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ESR Studies of the Ion Pairs of the Terephthalonitrile Anion with Alkali Metal Cations

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The behavior of the alkali metal ions, Li, Na, and K, in solutions of terephthalonitrile in ethereal solvents was studied by means of the electron spin resonance of the anion radical. The metal ions formed ion pairs by association with the anion in solution at one of the two cyano groups; the rate at which the cation is transferred between these two groups determines the detailed structure of the ESR spectrum. Within the limits of slow transfer, the spectrum was interpreted in terms of splittings due to two sets of proton pairs and two non-equivalent nitrogens. As the transfer rate increased, the spectrum exhibited an alternating line width, until finally the splittings were averaged within the limits of the fast transfer rate. The transfer rate of cations in the same solvent was found to increase in the order of the size of cations. It also depended on the solvating power for the cation. At low concentrations and low temperatures, the ion pair tended to dissociate, thus giving free anions. The hyperfine interactions with the nuclear spin of the cations were also observed.

Recent electron spin resonance (ESR) studies of anion radicals produced chemically in ethereal solvents have shown that there exists in most cases an ion-pair association between an anion and its counter cation. This association often leads to a hyperfine interaction involving a cation nucleus, and also sometimes to a spin distribution on an anion different from in its free state. If an anion has two sites which are capable of associating with a cation, the hopping of the cation between these two sites becomes especially possible. If the rate of hopping is sufficiently slow, the association at either one of the sites will modify the electron spin distribution, which may otherwise be predicted from the given geometrical symmetry of the free anion. If the hopping rate is faster, particularly when certain conditions are fulfilled, an isotropic modulation of line width, which is called "an alternating line width," may be observed.[1-6]

Although the ESR spectra of the free terephthalonitrile anion have been investigated by several workers,[7-9] no ESR studies of its ion-pair complex have been attempted. Stimulated by the possibility that the two cyano groups might work as the two sites referred to above, we have undertaken a study of the interactions of the terephthalonitrile anion with alkali metals. This paper will mainly deal with observations relating to the hopping of a cation between the two cyano groups. The dissociation of the ion-pair and the alkali metal hyperfine interaction will also be described.

Experimental

The terephthalonitrile anion was produced with potassium, sodium, or lithium metal in ethereal solvents, such as dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MeTHF), tetrahydropyran (THP), and ethyl ether. The temperature dependence of the ESR spectra was measured in the range from 20°C to about −80°C. The details of the experimental procedure have been described in a preceding paper.[10]

Results and Discussion

The Hopping of the Cations. Among the ion pairs of the terephthalonitrile anion with alkali cations examined, the lithium ion pair reveals most clearly the ESR spectrum associated with the hopping of a metal cation between the two cyano groups of the anion. Figure 1 shows the ESR spectrum of the ion pair with lithium in DME at 20°C. Only fifteen lines are visible in this spectrum, in contrast to the spectrum of the free anion, shown in

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1) R. L. Wards, *J. Am. Chem. Soc.*, **83**, 1296 (1961); *J. Chem. Phys.*, **36**, 1405 (1962).

2) E. de Bore and E. L. Mackor, *Proc. Chem. Soc.*, **1963**, 23; *J. Am. Chem. Soc.*, **86**, 1513 (1964).

3) N. M. Atherton and A. E. Goggons, *Mol. Phys.*, **8**, 99 (1964).

4) E. de Bore, *Recueil*, **84**, 609 (1965).

5) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **41**, 699 (1964).

6) E. A. C. Lucken, *J. Chem. Soc.*, **1964**, 4234.

7) R. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

8) P. H. Rieger and Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

9) A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1963).

10) K. Nakamura, This Bulletin, **40**, 1 (1967).

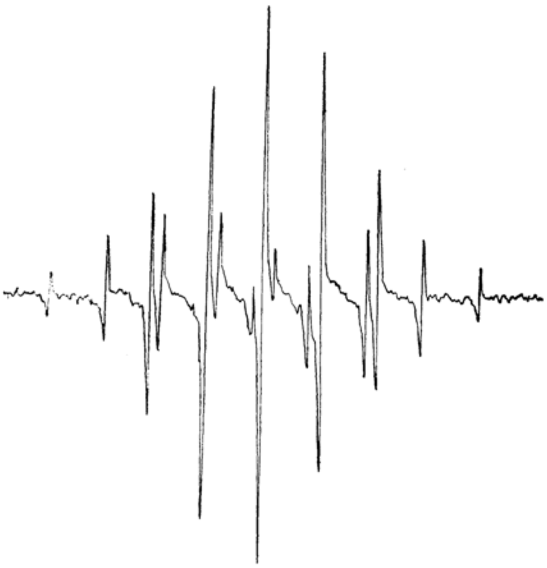


Fig. 1. ESR spectrum of the ion-pair with lithium in DME at 20°C.

