Thermodynamic and Electron Spin Resonance Studies of Ion Pairs in Mixed Solvents

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Abstract: Sodium and potassium naphthalenide ion pairs were studied in THP and THP + DME mixtures as well as in DEE and DEE + THF mixtures over a wide temperature range. The existence of various species was investigated by applying spectrophotometric methods to studies of the equilibria such as sodium metal + N (naphthalene) $\rightleftarrows$ $N\cdot^-,Na^+$ (in a solvent); $N\cdot^-,Na^+$ (in a solvent) + solvating agent X $\rightleftarrows$ $N\cdot^-,Na^+,X$ (in a solvent); $N\cdot^-,Na^+,X + X \rightleftarrows N\cdot^-,Na^+,X_2$, etc. These thermodynamic investigations were supplemented by esr studies. The stoichiometry of complexes, ΔH's and ΔS's of their formation, and their structures were deduced from the experimental results.

A technique permitting studies of equilibria such as in eq 1 was developed in this laboratory.[1] It utilizes

$$Ar\cdot^-,M^+ + nX \rightleftarrows Ar\cdot^-,M^+,X_n \qquad (1)$$

the following strategem. In a relatively poor solvating medium equilibrium is established between metal M and a suitable electron acceptor Ar yielding the M radical-anion pair, $Ar\cdot^-,M^+$, *i.e.*

$$\text{M(solid)} + \text{Ar(solution)} \rightleftarrows Ar\cdot^-,M^+\text{(solution)} \qquad K_1$$

Since $Ar\cdot^-,M^+$ pairs have intense absorption bands, usually in the visible region, K_1 may be determined spectrophotometrically utilizing the relation

$$K_1 = [Ar\cdot^-,M^+]/[Ar]$$

Addition of a solvating (coordinating) agent X to the above system may lead to the formation of new species, such as $Ar\cdot^-,M^+,X$; $Ar\cdot^-,M^+,X_2$; etc. It is often found that these species absorb at the same wavelengths and have the same extinction coefficients as the original pair $Ar\cdot^-,M^+$. Their formation leads, therefore, to increased optical absorption from which the sum

$$[Ar\cdot^-,M^+] + [Ar\cdot^-,M^+,X] + [Ar\cdot^-,M^+,X_2] + \text{etc.}$$

may be calculated. Denoting by K_{ap} the ratio

$$\{[Ar\cdot^-,M^+] + [Ar\cdot^-,M^+,X] + [Ar\cdot^-,M^+,X_2] + \text{etc.}\}/[Ar]$$

we may show that

$$K_{ap} = K_1 + K_1K_2[X] + K_1K_2K_3[X]^2 + \ldots$$

where K_2, K_3, etc., refer to the equilibria

$$Ar\cdot^-,M^+ + X \rightleftarrows Ar\cdot^-,M^+,X \qquad K_2$$

$$Ar\cdot^-,M^+,X + X \rightleftarrows Ar\cdot^-,M^+,X_2 \qquad K_3\text{, etc.}$$

(Under the conditions of our experiments less than 3% of the solvating agent is coordinated with ion pairs. Consequently, we may approximate the concentration of the free solvating agent by its total concentration.)

There are conditions when a particular solvated species, one involving n molecules of X, predominates in the equilibrium mixture. In such a case

$$K_{ap} \approx K_1 + K_1\ldots K_n[X]^n$$

and then the plot of log $(K_{ap} - K_1)/K_1$ *vs.* log [X] is linear, its slope being equal to n. The above relations are simplified further when $[Ar\cdot^-,M^+] \ll [Ar\cdot^-,M^+,X_n]$.

There are some important situations when only one solvated species is dominant in the equilibrium mixture, *e.g.*, if $K_2[X] > 1$ and $K_3[X] \ll 1$, etc., or if $K_2 \approx K_3$ and simultaneously $K_3[X] \gg 1$ and $K_4[X] \ll 1$, etc. In the first case only the monosolvated species is present in a significant concentration, while in the second case the disolvated species dominates under the conditions of the experiments.

Experimental Section

The apparatus used in these studies was described earlier.[1] It consists of a round-bottom flask linked through an all-glass centrifugal pump to an optical cell placed in the compartment of a Cary spectrophotometer. A heavy mirror of an alkali metal is deposited on the walls of the flask and thus the solution of the investigated electron acceptor, Ar, remains all the time in contact with the metal (electron donor). The flask is immersed in a dewar; the temperature of the solution may be kept constant for the desired time and then changed by heating or cooling the liquid in the dewar.

