Structure and Reactivities of Ion Pairs and Free Ions Studied by Electron Spin Resonance Spectroscopy. Effect of Coordination with Tetraglyme

K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc

Contribution from the Department of Chemistry,
State University College of Forestry at Syracuse University,
Syracuse, New York 13210. *Received March 15, 1969*

Abstract: Esr studies show that sodium naphthalene may be coordinated with one molecule of tetraglyme forming $Na^+,G,N\cdot^-$ loose ion pair. The ordinary tight $Na^+,N\cdot^-$ ion pair in THP is characterized by a_{Na} hfsc of about 1.4 G (decreasing to about 1.0 G at lower temperatures), whereas the a_{Na} hfsc of the loose, glyme-coordinated pair is 0.39 G at 47° (decreasing to zero at lower temperatures). At a sufficiently low glyme concentration both types of ion pairs ($Na^+,N\cdot^-$ and $Na^+,G,N\cdot^-$) may be seen simultaneously in the esr spectrum. Its analysis gives the equilibrium constant K of the process $Na^+,N\cdot^- + G \rightleftarrows Na^+,G,N\cdot^-$ (k_1, k_{-1}) ($K = 200\text{–}300\ M^{-1}$ at 27°), the rate constants of "glymation" ($k_1 = 10^8\ M^{-1}\ \text{sec}^{-1}$) and of the collapse of $Na^+,G,N\cdot^-$ pair ($k_{-1} = 10^6\ \text{sec}^{-1}$). Electron transfer between naphthalene and its free radical ion, k_{ex}, was investigated in HMPA over a wide temperature range. Comparison of the data reported for various solvents showed a good correlation between k_{ex} and the parameter λ of Marcus' theory. Studies of exchange involving the glyme-coordinated pairs revealed the presence of two species, one rapidly exchanging, the other relatively slowly. Conductance studies proved that the rapidly exchanging species is *not* the free $N\cdot^-$ ion, and hence two distinct glymated $N\cdot^-G,Na^+$ pairs are present in this system. From the broadening of the lines of the $Na^+,G,N\cdot^-$ esr spectrum, and from the electron exchange studies involving the glymated species, the rate constants of the interconversion were estimated to be of the order of $10^7\ \text{sec}^{-1}$ at room temperature. A possible structure was tentatively proposed for these two glymated ion pairs.

Our knowledge of ion pairs stems from various observations furnished by conductance studies of their solutions, kinetic investigations of their reactions, detailed examination of their spectra when recorded in various solvents and at various temperatures, studies of some relaxation phenomena, etc. The interested reader may find numerous references to the pertinent literature in a recent monograph.[1]

Esr spectroscopy provides perhaps the most powerful and penetrating tool for probing the nature of ion pairs. This avenue of investigation was opened by Weissman,[2] who showed that the original hyperfine lines of radical anions split into multiplets on their association with cations possessing nuclear spin. The magnitude of the new hyperfine splitting constant (hfsc) may yield valuable information about the location of the cation within the pair, and the width and shape of the lines may reveal details of the dynamic processes involving these species. A recent article by Symons[3] includes a lucid discussion of these phenomena.

Ion pairs are surrounded in solution by solvent molecules arrayed in various ways. Because of Brownian motion, such configurations will change from one to another with a frequency determined by the temperature and the nature of both the pair and the solvent. Hence, the observed properties of such ion pairs, like those of all molecular ensembles, are expected to vary continuously with temperature, *e.g.*, the hyperfine splitting constants a_M, calculated from the esr spectra of paramagnetic ion pairs, usually increase at higher temperatures.

Two extreme situations should be visualized. The structure of an ion pair may be nearly fixed at each temperature. This means that the position of cation in respect to anion and the locations of the surrounding solvent molecules do not deviate substantially from their average configuration, the deviations varying rapidly with a frequency greater than $10^{10}\ \text{sec}^{-1}$. Nevertheless, the *average* configuration may be profoundly modified within some range of temperatures causing temperature-dependent changes of the properties of the relevant ion pairs. Systems exhibiting such a behavior will be classified as *static* ones.[4]

In some systems ion pairs may have two, or more, distinct structures, *i.e.*, two or more distinct patterns produced by the pair and the neighboring solvent molecules may coexist, each pattern lasting for a relatively long time ($>10^{-10}$ sec). It is then advantageous to treat each set of similar patterns as a thermodynamically distinct type of ion pairs and the whole system as an equilibrium mixture of different types of pairs. Such a model is known as a *dynamic* one. The observed properties of the system depend again on temperature as well as on the lifetime of each type of ion pairs. For example, two sets of lines may be seen in the esr spectrum of paramagnetic ion pairs if they form two distinct and slowly interconverted types. The usual broadening, coalescence, and subsequent sharpening of the lines should be observed as the temperature rises and the rate of interconversion increases. Moreover, since the conversion of one type into another involves a heat term, generally different from zero, the proportion of the various pairs in the mixture varies with temperature.

It is customary to talk about different modes of solvation of ion pairs when the organizations of solvent molecules surrounding them are substantially

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[1] M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience Publishers, New York, N. Y., 1968; see Chapters V and VII.

