be 10^{-4} – 10^{-5} M, but no accurate concentration was determined. The solvents used in this work are 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), diethyl ether (DEE), and 2,5-dimethyltetrahydrofuran (DMTHF).

Detailed investigations on the alkali metal splittings and proton hyperfine splittings have been made. Some of the preliminary results of these investigations were reported in ref 11.

Results

1. Temperature Dependence of the Alkali Metal Splittings. The alkali metal and proton hyperfine splittings in various alkali metal naphthalenides and anthracenides were investigated under various conditions. The temperature dependence of the alkali metal splittings is given in Figures 1–3.

The temperature dependence of the metal splittings appears to be classified roughly into two categories: (1) decrease of the alkali metal splittings (A_M) with decrease of temperature (the systems are lithium, naphthalenide in DEE, MTHF, and THF, sodium naphthalenide in THF, DEE, and MTHF, sodium anthracenide in THF, MTHF, and DEE, and potassium anthracenide in MTHF; in many cases $|dA_M/dT|$ is relatively large); and (2) increases of the alkali metal splittings with decreases

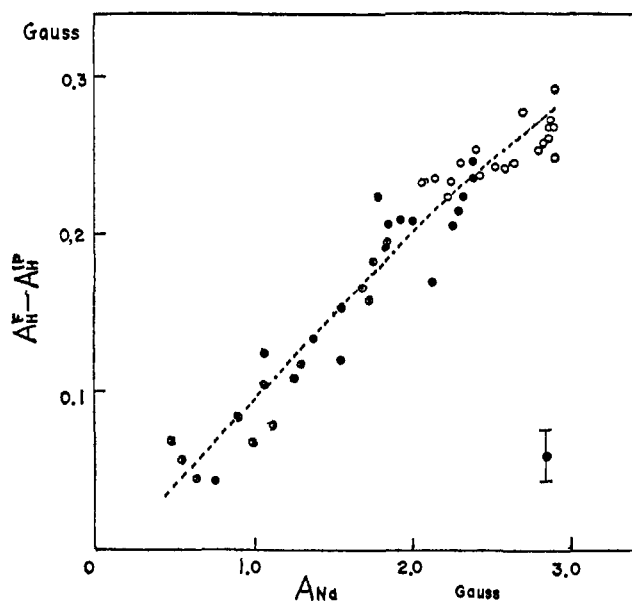


Figure 4. Correlation between sodium splittings and the perturbation to proton splittings ($A_H^F - A_H^{IP}$) in anthracenide: \circ , Na, DEE; \bullet , \odot , Na, DEE + THF; \otimes , Na, MTHF; \ominus , Na, MTHF + THF.

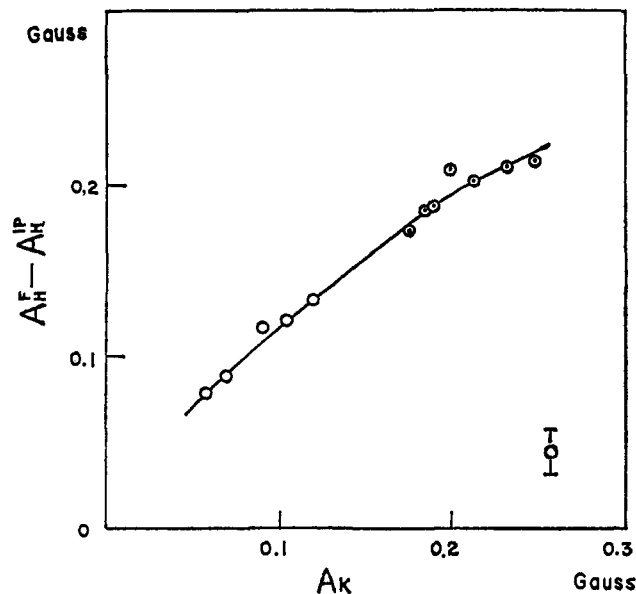


Figure 5. Correlation between potassium splittings and the perturbation to proton splittings ($A_H^F - A_H^{IP}$) in anthracenide: \odot , K, DEE; \ominus , K, MTHF.

of temperature. (The systems are lithium anthracenide in DEE, potassium anthracenide in DEE, rubidium naphthalene in THF and DME, rubidium anthracenide in DEE, cesium naphthalene in MTHF and THF, cesium anthracenide in MTHF and THF; generally $|dA_M/dT|$ is small with the exceptions of potassium anthracenide in DEE and rubidium naphthalene in THF.)