Most of the work was done with a sodium mirror. In view of the recent reports[2] that traces of potassium present in the commercial sodium are responsible for the formation of $Ar\cdot^-,M^+$, the sodium mirror was prepared by two techniques. Commercial sodium was distilled four times under high vacuum and eventually deposited on the walls of the flask. Alternatively, the recrystallized sodium azide was decomposed under high vacuum and the resulting sodium metal distilled twice and then deposited on the walls. As will be shown later, the results were virtually not affected by the modification of the technique of preparation of the mirror.

Potassium mirrors were obtained by depositing commercial metal which was distilled and then redistilled under high vacuum.

The purification of solvents followed the now routine procedure involving, as its final steps, digestion of the solvent with organoalkali followed by high-vacuum distillation.

The aromatic hydrocarbons (biphenyl and naphthalene) were high-purity commercial materials, recrystallized and then sublimed on a high-vacuum line.

The esr studies were carried out on a Varian V4500 spectrometer equipped with the Varian temperature controller. The concentrations of investigated solutions were determined by comparing the overmodulated signals with those obtained from solutions containing a known amount of sodium naphthalene kept at the

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[1] R. V. Slates and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 6043 (1967).

[2] P. Graceffa and T. R. Tuttle, *J. Chem. Phys.*, **50**, 1908 (1969).

Table I. System Metallic Sodium–THP Solution of Naphthalene (N) in the Presence of DME; $[N]_0 = 9.3 \times 10^{-3}$ M at 24°

Temp, °C	K_1	K_{ap} 0.19[a]	0.46[a]	0.96[a]	1.54[a]	K_2, M^{-1}	K_3, M^{-1}
25.4	0.75	0.86	1.06	1.47	2.07	0.75	0.35
21.1	0.99	1.13	1.40	1.96	2.74	0.75	0.4
16.6	1.32	1.51	1.87	2.66	3.63	0.75	0.5
12.5	1.79	2.04	2.53	3.68	4.92	0.75	0.7
8.5	2.44	2.82	3.48	5.30	7.0	0.80	0.4 (?)
4.6	3.37	4.06	5.04	8.1[b]	10.3[b]	1.0[b]	0.4[b]
0.8	4.80	6.1[b]	7.6[b]	14.4[b]	17.8[b]	1.5[b]	0.4[b]

[a] The numbers above the rule denote the concentration of DME at 25.4°. They increase slightly at lower temperatures due to contraction of volume on cooling the solution. The contraction of volume was taken into account in calculating $[N]_0$. [b] In view of high conversion of N into $N\cdot^-$, these values are of low accuracy.

same temperature. The coupling constants were determined after calibrating the chart by means of a Varian FH20 gaussmeter.

Results

The System Metallic Sodium–Tetrahydropyran (THP) Solution of Biphenyl (B). Although the concentration of B was ten times higher in the present investigation than in the previous one[1] (3.3×10^{-3} M compared to 3.9×10^{-4} M), basically the same results were obtained. The largest numerical deviation (~50%) was found for K_1 at about 20°.

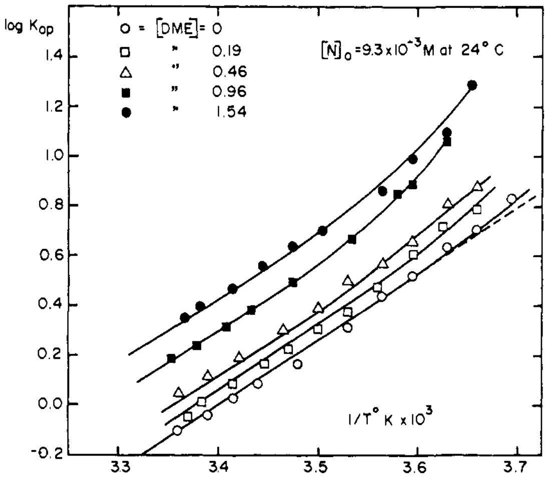

Figure 1. System metallic sodium–THP solution of naphthalene in the presence of DME; plots of log K_{ap} *vs.* $1/T$ for several DME concentrations.

The System Metallic Sodium–THP Solution of Naphthalene (N). These equilibria were studied in the presence and absence of dimethoxyethane (DME). The spectrophotometric investigation (determining the OD at 820 nm, ε $0.25.10^4$) covered temperatures ranging from 25 to −14°. At lower temperatures the conversion of N into $N\cdot^-$ was too high to permit reliable calculations of K_1 and K_2 (see footnote *b* in Table I). Esr studies were extended, however, to −38°.