[2] (a) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958); (b) N. M. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961).

[3] M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967).

[4] (a) P. Chang, R. V. Slates, and M. Szwarc, *ibid.*, **70**, 3180 (1966); (b) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969).

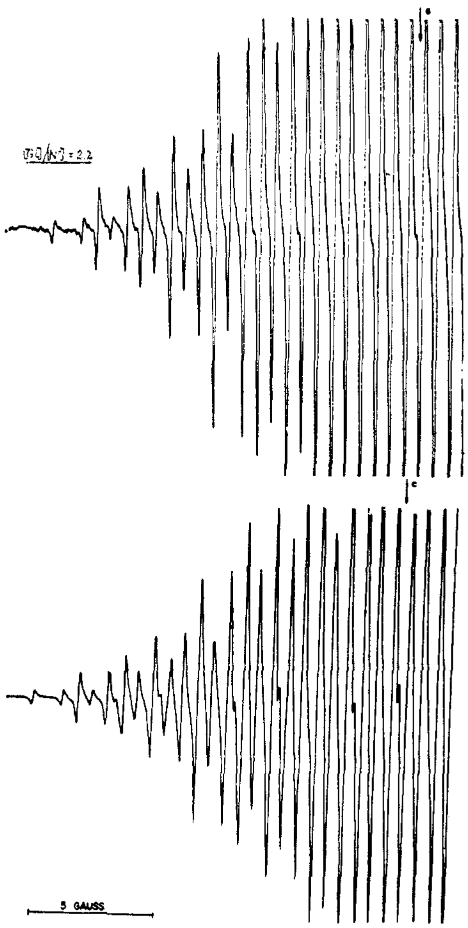

Figure 1. Esr spectrum of N·$^-$,Na$^+$ in THP at 27°: upper curve, the observed spectrum; lower curve, the computer-simulated spectrum.

different. Specifically, an increase in the number of solvent molecules between the ions increases their separation, and consequently the descriptive classification such as "tight" and "loose" ion pairs is often useful.

Distinction between the two models of ion pairs is not easy when only one splitting constant a_M is deduced from the spectrum. Such a result is always anticipated on the basis of the static model; it is also predicted by the dynamic model when the rate of interconversion between the various types of ion pairs is sufficiently fast.

An interesting method which makes the discrimination possible, at least under some conditions, was developed by de Boer, *et al.*[5] It utilizes the results of nmr studies of the alkali cations associated with paramagnetic anions, and it predicts different dependences of the line width upon the chemical shift for pairs described by the static and by the dynamic models. It was deduced from these studies that cesium biphenylide in diglyme is represented by the static and not by the dynamic model, although some assumptions incorporated in the treatment somewhat weaken this conclusion.

Another approach was employed by Hirota and his students,[6] who carried out an extensive esr study of alkali salts of naphthalenide and anthracenide ions. They stressed that the dynamic model of ion pairs predicts a characteristic dependence of a_M on temperature; namely, the plot of a_M *vs.* T should show two plateaus at extreme temperatures linked by an S-shaped curve. Thus, for an equilibrium, ion pair I $\rightleftarrows$ ion pair II, the respective equilibrium constants can be calculated from the experimental data if a_I and a_{II}, pertaining to the individual ion pairs, are temperature *independent.* A linear van't Hoff plot obtained for thus calculated equilibrium constants is considered as further strong evidence supporting the dynamic model. This approach seems to be plausible, although the derived numerical data may be questioned. The assumption of temperature independent a_I and a_{II} is somewhat doubtful, and if one of these constants (or both) were temperature dependent, the magnitudes of the calculated equilibrium constants would be modified. Such modifications strongly influence the ΔH and ΔS values derived from the data.

Finally, it should be stressed that the dynamic model predicts dependence of the width of the esr lines on M_z of the cation. Such dependence was thoroughly investigated by Hirota,[6] and the results led to an interesting method of calculation of the rate of interconversion.

Modification of Ion Pairs by Coordinating Agents. The character of ion pairs may be modified either by varying the solvent or the temperature of solution. It is also possible to modify the character of an ion pair at constant temperature in a virtually unchanged medium by the addition of small amounts of agents which strongly interact with the pair. For example, some polydentate ethers (glymes) react in a stoichiometric manner with various alkali salts producing well-defined adducts.[7-9] Therefore, it was decided to study the effect of tetraglyme (G) on the esr spectra of sodium naphthalenide in tetrahydropyran (THP).

The esr spectrum of sodium naphthalenide (N·$^-$,Na$^+$) in THP is shown in Figure 1. The hyperfine lines of naphthalenide are clearly split into quadruplets by the presence of ^{23}Na, the magnitude of the respective splitting constants varying from about 1.4 G at 47° to about 1.0 G at −37° (see Table I). Within the investigated range of temperatures the lines remain sharp and no clear-cut dependence of their width on M_z (Na) could be detected. It seems, therefore, that the temperature variation of a_{Na} observed here should be interpreted in terms of static model of ion pair.