2. Perturbation of Proton Hyperfine Splittings. It has been noted that a unique correlation between the proton hyperfine splittings and the sodium metal splittings exists in anthracenide systems.¹¹ We have investigated more thoroughly the systematic perturbation due to the counterions. The correlation is given in Figure 4 or 5 for anthracenide. Since the proton hyperfine splittings in free ion (A_H^F) are slightly temperature dependent, $|A_H^F - A_H^{IP}|$ is plotted against T in Figures 4 and 5. Here A_H^{IP} are the proton hyperfine splittings in ion pairs and A_H^F are those for free ions. The splittings due to the protons at the 1, 5, 7, and 8 positions (α splittings) were chosen for this study because of the ease of experimentation. Reddoch⁴ previously reported the systematic perturbation among different proton hyperfine splittings (α , β , and γ) in anthracenides. We have checked such correlation among α , β , and γ splittings in anthracenide and confirmed that the systematic perturbation similar to that reported by Reddoch exists in all the anthracenide systems we investigated. The correlation between different proton splittings in anthracenides is given in Figure 6. Figures 4 and 5 together with Figure 6 are enough to obtain the correlation between all the proton hyperfine splittings and the alkali metal splittings. Although the experimental points are slightly scattered, it appears that there exist good correlations between the proton hyperfine splittings and the alkali metal splittings within the limit of our experimental uncertainties.

Attempts to check whether or not a similar correlation between the proton and the sodium splittings exists

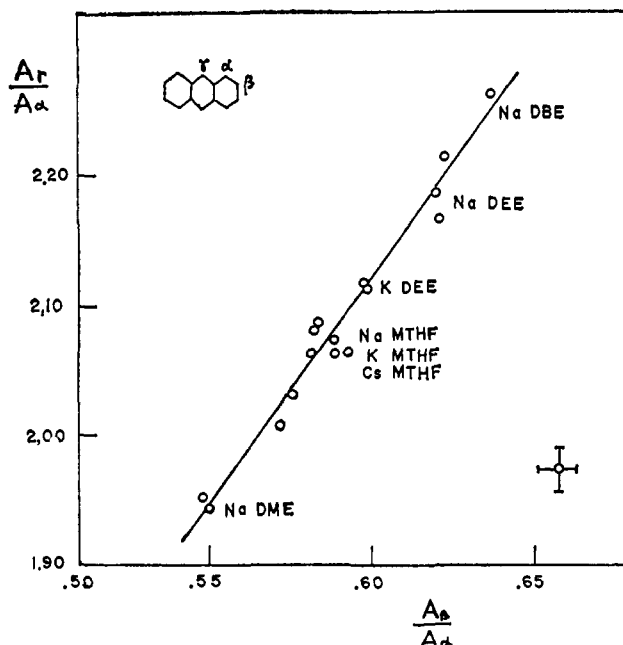


Figure 6. Correlation between α , β , and γ splittings in various anthracenides.

in naphthalene was made in a few cases. The magnitude of the perturbation, however, is smaller and the collection of the reliable data is considerably more difficult. Therefore, only a few cases (sodium naphthalene in DME, THF, mixture of THF and DEE, and DEE) were studied. Within our limited number of examples and limited experimental accuracy, we failed to detect any regular correlation between the proton and the sodium splittings.

3. Line Widths of the Hyperfine Components. The line widths of the components of alkali metal splittings often depend on the magnetic quantum number of the alkali metal nucleus (M_z^M). The details of the line-width analysis in case of the rapid equi-