It was established by separate experiments that the DME etherates studied in our experiments have spectra and extinction coefficients identical with those of $Na^+,N\cdot^-$ dissolved in pure THP. This was ascertained for the whole investigated temperature range. However, $Na^+,N\cdot^-$ dissolved in pure DME absorbs at longer wavelength (λ_{max} 860 nm, compared with λ_{max} 820 nm for the THP solution). These spectral changes indicate that DME solvates externally the tight $N\cdot^-,Na^+$ pair formed in THP, a conclusion confirmed by esr studies (see below).

The temperature dependence of K_1 is shown in Figure 1, its values being listed in Table I. The relevant OD's were measured at the required temperatures, both as they were approached by slow heating of the solution or by its slow cooling. This procedure permits us to check whether the ultimate equilibrium was attained. The linear portion of the van't Hoff plot corresponds to $\Delta H_1 = -12.0 \pm 0.5$ kcal/mol and $\Delta S_1 = -41$ eu.

The absorption due to $N\cdot^-$ increased on the addition of DME. The relevant K_{ap}'s are also listed in Table I and shown in Figure 1. The plots of log $(K_{ap} - K_1)/K_1$ *vs.* log [DME], calculated from the data obtained at several temperatures, are shown in Figure 2 and, for the sake of clarity, the repective lines are consecutively displaced upwards. It seems that they are linear, although their slopes randomly vary between 1.14 and 1.28. Apparently, the monoetherate, $N\cdot^-,Na^+,DME$, is the dominant solvated species, although not the only one.

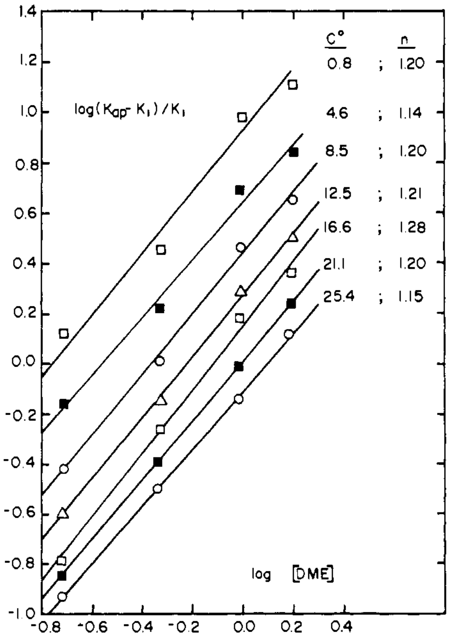

Figure 2. System metallic sodium–THP solution of naphthalene in the presence of DME; plots of log $[(K_{ap} - K_1)/K_1]$ *vs.* log [DME] at several temperatures.

We believe that the deviations of the slopes from unity are due to the formations of not insignificant amounts of $N\cdot^-,Na^+,DME_2$ complex which is present in equilibrium with the N·⁻,Na⁺,DME adduct. Hence, the system is governed by three equilibria, namely

$$\mathrm{Na(metal)} + \mathrm{N} \rightleftarrows \mathrm{N}\cdot^{-},\mathrm{Na}^{+} \qquad K_1$$

$$\mathrm{N}\cdot^{-},\mathrm{Na}^{+} + \mathrm{DME} \rightleftarrows \mathrm{N}\cdot^{-},\mathrm{Na}^{+},\mathrm{DME} \qquad K_2$$

$$\mathrm{N}\cdot^{-},\mathrm{Na}^{+},\mathrm{DME} + \mathrm{DME} \rightleftarrows \mathrm{N}\cdot^{-},\mathrm{Na}^{+},\mathrm{DME}_2 \qquad K_3$$

K_2 values were obtained by extrapolating the ratios $(K_{ap} - K_1)/K_1[\mathrm{DME}]$ to zero concentration of DME, and K_3 values were estimated from the equation $\log (K_{ap} - K_1)/K_1 = \log [\mathrm{DME}] + \log K_2 + \log (1 + K_3 \cdot [\mathrm{DME}])$. The results are listed in the last two columns of Table I. Apparently both solvation processes are thermoneutral, at least above 8°.

The lines shown in Figure 2 should be curved had a sufficiently wide range of concentrations of DME been investigated. Their slopes would then increase from unity at extremely low concentrations to two at a sufficiently high concentration of DME. However, technical reasons limited the range of concentrations accessible to our studies and, therefore, Figure 2 depicts only small sectors of the curves. This account for their apparent linearity.