Table I. Temperature Dependence of Hyperfine Splitting Constant of Na in Tight Ion Pair and in the Glymated Pair in THP

Temp, °C	a_{Na} (tight pair), G	a_{Na} (glymated pair), G
47	1.37	0.39
27	1.23	0.39
20	1.19	0.39
6	1.16	0.33
2.5	...	0.23
−2.5	...	0.17
−15	1.08	...
−32	...	~0.0
−37.5	1.01	~0.0

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(5) E. de Boer, G. W. Canter, B. M. P. Hendriks, and A. A. K. Klaessen, submitted for publication.

(6) (a) N. Hirota, *J. Am. Chem. Soc.*, **90**, 3603 (1968); (b) N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

(7) R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967).

(8) L. Chan and J. Smid, *ibid.*, **89**, 4547 (1967).

(9) M. Shinohara, J. Smid, and M. Szwarc, *ibid.*, **90**, 2175 (1968).

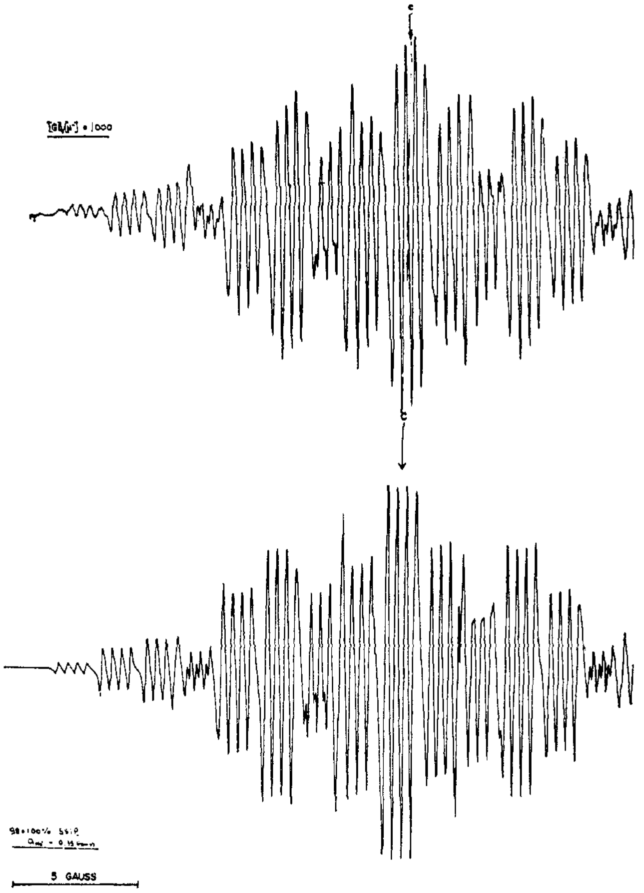

Figure 2. Esr spectrum of $N\cdot^-$,G,Na^+ in THP in the presence of 0.24 M tetraglyme at 27°: upper curve, the observed spectrum; lower curve, the computer-simulated spectrum.

On the addition of an excess of tetraglyme (~0.24 M) the a_{Na} is greatly reduced. The spectrum recorded at room temperature is shown in Figure 2, the relevant splitting constant being about 0.4 G. Lowering the temperature of solution reduces a_{Na} still further, and eventually at $-37°$ the four lines merge into one. The pertinent data are given in the last column of Table I.

At about 0° the widths of the lines of the glymated pairs show a clear dependence on M_z of the sodium nucleus. For example, at 1.2° the observed $a_{Na} = 0.21$ G and the lines show a width of 0.133 G for $M_z = \pm ^3/_2$ and 0.107 G for $M_z = \pm ^1/_2$. Therefore, the variation of a_{Na} recorded in the last column of Table I should be interpreted in terms of the dynamic model although, as will be shown later, the splitting constants of each type of ion pairs may substantially vary with temperature. The variation of line width permits us to calculate the rate constant of interconversion,[6] and the result of these calculations will be discussed later.

At room temperature and for intermediate concentrations of the glyme, two sets of lines are recognized in the spectrum: those characteristic of the "tight" pairs present in the pure THP and the other identified as the lines of the glymated pairs which were observed in the presence of an excess of glyme. This is shown in Figure 3b which depicts the low-field wing of the esr spectrum of $N\cdot^-$,Na^+ solution containing 0.006 M tetraglyme. The lines corresponding to the glymated pairs are marked in Figure 3b by arrows, and a stick model of the spectrum is shown beneath.