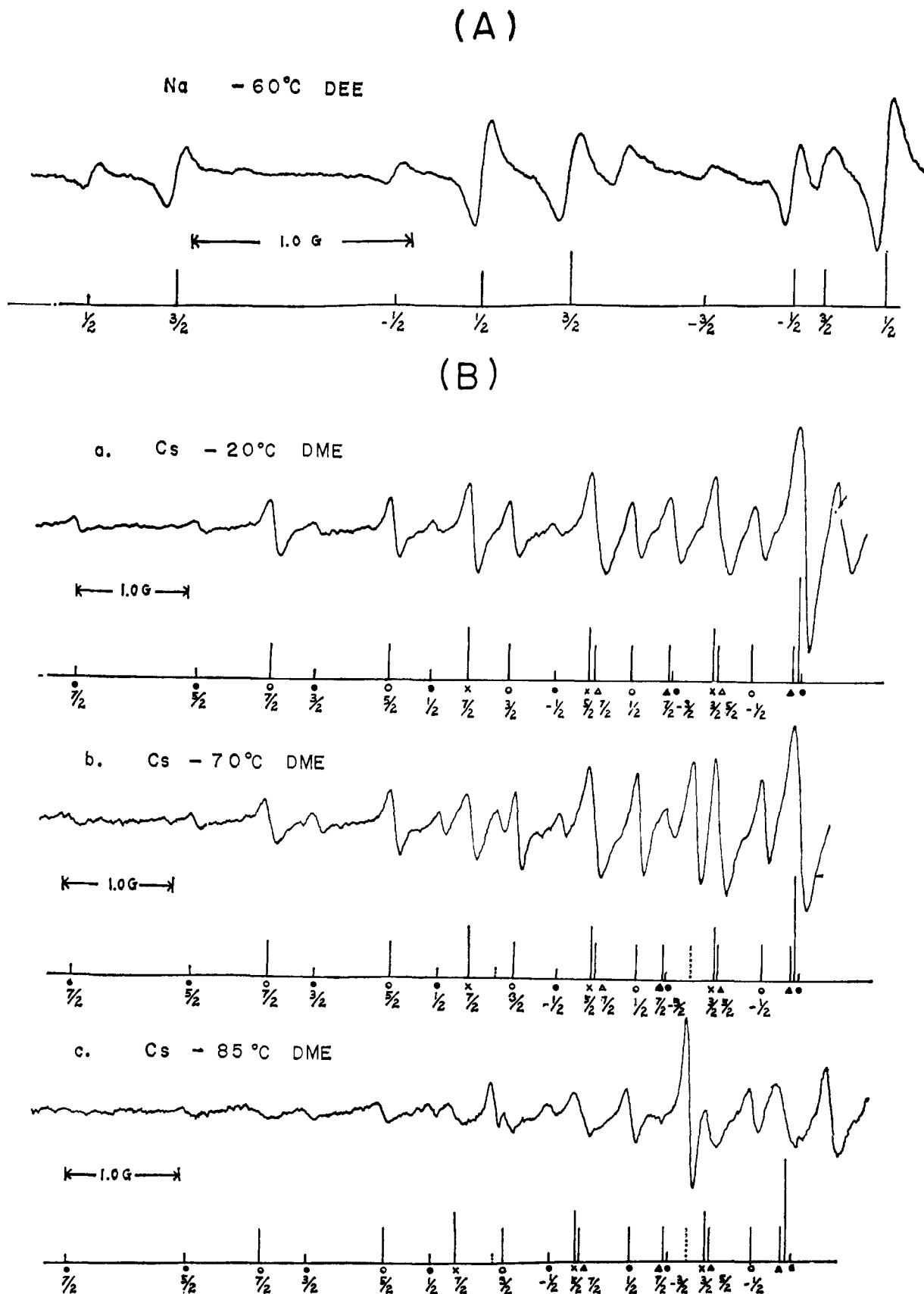


Figure 7. Epr spectra of ion pairs with $(M_2^M)^2$ -dependent line widths: (A) sodium naphthalenide in DEE at -60° ; (B) cesium naphthalenide in DME at (a) -20° , (b) -70° , and (c) -85° . - - - indicates the peaks due to dissociated species.

librium between tight and loose ion pairs in sodium naphthalenide is discussed in the accompanying paper. In the present article we mainly confine ourselves to

the tight ion pairs. Marked M_2^M dependences of the line widths were observed, however, in several tight ion-pair systems, indicating the existence of the rapid

process within tight ion pairs. Sodium naphthalenide in DEE and sodium anthracenide in DEE and in some mixtures of DEE and MTHF are these examples. Besides these and the cases reported in the previous papers,^{10,11} the systems in which marked M_2^M -dependent line-width changes were observed include lithium naphthalenide in DEE and mixtures of DEE and MTHF and cesium naphthalenide in DME. The spectra of cesium naphthalenide in DME and sodium naphthalenide in DEE are shown in Figure 7.

Discussion

1. Temperature Dependence of the Alkali Metal Splitting. The observed alkali metal splitting (A_M) is the weighted average of the splittings at different states, if the averaging process is rapid.² Different states can be structurally different ion pairs in one extreme or different vibrational states of an ion pair in the other extreme. The time required for averaging two or more structurally different ion pairs is usually much slower than the vibrational relaxation time (10^{-12} sec or shorter). Therefore, the averaging processes could be separated into two classes. Then

$$A_M = \sum_i P_i A_i \quad A_i = \sum_\nu P_\nu A_\nu \quad (1)$$

where P_i and P_ν represent the fractions of the states i and ν . The first sum goes over thermodynamically different states such as structurally different ion pairs. The second sum goes over all the vibrational states. The distinction into two classes is mainly for convenience, and clear separation may not be valid in some cases. However, if the system stays in one state longer than 10^{-10} sec, it is probably appropriate to talk about thermodynamically stable different structures. Temperature dependence of the splitting is brought in by the change of P_i and P_ν in the above summation.