In the absence of DME, the esr spectra of N·⁻,Na⁺ in THP (split by Na nuclei) are relatively sharp (60–70 mG at −37° increasing to about 100 mG at 36°), and the widths of the lines corresponding to $M_Z^{\mathrm{Na}} = \pm {}^1/_2$ and $\pm {}^3/_2$ are virtually identical. The sodium coupling constant increases with increasing temperature from 1.05 G at −37° to 1.23 G at 36° as shown in Table II.

Table II. Coupling Constants, a_{Na}, in the THP–DME System

Temp, °C	a_1, G 0^a	a_{obsd}, G 0.12^a	 0.28^a	 0.62^a	 1.03^a
36	1.23	1.20	1.19	1.19	1.12
26	1.23	1.21	1.15	1.14	1.10
17	1.20	1.18	1.13	1.08	1.08
9	1.18	1.17	1.12	1.06	1.00
0	1.15	1.11	1.06	1.03	0.93
−10	1.15	1.08	1.05	0.92	0.86
−19	1.09	1.06	1.00	0.86	0.80
−28	1.08	1.03	0.97	0.79	0.71
−37	1.05	1.00	0.90	0.75	0.60

[a] The numbers above the rule denote [DME], *M*.

The addition of DME (up to 1 *M*) hardly broadens the lines at higher temperatures (0 up to 36°), but the broadening is unmistakably observed at −37°; moreover, at this temperature and at higher concentrations of DME, the lines corresponding to $M_Z^{\mathrm{Na}} = \pm {}^3/_2$ are definitely broader than those for $M_Z^{\mathrm{Na}} = \pm {}^1/_2$. The sodium coupling constant is only slightly diminished by the addition of DME when the system is kept above 0°. However, in 1 *M* DME solution a_{Na} substantially decreases on lowering the temperatures below 0°. The pertinent results are collected in Table II.

The System Sodium Metal–Diethyl Ether (DEE) Solution of Naphthalene in the Absence and in the Presence of Tetrahydrofuran (THF). Metallic sodium reacts with naphthalene solution in rigorously purified diethyl ether giving, at sufficiently low temperatures, minute but still detectable amounts of sodium naphthalene. For a 2.9×10^{-2} *M* solution of naphthalene treated with sodium at −85° the concentration of N·⁻, Na⁺ was found to be 4.1×10^{-5} *M* by measuring its overmodulated esr signal. The equilibrium concentration of N·⁻,Na⁺ was subsequently measured at successively higher temperatures and the results led to the K_1 values listed in Table III. It was not feasible to observe the signal above −50°. The plot of log K_1 *vs.* $1/T$ is shown in Figure 3; it leads to $\Delta H_1 = -6$ kcal/mol and $\Delta S_1 = -44$ eu.

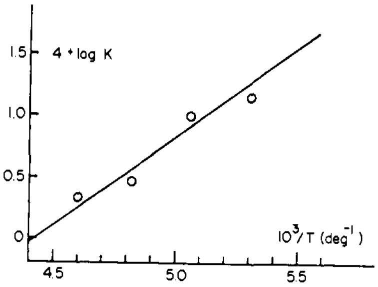

Figure 3. System metallic sodium–DEE solution of naphthalene; plot of log K_1 *vs.* $1/T$ obtained from esr data.

Table III. Sodium + N in DEE; $[\mathrm{N}]_0 = 2.9 \times 10^{-2}$ *M*

Temp, °C	$K_1 \times 10^4$	a_{Na}, G This work	 Hirota^a
−95		1.09	1.1
−85	14	1.20	1.2
−75	10	1.34	1.3
−65	2.9	1.42	1.4
−56	2.1	1.52	1.5
	$\Delta H_1 = -6$ kcal/mol	$\Delta S_1 = -44$ eu	

[a] The values of Hirota were taken from Figure 2 of ref 3. The accuracy of our reading was 0.1 G only.

The high-resolution esr spectra provided the relevant sodium coupling constant given also in Table III. The lines corresponding to $M_Z^{\mathrm{Na}} = \pm {}^1/_2$ or $\pm {}^3/_2$ were equally sharp at temperatures above −85°; however, a slight broadening of the outside lines of the sodium quadruplets was observed at −95°. Similar data extended up to 25° have been previously reported by Hirota,[3,4] and his results are included in Table III. Comparison of both sets of data is satisfactory.