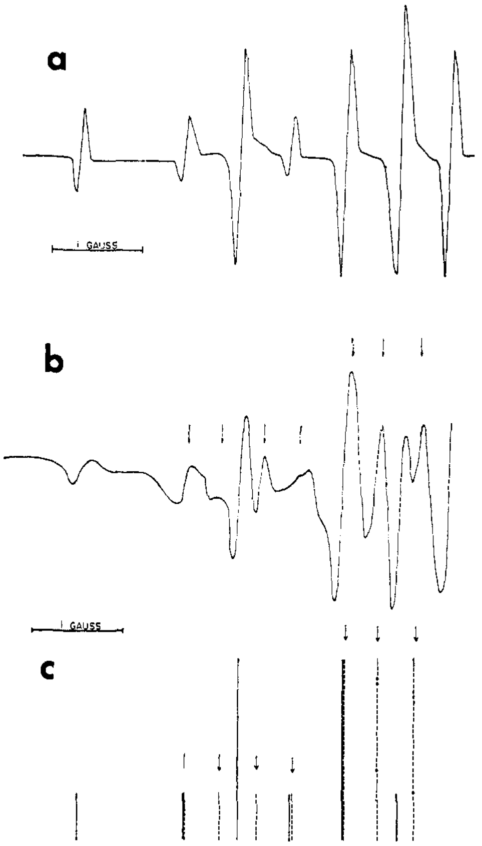

Figure 3. Low-field wing of esr spectrum of $N\cdot^-$,Na^+ in THP at 27°: (a) in the absence of tetraglyme; (b) in the presence of 0.006 M tetraglyme; (c) a stick model.

The spectra recorded for various concentrations of tetraglyme at 25° were simulated by computer. The Lorentzian line width was assumed to be 80 mG for the "tight" pair and 100 mG for the glymated one, the a_m of the latter being taken as 0.39 G and that for the former as 1.23 G. The proportions of each pair at various glyme concentrations were estimated by comparing the simulated and recorded spectra. The results are shown in Table II. They are consistent with the equilibrium

Table II. Equilibrium between Glymated and Nonglymated Sodium Naphthalenide at Room Temperature[a]

[Sodium naphthalenide] × 10^4 M	[Glyme], M	[Glyme]/[Sodium naphthalenide]	$N\cdot^-$,Na^+/$N\cdot^-$,G,Na^+	K_1, M
3.2	0.0007	2.1	6.1	230
3.0	0.0057	19	0.67	260
2.1	0.0244	118	0.18	230
3.2	0.1140	350	0.042	210
2.4	0.2390	1010	0.020	240

[a] Solvent THP, concentration of tetraglyme 0.015–5%. Relative concentrations of $N\cdot^-$,Na^+ and $N\cdot^-$,G,Na^+ were obtained by comparing the computer-simulated spectra with the experimental ones.

$$N\cdot^-,Na^+ + G \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N\cdot^-,G,Na^+ \qquad K_1$$

where $N\cdot^-$,G,Na^+ denotes the adduct containing one

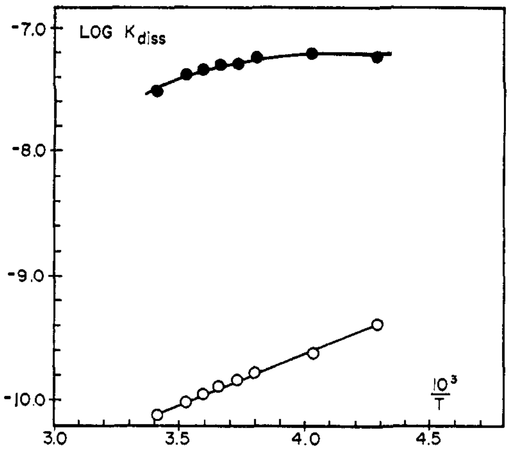

Figure 4. van't Hoff plot of K_{Diss} of $N\cdot^-,Na^+$ (lower line) and $N\cdot^-,G,Na^+$ (higher line) in THP.

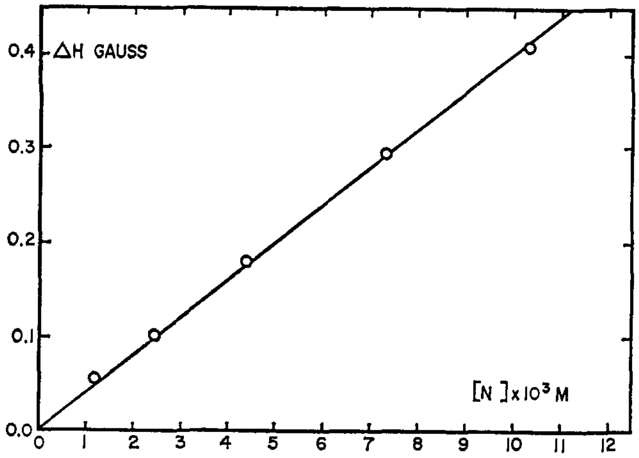

Figure 5. Dependence of ΔH on $\Delta[N]$ in the slow exchange $N\cdot^- + N \rightleftarrows N + N\cdot^-$ in HMPA (free ion).

molecule of glyme. The value of K_1 is in the range 200–300 M^{-1}; a more precise estimate is not feasible in view of the experimental difficulties and the assumptions involved in the computation.

The width of the lines seen in Figure 3b permits us to calculate the values of k_{-1} and k_1, namely, $\sim 10^6$ sec^{-1} and $\sim 10^8$ M^{-1} sec^{-1}, respectively. Therefore, the glymated pair lasts, on the average, for about 10^{-6} sec before it collapses into a tight one and relieves the glyme. Recent studies of Hirota, *et al.*,[6b] demonstrated that the collapse of loose $Na^+,N\cdot^-$ ion pairs formed in mixtures of diethyl ether and tetrahydrofuran (THF) is faster. Extrapolation of his data, reported for −70°, to +25° would lead to rate constants of collapse as high as 10^{12} sec^{-1} if the activation energy reported by Hirota is accepted. This may be surprising albeit the complexing of Na^+ with tetrahydrofuran is much weaker than with tetraglyme.