Practically the most important case is the rapid equilibrium between two different ion pairs A and B. As already discussed in the previous papers, the observed splitting A_M is given by^{10,11}

$$A_M = \frac{A_M(A) + K A_M(B)}{1 + K} \quad (2)$$

with the equilibrium constant K . In case of the rapid equilibrium between two different ion pairs, the line width of each hyperfine component is given by the well-known formula¹⁶

$$\frac{1}{T_2} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} + P_A^2 P_B^2 (W_A - W_B)^2 \tau_A (1 + K) \quad (3)$$

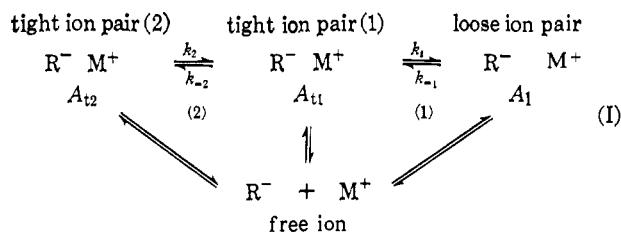
where W_A and W_B are the resonant frequencies of the ion pairs A and B. As already discussed in previous papers,^{10,11} ion-pair equilibrium makes significant contributions to the line widths in many systems, when τ_A is the order of 10^{-8} sec or longer. Since the line-width contribution from this mechanism depends strongly on $(M_2^M)^2$, such a broadening gives strong support for the existence of the rapid ion-pair equilibria. The contribution to the line width from the usual vibrational motion is likely to be negligibly small. Thus each component of the alkali metal splitting is expected to have the

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 222.

same line width, if no ion-pair equilibrium exists. In this article different behaviors of the different types of ion pairs are discussed based on the temperature dependence of the magnitude and the line width of the alkali metal splitting.

a. Rapid Equilibrium between Different Ion Pairs. Most convincing evidence for the existence of rapid equilibrium between different ion pairs should be the line-width dependence on M_2^M as described above. However, if the equilibration is very rapid, the line-width effect may not be detected. The ion-pair equilibrium is often accompanied by the large change in ΔH° and ΔS° , but the possibility of the very small ΔH° and ΔS° should not be excluded.

The prototype of this class is well exemplified by sodium anthracenide in various ethereal solvents. The equilibrium processes in this system appear to be adequately described by the scheme in eq I. The position



of the equilibrium strongly depends on factors such as temperature and nature of the solvent. The dissociation of ion pairs into free ions have been studied extensively by Szwarc and his coworkers.^{13a} Although we did not make any quantitative measurements, we have often detected the peaks due to free ions. Our rough estimates of the order of magnitudes of dissociation constants seem to agree reasonably well with Szwarc and his coworkers' values.

The equilibrium process 1 (in eq I) has been described in detail in the previous papers^{10,11} and is not discussed in this paper. No alkali metal splitting was observed for loose ion pair, and it is considered that they are solvent-separated ion pairs. The magnitudes of the alkali metal splittings in the tight ion pair (1) depends on the nature of the solvent; ~ 1.5 – 2 G for sodium anthracenide and ~ 0.6 – 1.2 G in sodium naphthalenide were observed depending on the solvent. The existence of the second equilibrium (2) in eq I appears to be very clear in sodium anthracenide in DEE from the temperature dependence of the alkali metal splitting and the line-width dependence on M_2^M . The temperature dependence of the sodium splitting in sodium anthracenide in DEE and in the mixed solvents of DEE and THF can be analyzed by the use of eq 2 with $A_M(A) = 2.95$ G and $A_M(B) = 2.02$ G for DEE. The plot of $\log K_2$ vs. $1/T$ is shown in Figure 8, and the analysis in terms of eq 2 appears to be quite satisfactory. Similar analysis can be applied to sodium naphthalenide in DEE but the equilibrium processes 1 and 2 in eq I do not seem to be clearly separated, and we were unable to obtain the limiting values of $A_M(A)$ and $A_M(B)$ accurately. Nevertheless, the plot of $\log K_2$ vs. $1/T$ gave a good straight line with the choice of $A_M(A) = 2.45$ G and $A_M(B) = 0.75$ G. In both cases the line width depends on the quantum number of the alkali metal nucleus at low temperatures. k_2 and k_{-2} were determined for sodium naphthalenide in DEE by making use of eq 3 for the second equilibrium process. The