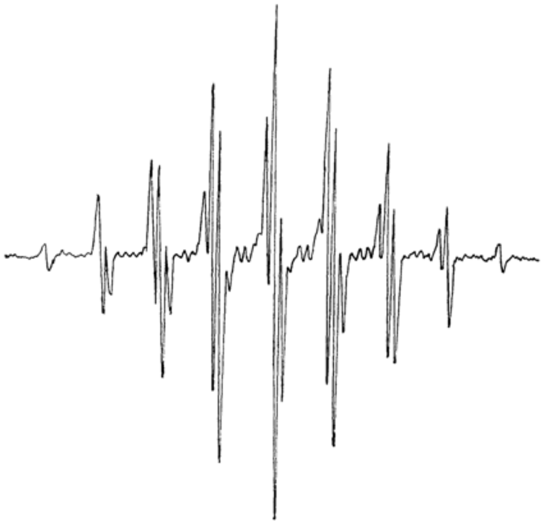


Fig. 2. ESR spectrum of the terephthalonitrile anion produced with potassium in DME at 20°C.

Fig. 2, which exhibits the twenty-five lines expected from four equivalent protons and two equivalent nitrogens of the anion. Each line of the spectrum may be conveniently identified by denoting it with a particular set of M_H and M_N values, where M_H and M_N are the sum of the nuclear magnetic quantum numbers of the four protons and the analogous sum for the two nitrogen nuclei respectively. Now, it is shown that the missing ten lines are those for $M_H=\pm 1$, and also that the intensity ratio of a line for $M_N=0$ to a line for $M_H=\pm 2$ is, experimentally, 4 within a family of the same M_N values, while the corresponding ratio of the statistical weights is 6. On the other hand, the intensity ratios of the lines for different M_N values but the same M_H values accord with the ratios of the statistical weights of these lines. These features may easily be seen in Fig. 3, a schematical reconstruction corresponding to Fig. 1. Similar features of the spectrum were also observed in the THF solution.

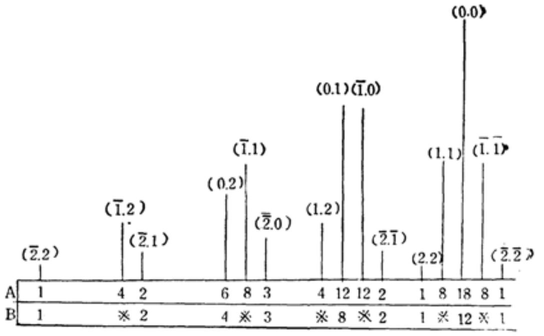


Fig. 3. The schematic reconstruction corresponding to the low-field halves of Figs. 1 and 2. Figures in parentheses denote values of M_H and M_N in this order. The bar above the figure represents a negative sign. The row A represents the statistical weight, which is seen to be equal to the relative amplitude of the lines in Fig. 2, and the row B is the relative amplitude of the lines in Fig. 1. A negative sign of the proton coupling constants and a positive sign of the nitrogen coupling constant are assumed.
※ : Lines not observed in Fig. 1.

On the contrary, the spectrum of the ethyl ether solution shown in Fig. 4 is much more complex. In order to explain this spectrum, it will be necessary to consider two sets of pair protons and two non-equivalent nitrogens, whose coupling constants are listed in Table 1. These coupling constants give the reconstruction diagram depicted in Fig. 5, which should be compared with Fig. 4.

Table 1. Hyperfine coupling constants and g values of the terephthalonitrile anion radical (with peroxylaminedisulfate as a standard)

Species*	g-Value	a_H, gauss**	a_N, gauss**
Free anion	2.00255	1.576	1.812
Potassium	2.00253	1.595	1.812
Sodium	2.00253	1.595	1.812
Lithium (a)	2.00251	1.625	1.800
Lithium (b)	2.00251	a_{H_1} 2.46 a_{H_2} 0.80	a_{N_1} 1.98 a_{N_2} 1.63

* Where the solvent is not specified, the value were independent of the solvent employed.
** The proton and nitrogen coupling constants, respectively.
(a) In DME or THF, solution.
(b) In THP, MeTHF, or ethyl ether solution.
For suffixes 1 and 2, see Fig. 6.

The results presented so far may be understood in

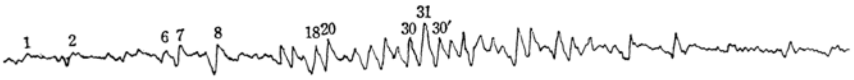
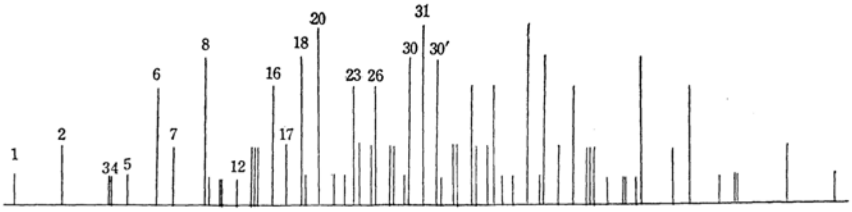


Fig. 4. ESR spectrum of the ion-pair with lithium in ethyl ether at 20°C. The lines are numbered in consistency with Fig. 5.