A direct determination of the activation energy of the collapse was not possible because a_{Na} of the glymated pair decreases nearly to zero at lower temperatures. Assuming 10^{14} sec^{-1} for the frequency factor of the collapse process, one calculates E_{-1} to be about 8 kcal/mole. This estimate is consistent with the results of other studies carried out in this laboratory which showed that the coordination of glyme with sodium salts is exothermic by about 6 kcal/mole.

According to Hirota,[6] the collapse of a loose, THF solvated $Na^+,N\cdot^-$ is associated with a high A factor of about 10^{18} sec^{-1}. If the degree of solvation in the transition state is lower than in the initial state, then a higher positive entropy of activation is expected for the collapse of an ion pair coordinated with several (say four) molecules of THF than for a pair associated with one molecule of glyme. Hence, a large increase in $\Delta S^{\ddagger}$ may be the main factor responsible for a high rate of collapse of the loose ion pairs studied by Hirota as compared to the relatively slow process observed in our studies. However, it should be stressed that Hirota assumes the a_{Na} of each type of ion pair to be temperature independent. Any decrease of the splitting constant of the tight ion pairs with decreasing temperature would affect his calculation, reduce the respective rate constants, and, hence modify $E^{\ddagger}$ and $\Delta S^{\ddagger}$.

Conductance of $N\cdot^-,Na^+$ in THP in the Absence and Presence of Glyme. Not always is it possible to discriminate between ion pairs and free ions on the basis of esr observations. For loose pairs the hfsc due to cations are often indistinguishable from zero; consequently, many investigators mistake them for free ions. A reliable criterion which permits us to distinguish pairs from free ions is provided by conductance studies. We investigated, therefore, the conductance of $N\cdot^-$, Na^+ in THP in the absence and presence of tetraglyme. The technique described elsewhere[4a,10,11] was adopted.

The results are summarized in Table III. The extremely low degree of dissociation of $N\cdot^-,Na^+$ in THP (in the absence of glyme) prevented the direct determination of the relevant Λ_0's. These were calculated by applying Walden's rule to the data obtained in THF.[4a] The degree of dissociation of the glymated pair is much higher than that of the tight $N\cdot^-,Na^+$, and for this salt Λ_0's were derived from the Fuoss plots. These values favorably compare with those calculated by the Walden rule.

Table III. Dissociation of Glymated and Nonglymated Sodium Naphthalenide in THP

Temp, °C	Λ_0 Non-glymated	 Glymated[a]	$K_{diss} \times 10^{11}$ M Non-glymated	$K_{diss} \times 10^8$ M Glymated[a]
20	71	69	7.7	3.0
10	62	59	9.8	4.1
5	57	55	11.3	4.4
0	53	50	12.8	4.9
−5	48	47	14	5.0
−10	44	42	16.3	5.8
−25	33	31	25	6.1
−40	24	22	41	5.5 (?)

[a] $[G] = 5 \times 10^{-2}$ M.

Inspection of Table III shows that K_{diss} of the glymated pair, although by two orders of magnitude greater than that of the tight pair, is still very low. The van't Hoff plots shown in Figure 4 reveal that $-\Delta H_{diss}$ of the latter pair is about 3.8 kcal/mole corresponding to ΔS_{diss} of ~ -60 eu. This indicates that a substantial degree of solvation takes place on the dissociation of

(10) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(11) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 5743 (1967).

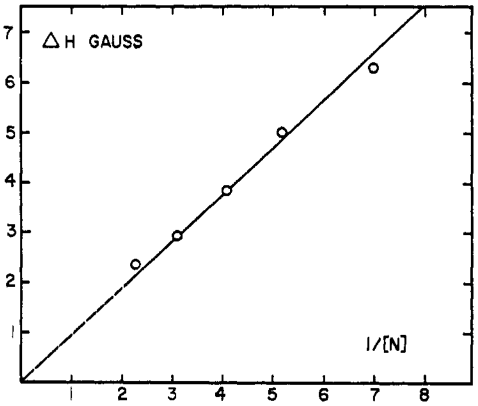

Figure 6. Dependence of ΔH on $1/[N]$ in the fast exchange $N\cdot^- + N \rightleftarrows N + N\cdot^-$ in HMPA (free ion).

the tight pair. The $-\Delta H_{diss}$ of the glymated pair approaches 0 at lower temperatures, the relevant ΔS_{diss} being only ~ -30 eu. This is consistent with the loose structure of the glymated pair and shows that the degree of cation solvation is relatively high in that pair and, therefore, it increases only slightly on its dissociation. The reason for the temperature dependence of the ΔH_{diss} observed for the glymated pair will be discussed later.