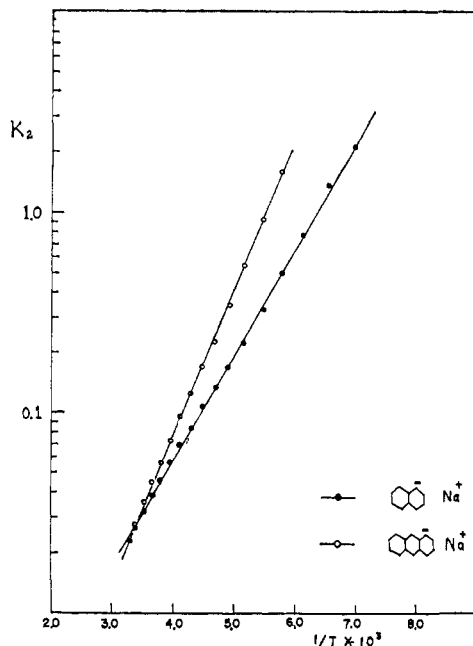


Figure 8. $\log K_2$ vs. $1/T$. Equilibrium constant for the equilibrium tight ion pair (2) \rightleftharpoons tight ion pair (1): \bullet , sodium naphthalenide in DEE; \circ , sodium anthracenide in DEE.

temperature dependence of k_2 and k_{-2} are shown in Figure 9. Thus the tight ion pairs in these systems seem to be adequately described by the rapid equilibrium model.

The estimates of the kinetic and the thermodynamic quantities involved in the equilibria listed above are summarized in Table I. Sodium anthracenides and

Table I. Thermodynamic Data for Interconversion

System	(A) tight ion pair (1) $\xrightleftharpoons[k_{-1}]{k_1}$ loose ion pair					
	ΔH_1° , kcal	ΔS_1° , eu	ΔH_1^\ddagger , kcal	ΔS_1^\ddagger , eu	ΔH_{-1}^\ddagger , kcal	ΔS_{-1}^\ddagger , eu
Na, naphthalene, THF	-5.6	-24
Na, anthracene, MTHF	-4.5	-26	-2.8	-8.3	7.2	14.4
System	(B) tight ion pair (2) $\xrightleftharpoons[k_{-2}]{k_2}$ tight ion pair (1)					
	ΔH_2° , kcal	ΔS_2° , eu	ΔH_2^\ddagger , kcal	ΔS_2^\ddagger , eu	ΔH_{-2}^\ddagger , kcal	ΔS_{-2}^\ddagger , eu
Na, naphthalene, DEE	-2.4	-11	0.9	-12	3.1	-2.4
Na, anthracene, DEE	-3.4	-14

sodium naphthalenides in various ethereal solvents can be described by the present equilibrium scheme. Lithium naphthalenide in DEE, MTHF, and THF and lithium anthracenide in MTHF seem to be explained by the similar equilibrium scheme. Perhaps many other systems can be described by this type of scheme. The negative ΔH° and the large negative ΔS° are characteristic in these ion-pair equilibrium systems. The tight ion pair (1) is more solvated than the tight ion pair (2), and the solvation appears to be primarily responsible for the negative ΔH° and ΔS° . However, this may not

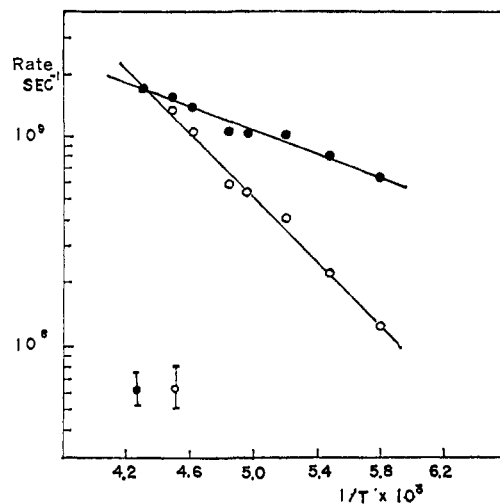


Figure 9. Temperature dependence of the interconversion rates between two different tight ion pairs. Sodium naphthalenide in DEE: \bullet , k_2 ; \circ , k_{-2} .