Addition of THF to the diethyl ether solution greatly increased the optical density at $\lambda_{\max}$ 820 nm without changing the shape of the spectrum. The pertinent values of K_{ap} are listed in Table IV. Plots of log K_{ap} *vs.* log [THF] are linear at all temperatures, as shown by Figure 4, their slopes being virtually equal to 2.0. It seems, therefore, that under our experimental conditions the complex N·⁻,Na⁺,THF₂ is the dominant species, the concentration of N·⁻,Na⁺ being vanishingly small, and apparently the concentration of N·⁻, Na⁺,THF was also minute. For each constant concentration of THF, K_{ap} increases with decreasing temperature, the respective van't Hoff plots being linear, as exemplified in Figure 5. The respective ΔH's are virtually identical, the pertinent values being given at the bottom of Table IV.

In terms of our scheme, the results give $K_1K_2K_3 = K_{ap}/[\mathrm{THF}]^2$. Extrapolation of the data collected in Table III gives $K_1 = 5.5 \times 10^{-5}$ and 1.8×10^{-5} at

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(3) N. Hirota, *J. Phys. Chem.*, 71, 127 (1967).
(4) N. Hirota, *J. Amer. Chem. Soc.*, 90, 3603 (1968).

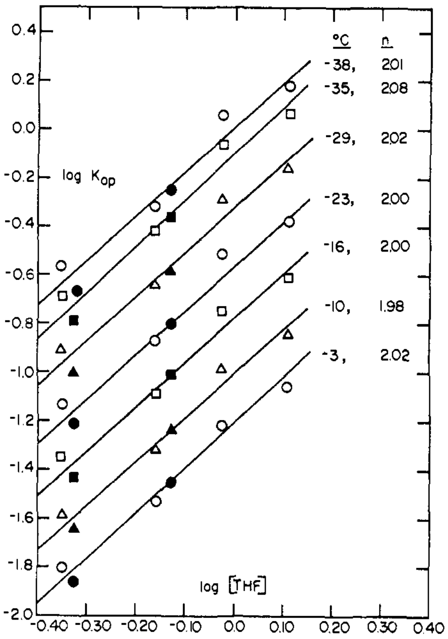

Figure 4. System metallic sodium-DEE solution of naphthalene in the presence of THF; plots of log K_{ap} vs. log [THF] at various temperatures; solid symbols refer to experiments performed with sodium formed by decomposing the azide.

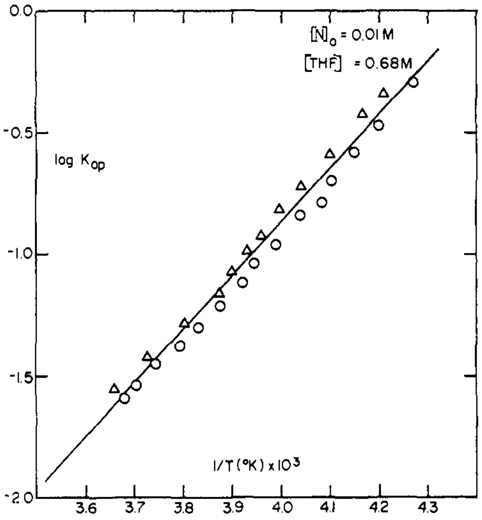

Figure 5. System metallic sodium-DEE solution of naphthalene in the presence of THF; a representative plot of log K_{ap} vs. $1/T$: ○, rising temperature; △, falling temperature.

-38 and -3°, respectively. By averaging the $K_{ap}/[THF]^2$ values given in Table IV, we find $K_1K_2K_3$ to be 1.1 M^{-2} and 0.07 M^{-2} at the above temperatures. Hence, K_2K_3 is 2×10^4 and 4×10^3 M^{-2} at -38 and -3°, respectively.

The esr spectra obtained in the presence of THF give a_{Na} values lower than those observed in the absence of THF. Their values increase with temperature and, to a lesser extent, with decreasing concentrations of THF. These findings are presented in a graphical form in Figure 6. All the esr spectra obtained in the presence of THF show no variation of the widths of the sodium lines.

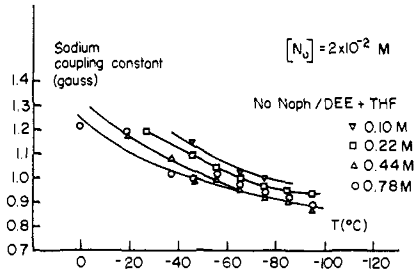

Figure 6. System metallic sodium-DEE solution of naphthalene in the presence of THF; the variation of a_{Na} with temperature at different THF concentrations.

System Potassium Metal-DEE Solution of Naphthalene in the Absence and in the Presence of THF. Potassium metal reacts with naphthalene in pure DEE giving $N\cdot^-,K^+$. Its concentration was determined spectrophotometrically; the conversion was found to be about 13%, virtually independent of temperature (from -22 to $+22$°). Also, a negligible change in conversion (up to 17%) was observed on the addition of THF ([THF] varied from 0.47 to 0.93 M). Again, the conversion in the presence of THF remained unaffected by temperature within the range -60 up to $+20$°.