Table IV. Rate Constant of Exchange, $N\cdot^- + N \rightarrow N + N\cdot^-$ ($k_{ex,1}$) for Free $N\cdot^-$ Ions in HMPA[a]

	$k_{ex,1}$ 10^{-8} M^{-1} sec^{-1}	
Temp, °C	Slow exchange	Fast exchange
16.4	...	4.5
20	4.1	...
25.3	...	4.7
26.7	5.0	...
36.8	...	5.9
37.3	5.3	...
46.8	6.1	...
47.4	...	7.4
57.3	6.3	8.4
68.6	7.2	9.7
78.4	7.1 (?)	11.7

[a] Rate constant at slow exchange was calculated for Lorentzian lines, $k_{ex} = 1.52 \times 10^7 \Delta H/\Delta[N]$. Each result was obtained from five experiments with [N] varying from 0 to 10^{-2} M; an average width of four or five lines was used in the calculation (α −4, β −2; α −4, β 0; α 0, β −2; α 0, β 0; α 4, β 0). Rate constant at fast exchange was calculated from the equation $k_{ex} = 2.02 \times 10^7 \nabla \{\Delta H/\Delta(1/[N])\}^{-1}$ where the second moment ∇ was calculated from the stick model. ∇ varies from 22.05 at 16° to 21.30 at 78°, corresponding to hfsc β = 1. 74–1.69 and α = 4.70–4.65, respectively. Each k_{ex} value was determined from five experiments in which [N] varied from 0.14 to 0.4 M. No corrections were introduced for modulation broadening since its amplitude was low (~80 mG).

The Effect of Ionic Association on Kinetics of Electron Exchange. The pioneering work of Weissman and his coworkers[12] demonstrated that the rate of electron exchange between naphthalenides and naphthalene depends on the state of ionic association of the radical ions. Since alkali salts of many radical ions are virtually dissociated in hexamethylphosphoramide[13] (HMPA), even at concentrations as high as 10^{-2} M, the exchange between free $N\cdot^-$ ions and N can be conveniently studied in this solvent.

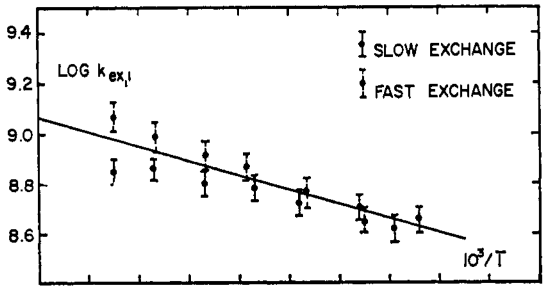

Figure 7. The Arrhenius plot of log k_{ex} *vs.* $1/T$. The results obtained at the slow- and fast-exchange limit for the process $N\cdot^- + N \rightleftarrows N + N\cdot^-$ in HMPA (free ion).

The rate of electron transfer was determined from broadening of the esr lines at slow- and at fast-exchange limits. The pertinent data and the details of experimentation and calculations are given in Table IV. For the sake of illustration a typical plot of ΔH(gauss) *vs.* Δ[N] derived from the experiments performed at slow exchange limit is shown in Figure 5, and a typical result obtained at fast exchange limit is shown in Figure 6.

The Arrhenius plot of log $k_{ex,1}$ *vs.* $1/T$ is shown in Figure 7.

$$N\cdot^- + N \xrightarrow{k_{ex,1}} N + N\cdot^-$$

The activation energy, $E_{ex,1}$, is calculated to be 2.7 ± 0.5 kcal/mole corresponding to $A_{ex,1} = 4 \times 10^{10}$ M^{-1} sec^{-1}. Similar studies were performed by Hirota, *et al.*,[6b] who used a mixture of THF and DME as the solvent. Their results led to E_{ex} = 2.5 kcal/mole corresponding to $A_{ex} = 8 \times 10^{10}$ M^{-1} sec^{-1}.

The rates of exchange of free $N\cdot^-$ ions are reported in the literature for several solvents. The relevant rate constants and references are given in Table V.

Table V. Exchange Involving the Free Ions, $N\cdot^- + N \rightleftarrows N + N\cdot^-$, in Various Solvents

Solvent	10^{-8} $k_{ex,1}$ (~25°) M^{-1} sec^{-1}	λ, kcal/mole	Ratio of k_{ex}'s Obsd	Calcd	Ref
Isopropyl alcohol	1[a]	16.0	0.2	0.5	*b*
HMPA	5	14.5	1.0	1.0	This work
THF–DME	12	~12.5	2.4	2.3	*c*
THF	30	12.2	6.0	2.6	*d*

[a] The value for the reaction $B\cdot^- + N \rightleftarrows N\cdot^- + B$ is given in ref *b*. We calculated from it the k_{ex} by introducing the correction which accounts for the thermoneutrality of the exchange. [b] S. Arai and L. M. Dorfman, Advances in Chemistry Series No. 82, American Chemical Society, Washington, D. C., 1968, p 378. [c] N. Hirota, R. Carraway, and W. Schook, *J. Am. Chem. Soc.*, **90**, 3611 (1968). [d] R. Chang and C. S. Johnson, *ibid.*, **88**, 2338 (1966).