be always true. In cesium naphthalenide in DME, cesium splitting changes very little with temperature. However, the line width of the cesium splitting depends on the quantum number of Cs nucleus (Figure 7B). This appears to indicate that the system is actually undergoing some averaging process with the lifetime of $\sim 10^{-8}$ sec, although the Cs splitting is temperature insensitive. The magnitude of the Cs splitting in DME is considerably smaller than that in THF or MTHF. If one assumes the existence of the rapid ion-pair equilibrium in this system, one has to assume $\Delta H^\circ \sim 0$. In some cases, alkali metal splittings increase considerably at lower temperatures. They are potassium anthracenide in DEE and rubidium naphthalenide in THF. In potassium anthracenide the perturbation on the proton splittings increases considerably at lower temperatures indicating the stronger cation-anion interaction at lower temperatures. Thus closer approach of cation and anion at lower temperatures appears to exist in this case, and one has to assume positive ΔH° , if the similar rapid equilibrium scheme is to be applied. ΔH° for this system is given by $\Delta H^\circ = \Delta H^\circ_{\text{ion-ion}} + \Delta H^\circ_{\text{ion-solvent}} + \Delta H^\circ_{\text{solvent-solvent}}$. For the change from less solvated species to more solvated species, $\Delta H^\circ_{\text{ion-ion}}$ is positive, but $\Delta H^\circ_{\text{ion-solvent}}$ is negative. In most systems $|\Delta H^\circ_{\text{ion-solvent}}|$ is larger than $|\Delta H^\circ_{\text{ion-ion}}|$ and the resultant negative ΔH° is obtained. However, it would be possible that in the systems with weaker $\Delta H^\circ_{\text{ion-solvent}}$, $|\Delta H^\circ_{\text{ion-ion}}|$ could be larger than $|\Delta H^\circ_{\text{ion-solvent}}|$ with the resultant positive ΔH° . In potassium anthracenide in DEE and rubidium naphthalenide in THF, solvation is expected to be relatively weak, and the resultant positive ΔH° does not seem to be unreasonable. Therefore, these two cases may also be described by the rapid ion-pair equilibria, although the temperature dependence of the alkali metal splitting is quite different.

b. Slow Equilibrium between Different Ion Pairs. Even if the equilibrium scheme described in the previous section is applicable, one obtains completely different types of epr spectra, when the rate of interconversion is slow ($< 10^5$ sec). This situation, however, was not observed in most cases here, but at least one example

falls in this category. The spectrum of lithium anthracenide in DEE at lower temperatures shows the superposition of two spectra, one with large splitting and the other without Li splitting. At -100° the spectrum completely changes to that without Li splitting. The species without Li splitting at low temperatures appears to be a solvent-separated ion pair and not a free ion, because the value of the proton hyperfine splittings is slightly different from those for free ions. Therefore, this system gives an example of slow equilibrium between tight and solvent-separated loose species. Sodium naphthalenide in DEE reported in the previous paper¹¹ also gives an example of slow equilibrium between different ion pairs. However, more detailed studies on this system showed that the concentration of species with the small splitting depends strongly on the preparation. Accordingly we reserve the definite statement on this system at this point.

c. Static Ion-Pair Systems. Alkali metal splittings in cesium anthracenides in THF and MTHF, rubidium anthracenide in DEE, and cesium naphthalenide in THF and MTHF increased only very slightly at lower temperatures. Such a slight increase of the alkali metal splitting at lower temperatures has been reported by other workers previously.³ No dependence of the line widths on M_2^M were observed in these systems. Therefore it seems that no ion-pair equilibrium is taking place, except the possibility of very rapid equilibrium with $\Delta H^\circ \sim 0$. It was thought that the slight increase of the alkali metal splittings at lower temperatures might mean that two ions are coming closer at lower temperatures. Therefore the temperature dependence of the perturbation to the proton hyperfine splittings was studied. Within the range of the experimental error the perturbation was found to be almost constant. The small increase of the alkali metal splitting with decrease of temperature could be interpreted as the change in the relative population of the various vibrational states as suggested by Atherton and Weissman.² Also the degree of solvation may change slightly with temperature. However, the ion-pair structures in these systems are considered to be more static and fixed. The magnitude of the alkali metal splitting is also relatively insensitive to temperature and the nature of solvent.

2. Perturbation of Proton Splittings and the Structures of Ion Pairs. As described in section 2 of the Results, a clear correlation between the perturbation to the proton hyperfine and alkali metal splittings was found to exist in anthracenide. The perturbation is due to the electrostatic interaction between positive and negative ions. Suppose that the relative position of the positive ion with respect to the negative ion does not change much from one system to the other, but the distance between the positive and the negative ions changes from one ion pair to another. Then the correlation between the perturbation to the proton hyperfine splittings and the magnitudes of the alkali metal splittings would be expected. This appears to be the case in anthracenides. As shown in Figure 8, the perturbation depends on the alkali metal, the nature of solvent, and temperature. Although the maximum perturbation observed with certain positive ions increases in the following order, $Cs < Rb < K < Na < Li$, the metal dependence of the perturbation in one solvent does not necessarily follow this order. Since the rela-