Table IV. System Metallic Sodium-DEE Solution of N in the Presence of THF; $[N]_0 = 0.01\ M$

Temp, °C	K_{ap} for variable [THF] (intrapolated values) 0.45 M	0.47 M^a	0.68 M	0.70 M^a	0.89 M	1.13 M
-3	0.016	0.014	0.030	0.036	0.060	0.087
-10	0.026	0.023	0.049	0.059	0.102	0.145
-16	0.045	0.038	0.081	0.098	0.178	0.245
-23	0.074	0.062	0.135	0.159	0.302	0.417
-29	0.123	0.100	0.229	0.263	0.513	0.692
-35	0.204	0.162	0.380	0.437	0.87	1.18
-38	0.269	0.214	0.479	0.562	1.15	1.51
ΔH, kcal/mol	-10.3	-9.9	-10.1	-10.0	-11.2	-9.6

[a] Denotes results obtained with a mirror obtained from sodium azide. All the other values were obtained with commercial sodium. All THF concentrations were measured at 25°.

The esr spectra show 25 lines and no splitting by potassium was observed under any conditions. However, the lines were broad, *e.g.*, ~0.2 G at -95°, and hence a small splitting would remain undetected under our conditions.

Systems Sodium Metal-THP Solution of Naphthalene in the Presence and Absence of Tetraglyme. This system was investigated by Höfelmann, *et al.*,[5] who found different esr spectra for the $N\cdot^-,Na^+$ pair in THP and for its 1:1 complex with the tetraglyme. Following the reports[2] that traces of potassium present in the commercial sodium may lead to the formation of $N\cdot^-$, K^+ together with $N\cdot^-,Na^+$, the problem was raised whether the glyme complex could not be a potassium salt. We repeated, therefore, their studies using recrystallized sodium azide as a source of sodium and thus eliminated any spurious potassium in the mirror. The observations of Höfelmann were fully confirmed, proving that the spectrum showing the 0.4-G sodium coupling constant is due to a genuine $N\cdot^-,Na^+$,tetraglyme complex. Moreover, since the $N\cdot^-,K^+$ spectrum does not show splitting due to potassium cation in

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[5] K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, 91, 4645 (1969).

DEE, it certainly should not reveal any splitting by K in THP. Hence, the observations of Höfelmann, *et al.*,[5] cannot be attributed to the presence of traces of potassium.

Discussion

In the systems studied in the course of this investigation, sodium naphthalene forms ion pairs, and any significant concentration of free ions is precluded by the relatively low dielectric constants of the solvents used in this work. Ion pairs interact with the neighboring solvent molecules or the molecules of the added solvating agent, and such interactions lead to the formation of more or less rigid solvation shells. The solvating molecules may reside on the periphery of a pair, their presence affecting only slightly the relative position of the cation in respect to its anion. Such pairs are referred to as tight ion pairs. Alternatively, the ions may be surrounded by solvent molecules; in that case loose ion pairs are formed. In mixed solvents, or in the presence of small amounts of powerfully solvating agents, different types of tight or loose ion pairs should be distinguished, each type characterized by the composition of a shell formed by the solvent molecules neighboring the pair.

The array of solvent molecules surrounding an ion pair varies within some limits due to Brownian motion; consequently, their average array-determined properties are temperature dependent. Nevertheless, each pattern of arrays persists for a sufficiently long time to justify its treatment as a thermodynamically distinct species endowed with its own characteristic observable properties. This implies that the intermediate arrays, not belonging to any of the patterns characterizing the thermodynamic species, are virtually excluded, a situation often encountered in the real systems. Classification of ion pairs surrounded by shells of different composition as thermodynamically distinct species is also frequently justified because in many systems the composition of a shell remains constant for long times as compared with the periods of vibrations. The ideas outlined above were discussed previously, although sometimes in slightly different terms.[3,4,6,7]

Having this framework in mind we may discuss the present findings. In THP and in DEE, sodium naphthalene forms tight pairs surrounded by molecules of the respective solvents. Their interaction with the pair is different for DEE and THP, the latter interacting more strongly than the former. The difference of the respective interaction energies is given by ΔH_1(THP) − ΔH_1(DEE) = −6 kcal/mol (note that ΔH_1's involve other terms independent of solvent). This difference accounts for the large ratio K_1(THP)/K_1(DEE), because ΔS_1's remain virtually constant (−41 and −44 eu, respectively).