According to Marcus[14] the solvent effect arises from the change of λ. The latter is given by the equation

$$\lambda = ({}^1/_2a_1 + {}^1/_2a_2 - 1/r)(1/D_{op} - 1/D_s)(\Delta e)^2$$

where a_1 and a_2 are the radii of the exchanging partners

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(12) (a) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957); (b) P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962).

(13) A. Cserhegyi, E. Franta, J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **89**, 7129 (1967).

(14) R. A. Marcus, *J. Chem. Phys.*, **26**, 867 (1957).

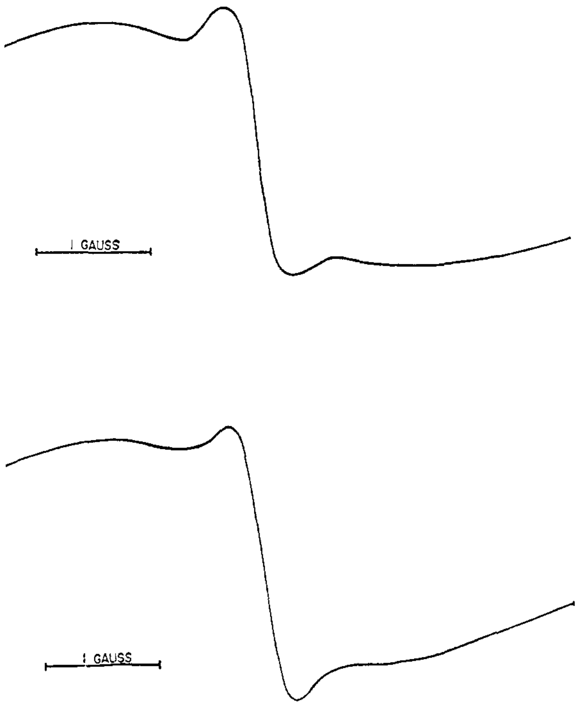

Figure 8. Esr spectrum of N·⁻,G,Na⁺ (about $2 \times 10^{-4}M$) in the presence of a large excess of N (at 37°): upper curve, the observed spectrum; lower curve, the computer-simulated spectrum having the slope of the middle line and the widths of the peaks identical with the observed one.

and r is their distance in the transition state. We shall assume that the value of the entity given in the first bracket is constant for all the investigated solvents and equal to $1/10A$. Although this estimate is somewhat arbitrary, the "true" value is not expected to differ by more than 20 or 30% from the chosen one. $D_{\text{op}} = n^2$ is the optical dielectric constant and D_s the static dielectric constant of the investigated solvent, and Δe is the transferred charge. For exchange reactions the free energy of activation is given by $\lambda/4$.

The values of λ are listed in the third column of Table V. On this basis we calculated the ratios of k_{ex}(in a solvent)/k_{ex}(in HMPA). The observed and calculated ratios are given in the fourth and fifth columns of Table V. The fair agreement indicates that Marcus' treatment is applicable for these processes.

Studies of electron exchange of glymated pairs, *i.e.*

$$N\cdot^-,G,Na^+ + N \rightleftarrows N + N\cdot^-,G,Na^+$$

led to some unexpected results. The experiments were performed in a solution containing enough glyme to convert virtually all $Na^+,N\cdot^-$ pairs into $N\cdot^-,G,Na^+$. Due to technical reasons only the fast exchange limit was studied. At three temperatures, *viz.* 27, 37, and 47°, the esr spectrum revealed the presence of two species, one exchanging rapidly, the other more slowly. This is seen from inspection of Figure 8 which depicts the spectrum observed at 37° (the upper curve) and the simulated spectrum drawn by computer (the lower curve). The simulation of the spectrum was performed on the assumption that the esr spectrum of the slower species collapses into four overlapping lines ($a = 0.4$ G), whereas that of the rapidly exchanging one collapses into a single line ($a \approx 0$). Such simulations were done for various proportions of the two species, *viz.*, from 1.5 to 15% of the fast exchanging one, and for various line widths (0.22–0.44 G for the fast one and 1.4–2.4 for the slow one). The selection of the proper simulated spectrum was made on the basis of the following criteria: (1) the over-all shape of the line; (2) the relative heights of the two peaks; (3) the magnitude of the maximum slope of the center line (a very sensitive test); (4) the apparent line widths of the broad and narrow lines. On this basis the proportion of the fast exchanging species was determined to be 10 ± 3%. All the simulated spectra corresponding to less than 7% of those species are definitely not acceptable. The agreement between the simulated and experimental spectrum was slightly improved by assuming a 50-mG shift in the g value. This accounts for some asymmetry noted in the observed spectrum. The actual widths of the two lines, superimposed in the observed spectrum, were determined thus as 2.4 and 0.42 G, respectively, and hence the rate constants of exchange at 37° were calculated to be 5×10^8 sec^{-1} for the slower pair and 3×10^9 sec^{-1} for the faster one, respectively. Analysis of the two-peak spectrum observed at 47° proves that the proportion of the rapidly exchanging species decreases with increasing temperature. We did not attempt to analyze the spectra observed at lower temperatures (<20°) in which both peaks coalesce.