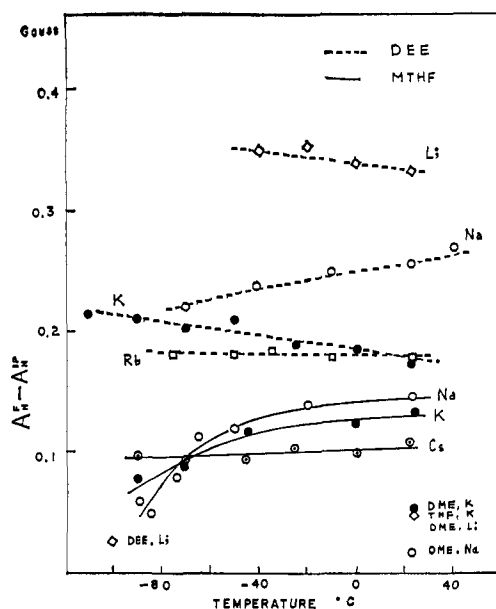


Figure 10. Perturbation to proton hyperfine splittings ($A_H^F - A_H^{IP}$) by counterions. Relative strength of cation-anion interaction in different systems: ----, DEE solvent; —, MTHF solvent; \diamond , Li; \circ , Na; \bullet , K; \square , Rb; \circ , Cs.

tive strength of the cation-anion interaction should be represented by the perturbation to the proton splittings, Figure 10 indicates the relative strength of the cation-anion interaction assuming that the ion-pair structures are similar. Thus the interaction in sodium anthracenide in MTHF at 24° is much weaker than that in potassium anthracenide or rubidium anthracenide in DEE and is close to the interaction in cesium anthracenide in MTHF or potassium anthracenide in MTHF. This indicates that the tight ion pair (1) of sodium anthracenide in MTHF is solvated, and the separation between the positive and the negative ions in this ion pair is considerably larger than one would expect from the real contact ion-pair structure with two ions in contact with their respective van der Waals and ionic radii. The solvation would also reduce the effective charge of the cation and reduce the electrostatic interaction between cation and anion. The words "contact ion pair" is widely used to represent our tight ion pair. However, the solvation in the tight ion pair is still significant and the structure of the ion pair and the interaction between the positive and the negative ions strongly depends on the nature of the solvent and temperature. Even in the most tightly bound ion pair the solvation appears to be important for the stable formation of the ion pairs in solution. Even in cesium anthracenide solvation appears to be important from the following observations. Cesium reacts very easily with anthracene in THF and MTHF but Cs does not react with anthracene in DEE. This seems to suggest that THF and MTHF solvates toward Cs to a certain extent and the stable ion pair is formed. The solvation of DEE toward Cs is too weak to allow the formation of stable ion pair in solution. Therefore we think that the so-called "contact ion pair" is significantly solvated and the degree of solvation and the structure of contact ion pair strongly depend on solvent.

Structure and Equilibrium of Tight Ion Pairs in Mixed Solvents. The importance of solvation in the

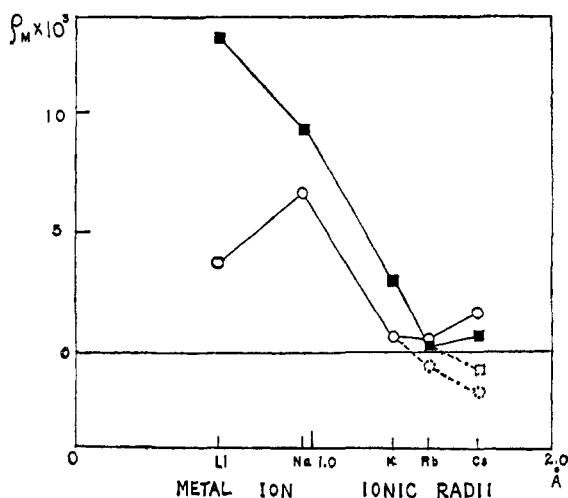


Figure 11. Observed maximum spin densities at alkali metal nuclei vs. ionic radii: ■, anthracenide; ○, naphthalenide.

tight ion pair (1) in sodium anthracenide is also shown in a series of experiments made on the mixture of MTHF and DEE. The sodium splitting of the tight ion pair (1) gradually changes with the mixing ratio from 1.55 G in pure MTHF to 2.02 G in pure DEE. The preferable solvation of MTHF in the mixed solvent is clearly seen from the fact that only 5 vol % of MTHF changes its splitting from 2.02 to 1.75 G. The thermodynamic analysis of the solvent exchange between MTHF and DEE can be made similar to that of Luckhurst.¹⁷ The perturbation to the proton splittings by the sodium ion increases as the mole fraction of DEE increases. This implies poorer solvation and stronger interaction between ions in the ion pairs in DEE.