The $N\cdot^-$,Na^+ ion pairs formed in THP or DEE are designated as tight ones because their sodium coupling constants are relatively large (see Tables II and III). In pure DME loose ion pairs are formed. This is indicated by the change in the optical spectrum of $N\cdot^-$,Na^+ (see the Experimental Section) and by Hirota's esr results ($a_{Na} = 0.2$ G). He and his coworkers reported a thorough study of esr spectra of naphthalenides and anthracenides in a variety of solvents over a wide temperature range.[3,4,8,9] We confirm their findings, although we suggest a slight modification of their approach. Hirota assumed that each type of ion pair is characterized by a *temperature-independent* metal coupling constant and this was the foundation for his thermodynamic calculations. (The appearance of the quadruplet with $a \sim 0.06$ G shown in Figure 3 of ref 3 is due to the contamination of sodium by potassium (see ref 2). We did not detect such a species in our system.) We believe, as was explained in the beginning of our discussion, that the relevant a_{Na}'s are still temperature dependent, a point previously discussed by Höfelmann, *et al.*[5] Such temperature dependence affects the numerical values of the equilibrium constants and substantially reduces the calculated ΔH values reported by Hirota. This problem was, in fact, partially recognized by him and discussed in ref 9.

It cannot be stated definitely whether loose $N\cdot^-$,Na^+ pairs are formed in THP in any detectable amounts. Our data do not reveal their presence, even at −37°, the lowest temperature attained in our study (THP freezes below −40°), and the decrease of a_{Na} is interpreted as being caused by the temperature dependence of the coupling constant of a tight ion pair. Undoubtedly, the loose pairs should be formed at lower temperatures which unfortunately could not be attained in this work.

The addition of DME to THP yields new pairs, *viz.*, $N\cdot^-$,Na^+,DME and $N\cdot^-$,Na^+,2DME. Both are classified as tight ion pairs because the respective $-\Delta H_2$ and $-\Delta H_3$ values are very small. Formation of loose pairs should be associated with a $-\Delta H$ of 5–8 kcal/mol. A similar conclusion may be drawn from consideration of the relevant a_{Na}. It seems that a_{Na} of the $N\cdot^-$,Na^+,DME pair is insignificantly smaller than that of $N\cdot^-$,Na^+ surrounded by THP only (see Table II). Hence, we may calculate a_{Na} of the $N\cdot^-$,Na^+,2DME pair by assuming that its presence accounts for the observed decrease of a_{Na} reported in Table II. Thus, we find a_{Na} of that pair to be 0.7 G at room temperature, still too high a value for a truly loose pair (see, *e.g.*, ref 5). However, loose $N\cdot^-$,Na^+,2DME pairs apparently are formed at lower temperatures, and this accounts for the substantial decrease of the observed a_{Na} at lower temperatures and at higher concentrations of DME. We deal here with an isomerization process described symbolically by

$$\mathrm{Na}\cdot^-,\mathrm{Na}^+,2\mathrm{DME} \rightleftarrows \mathrm{N}\cdot^-,\mathrm{DME},\mathrm{Na}^+,\mathrm{DME}$$

The isomeric ion pairs were first reported by Slates and Szwarc,[1] and the phenomenon of isomerization was confirmed subsequently by other studies carried out in our laboratory.[10]

Our results imply that the interaction energies of DME and THP with the periphery of the $N\cdot^-$,Na^+ pair are similar and that one DME displaces only one THP. The latter conclusion is justified by the nearly 0 value of the respective ΔS. This is rather surprising, but presently we cannot offer any comments on this subject.

The interaction of THF with $N\cdot^-$,Na^+ pairs in DEE yields mainly the $N\cdot^-$,Na^+,THF_2 complex. In view of the large K_2K_3 values this is understandable. It is

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(6) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

(7) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969).

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

(9) N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

(10) L. L. Chan, K. H. Wong, and J. Smid, *ibid.*, **92**, 1955 (1970).

plausible to assume $K_2 \approx K_3$ and, thus, $K_3 \approx 140$ and $\approx 65\ M^{-1}$ at -38 and $-3°$, respectively. Hence, the mono complex, $N\cdot^-,Na^+,THF$ forms only 1.5% of all the pairs at $-3°$ and 0.7% at $-38°$, when [THF] = 1 M. Its proportion increases to about 15 and 7%, respectively, at the above-mentioned temperatures when [THF] = 0.1 M.