Spectra observed by Chang and Johnson[15] in the course of their studies of fast exchange between N and its radical ion resemble those shown in Figure 8. However, these workers claim that the free $N\cdot^-$ ions are the rapidly exchanging species. It seems that such an explanation is not applicable in our case. The salt concentration in our experiments was 2×10^{-4} M and the relevant dissociation constant at 37° is 2×10^{-8} M^{-1} (see Table III). Hence, only 1% of the free ions was present in the solution while the fraction of the reactive species had to be greater than 7%. One concludes, therefore, that the rapidly exchanging species forms another type of glymated ion pair having $a_{\text{Na}} \approx 0$ and it cannot be a free $N\cdot^-$ ion.

The hypothesis of two loose pairs gains further support from conductance studies. These showed a decrease in the heat of dissociation of glymated ion pairs on cooling the solution (see Figure 4). Apparently, on lowering the temperature of the solution the pair which predominates at higher temperatures is converted into another one which dissociates more readily. The latter could, perhaps, be identified with the more rapidly exchanging ion pair characterized by a lower a_{Na} hfsc.

It is not possible at present to determine the structures of these two loose, "glymated" pairs. Nevertheless, the following tentative suggestion may be considered. Let us assume that the sodium ion is located above the plane of the $N\cdot^-$ moiety. Inspection of models shows that a tetraglyme molecule could encircle the Na^+ ion and form a bulky ring around it. Therefore, two structures, schematically depicted in Figure 9, may be visualized, and we propose that one of them (I) represents the slower pair while the other (II) is the one which exchanges more rapidly with naphthalene molecule.

This model is appealing. Pair I should have a larger a_{Na} hfsc than pair II, its degree of solvation is lower than that of II and, hence, the conversion of I into II should

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[15] R. Chang and C. S. Johnson, *J. Am. Chem. Soc.*, **88**, 2338 (1966).

be exothermic. The electron transfer from II to naphthalene should proceed without any rearrangement of solvent molecules around the Na$^+$ ion, whereas THP molecules have to be removed from above Na$^+$ and squeezed in below when the exchange involves ion pair I. Thus, the exchange would be faster for II than for I. The proposed model accounts, therefore, for the conclusions deduced from our experiments.

The conversion of pair I into II is associated with the rotation of the solvated Na$^+$ ion coupled with its further coordination with solvent molecules. The rate constant of this conversion must be greater than 10^6 sec^{-1}, judging from the sharpness of the lines seen in Figure 2, but it should be smaller than 10^8 sec^{-1} because two distinct species could be observed in the fast electron-transfer process. The most probable value of conversion of I into II is about 10^7 sec^{-1}. The rate constant of conversion of pair II into I is approximately 10 times greater.

The decrease of the a_{M} values of the glymated species observed at lower temperatures (see Table I) cannot be interpreted in terms of dynamic model only. The splitting constant of ion pairs I must be temperature *dependent* otherwise unacceptable values would be obtained for ΔH and ΔS of the conversion

$$\text{ion pair I} \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} \text{ion pair II}$$

Assuming a plausible value of 3 kcal/mole for ΔH (justified by our conductance measurements), we calculate that a_{I} decreases from about 0.4 G at 47° to about 0.25 G at 0°. Accepting this estimate and utilizing the observation that at 0° the lines corresponding to $M_z(\mathrm{Na}) = {}^1/_2$ have different width from the lines corresponding to $M_z = {}^3/_2$, we find from eq 6 of ref 6 that $k_c \approx 2 \times 10^6$ sec^{-1} at that temperature. This is reasonable in view of our previous estimate of k_c at 37° which was based on the result of fast exchange.

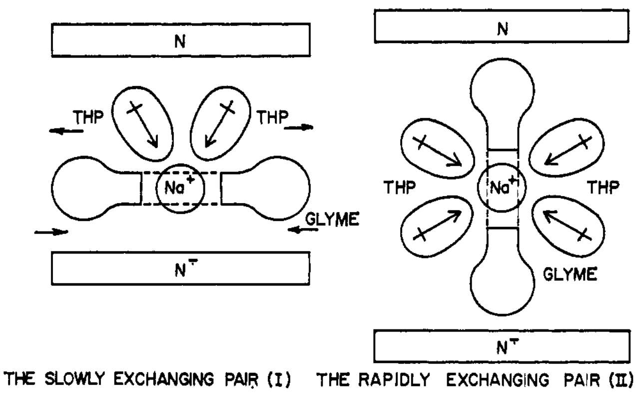

Figure 9. Schematic drawing representing tentatively the two loose glymated N$\cdot^-$,G,Na$^+$ ion pairs and their exchange with N: (I) the slowly exchanging pair; (II) the rapidly exchanging pair.

Finally, we investigated the rate of electron transfer from the tight Na$^+$,N$\cdot^-$ ion pair to N at room temperature in THP. Studies in the slow-exchange limit led to the rate constant of 2×10^6 M^{-1} sec^{-1}. Hence, the tight ion pair is the least reactive. The transfer involving tight ion pairs in several solvents was investigated by Hirota.[6] His rate constant is similar to ours when the reaction takes place in DMTHF, although higher values were obtained in other solvents.

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