Suppose that the ion pair has n average coordination number; then the equilibrium is given by



The equilibrium constant is given by¹⁷

$$K = \frac{(A_{\text{Na}}^{\text{DEE}} - A_{\text{Na}})(1 - \chi)}{(A_{\text{Na}} - A_{\text{Na}}^{\text{MTHF}})\chi} \quad (4)$$

where χ is the mole fraction of MTHF. $A_{\text{Na}}^{\text{DEE}}$ and $A_{\text{Na}}^{\text{MTHF}}$ are the magnitudes of the sodium splittings in DEE and MTHF. K estimated from the above formula is 17 ± 3 at -80° . Thus MTHF preferably solvate to the tight ion pair (1). Over the temperature ranges from 24 to 100° the line width of the spectra in mixed solvents are generally fairly sharp, and the magnitude of the sodium splitting is only the function of the bulk mixing ratio of the solvent. As the mixing ratio increases, the composition of the solvation sphere must change gradually. However, the microscopic structure of the solvation sphere would be fluctuating from time to time. Since the line width is very sharp, the microscopic fluctuation of the solvation sphere is time averaged and only sharp hyperfine lines are observed. The line width in the mixed solvents is 0.1 G or smaller and the upper limit of the contribution to the line width from the solvent-exchange process should not exceed 0.03 G. Assuming that the solvent-exchange reaction, such as eq II, contributes to the line width, the solvent-

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exchange rate is $>5 \times 10^8 \text{ sec}^{-1}$, which seems to be reasonable.

Perturbation to the Proton Splittings and the Structure of Ion Pair in Naphthalenide. Although our experimental data are very limited, no systematic correlation between metal splittings and the proton hyperfine splittings was observed in sodium naphthalenide. Contrary to the case of anthracenides, the sodium splitting of the tight ion pair (1) drops from 1.10 G in THF to 0.75 G in DEE, although the solvation power of DEE is weaker. Also the perturbation to the proton splittings in THF and DEE is quite different. These observations may be understood by assuming that the relative position of the positive ion with respect to the negative ion varies from one ion pair to another depending on the nature of solvent and temperature, and the perturbation cannot be a function of only distance between positive and negative ions.

3. Magnitude and Sign of the Alkali Metal Splittings.

There have been a number of reports on the alkali metal splittings,⁹ and some attempts of theoretical analysis have been made.^{2,5,18,19} However, the distinctions in different ion-pair structures were not clearly made in most cases. The magnitude of the alkali metal splitting, of course, depends very much on the structure of the ion pair. Since the structure of ion pair and the exact separation between positive and negative ions was never known, it is not possible to estimate what the magnitude of the alkali metal splitting should be in certain ion pairs. We thought that more systematic study of the alkali metal splitting is necessary before any theoretical analysis is made. In order to minimize the effect of solvation on the alkali metal splitting, we tried to obtain the splitting in a solvent of poor solvating power. These splittings represent the largest splittings observed with particular metal ions. The maximum observed spin density at the metal nuclei (obtained by dividing the observed alkali metal splitting by the respective atomic splitting) is given in Figure 11, which seems to show some trend among spin densities. The spin density at the metal nuclei is generally small in the ion pair with large cations. It has been suggested that the alkali metal splitting can be either positive or negative.⁵ If one assumes that the sign of spin density is negative for rubidium naphthalenide, cesium naphthalenide, and cesium anthracenide, there exists a regular trend that the spin density at the alkali metal nucleus decreases with the increase in the size of metal cation (or atomic number of metal ion) with the exception of lithium naphthalenide. In lithium naphthalenide in DEE the relative position of Li with respect to negative ion may be different from the rest of the ion pairs. Also the spin density at the metal nucleus is regularly larger for anthracenide than for naphthalenide. Systematic decrease of the spin density with the increase in the size of cation has been noted previously by Herold, *et al.*, in *O*-dimesitylbenzene.²⁰ However, the change in the spin density in going from Li to Cs is much more drastic in the present case than in *O*-dimesitylbenzene.

Several theoretical studies on the mechanisms of producing metal splittings and the magnitude of the alkali

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metal splittings have been made. Atherton and Weissman discussed the admixing of S orbitals of alkali metal ions with π orbitals of anion because of the nonorthogonality of the molecular and atomic orbitals.² 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 $\psi_0 = \psi(\text{Ar}^-\text{Na}^+)$.¹⁸ They obtained a splitting of the order of ~ 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 Boer⁵ 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.

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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^{1a} 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.^{1b} 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.² 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,³ 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.³⁻¹¹ Although the role of ion-pair formation in determining the rate of electron transfer has been noted for some time,^{5,12} there have been no detailed studies reported on the relationships between the reaction rates and the ion-pair structures. In 1962 Zandstra and Weissman⁵ 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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