The presence of $N\cdot^-,Na^+,THF$ is reflected by the esr data presented in Figure 6. It is plausible to expect a_{Na} to be slightly larger for $N\cdot^-,Na^+,THF$ than for $N\cdot^-,Na^+,2THF$. Hence, the trends shown in Figure 6 become rationalized (note the increase of the observed a_{Na} at higher temperatures and with *decreasing* concentration of THF). Nevertheless, the relatively high values of a_{Na} even at $-90°$ indicate that both complexes, $N\cdot^-,Na^+,THF$ and $N\cdot^-,Na^+,2THF$, are virtually tight pairs at the investigated concentrations of THF. However, as shown by Hirota,[3,4] at still higher concentrations of THF loose pairs (presumably $N\cdot^-,Na^+,4THF$) are formed at sufficiently low temperatures ($a_{Na} \sim 0.2$ G).

Our results indicate that the process

$$N\cdot^-,Na^+ \text{ (in DEE)} + 2THF \rightleftarrows N\cdot^-,Na^+,2THF \text{ (in DEE)}$$

is exothermic to an extent of 4 kcal/mol but the respective $\Delta S \sim 0$. (We should consider "corrected" ΔS's which take into account the fact that THF (or DME in the THP + DME system) molecules are with drawn from 1 M solution, while the released DEE (or THP) molecules return to about 10 M solution. The corrected ΔS's are larger by about 4.6 eu than the one quoted above.) The interaction of THF molecules with $N\cdot^-,Na^+$ is therefore stronger than that with DEE, and in the formation of the $N\cdot^-,Na^+,2THF$ complex two of the DEE molecules were replaced by two THF molecules. The low value of ΔS is again indicative of the formation of tight pairs, because the formation of the loose pair leads to a negative and absolutely large ΔS. Hence, the thermodynamic results confirm the esr observations.

Finally, the behavior of $N\cdot^-,K^+$ ion pairs calls for some comments. It seems that the interaction of $N\cdot^-,K^+$ with DEE or even THF is weak. It is significant that in spite of the lower ionization potential and heat of sublimation of potassium, when compared with sodium, the relevant ΔH_1 is about 0. Also, the addition of THF led to hardly any increase in $N\cdot^-,K^+$ concentration and again the system was not affected by temperature variation. The low a_K value observed by Hirota and by ourselves is not diagnostic of loose ion pairs; it reflects the much weaker magnetic moment of the ^{39}K nucleus. In view of the weak interaction of $N\cdot^-,K^+$ with the solvent, it may not be justified to treat the ion pairs surrounded by a solvation shell of different composition as distinct thermodynamic species.

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Electron Paramagnetic Resonance Investigation of Transition Metal Complexes. XV. Complexes of Vanadyl Chloride with Tertiary Phosphines[1]

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Abstract: A family of vanadyl–phosphine complexes $VOCl_2 \cdot 2(PR_3)$, with varying bulkiness of the substituents R, have been investigated. The epr spectra show increasing line width with increasing molecular volume. The line-width variation can be described by using an equation derived by Kivelson, *et al.*, assuming that the only essential variable is the equivalent spherical hydrodynamic radius of the compounds. Structural information was obtained favoring a trigonal-bipyramidal *vs.* a square-pyramidal arrangement.

Recently[1] we reported briefly on the epr spectrum observed in the reaction solution if $VOCl_2$ is solubilized in toluene by an excess of tertiary phosphine. The signal (see Figure 1a) shows the interaction of the unpaired electron of V^{IV} with the ^{51}V nucleus (nuclear spin $I = {}^7/_2$). Each of the eight vanadium lines is further split into a 1:2:1 triplet. This hyperfine structure can be attributed unambiguously to two equivalent phosphorus nuclei, since the corresponding complex with arsine (^{75}As, $I = {}^3/_2$) has a spectrum in which the triplets are replaced by septets (thus excluding hydrogen).[2] The epr signal was thus ascribed to the complex $VOCl_2 \cdot 2(C_2H_5)_3P$. From the signal intensity it could be estimated that essentially all vanadium was present in the signal giving form.

The present paper deals with a family of similar complexes which only differ by the substituents at the phosphorus in the phosphine ligands. The epr spectra of these complexes show marked differences in line width

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[1] Part XIV: G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **82**, 955 (1970); *Angew. Chem. Int. Ed. Engl.*, **9**, 957 (1970).

[2] (a) G. Henrici-Olivé and S. Olivé, *Chem. Commun.*, 596 (1969). (b) The arsine spectrum was first observed with a VCl_3 solution.[2a] Experiments with $VOCl_2$ suggest that the reported signal is due to $VOCl_2 \cdot 2AsR_3$.