(a)



(b)

1. $(\bar{1}.\bar{1}.1.1)$
2. $(\bar{1}.0.1.1)$
3. $(\bar{1}.1.1.1)$
4. $(\bar{1}.\bar{1}.1.0)$
5. $(\bar{1}.\bar{1}.0.1)$
6. $(0.\bar{1}.1.1)$
   $(\bar{1}.0.1.0)$
7. $(\bar{1}.0.0.1)$
8. $(\bar{1}.1.1.0)$
   $(0.0.1.1)$
9. $(\bar{1}.\bar{1}.1.\bar{1})$
10. $(\bar{1}.1.0.1)$
11. $(\bar{1}.\bar{1}.0.0)$
12. $(\bar{1}.\bar{1}.\bar{1}.1)$
13. $(0.1.1.1)$
14. $(0.\bar{1}.1.0)$
15. $(\bar{1}.0.1.1)$
16. $(0.\bar{1}.0.1)$
    $(\bar{1}.0.0.0)$
17. $(\bar{1}.0.\bar{1}.1)$
18. $(0.0.1.0)$
    $(1.\bar{1}.1.\bar{1})$
19. $(\bar{1}.1.1.\bar{1})$
20. $(0.0.0.1)$
    $(\bar{1}.1.0.0)$
    $(\bar{1}.\bar{1}.0.\bar{1})$
21. $(\bar{1}.1.\bar{1}.1)$
22. $(\bar{1}.\bar{1}.\bar{1}.0)$
23. $(0.1.1.0)$
    $(1.0.1.1)$
24. $(0.\bar{1}.1.\bar{1})$
25. $(0.1.0.1)$
26. $(0.\bar{1}.0.0)$
    $(\bar{1}.0.0.\bar{1})$
27. $(0.\bar{1}.\bar{1}.1)$
28. $(\bar{1}.0.\bar{1}.0)$
29. $(1.1.1.1)$
30. $(1.\bar{1}.1.0)$
    $(0.0.1.\bar{1})$
31. $(0.0.0.0)$
    $(1.\bar{1}.0.1)$
    $(\bar{1}.1.0.\bar{1})$

Fig. 5. (a) The reconstruction corresponding to Figs. 4, 7 and 8.
(b) The table of the nuclear spin states for each line of the low field half in Fig. 5 (a). Each line is denoted by number. Four figures in parentheses of (b) represent the values of M_{H_1}, M_{H_2}, M_{N_1} and M_{N_2} in this order.

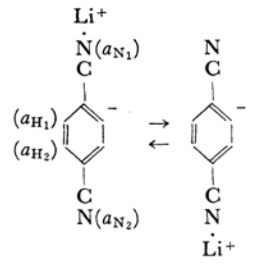


Fig. 6. a's: The proton and nitrogen constant at each position. See Table 1.

terms of the hopping of the lithium ion between the two cyano groups, as is shown in Fig. 6, a hopping analogous to the mechanism postulated by the Boer and Mackor for the pyracene-alkali metal system[2,4] and by Atherton and Goggins for the pyrazine-sodium system.[3]

If a cation hops between two sites, A and B, of an anion, with the same life-time, t, at each site, and if a particular nucleus of the anion is associated with different coupling constants, a_A and a_B, according as the cation is at Site A or B respectively, the observed splitting will depend on the transfer rate of the cation between the two sites. When $a_A - a_B$ is larger than the line-width, w, the spectrum will exhibit both splittings, a_A and a_B, within the limits of slow transfer rate, $t \gg |\gamma(a_A - a_B)|^{-1}$, and an averaged splitting, $a = (a_A + a_B)/2$, within the limits of fast transfer, $t \ll |\gamma(a_A - a_B)|^{-1}$, where γ is a magneto-gyric ratio of an electron. In such extreme cases, the transfer rate does not influence the line width. When the transfer rate increases from the former to the latter, it begins to make a contribution to the line width in the range $t \approx (\gamma w)^{-1}$; a further increase in the rate will make it progressively impossible to distinguish between a_A and a_B, and the spectrum will come to an averaged splitting when $t \approx |\gamma(a_A - a_B)|^{-1}$. Thus, the spectrum resembles the one within the limits of fast transfer except for the greater line widths of the line in question. With a still further increase in the transfer rate, the line width is reduced as the result of a mechanism similar to the motional narrowing.[2,11-13]

From this point of view, the spectrum of the ethyl ether solution (Fig. 4) can be regarded as exhibiting the locking of the lithium ion in the proximity of a cyano group, corresponding to the limit of slow transfer. The spectrum of the DME or THF solution is a typical example of alternating line widths, corresponding to the case of an intermediate transfer rate, $t \approx |\gamma(a_A - a_B)|^{-1}$.

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11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York (1959), p. 218.
12) A. Carrington, *Mol. Phys.*, **5**, 426 (1962).
13) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

It is well known that, for the alternating line widths of a two-jump system, as in the present case, the contribution of the transfer rate to the line-width parameter, T_2^{-1}, is given by:

$$\Delta T_2^{-1} = \frac{1}{8} t\gamma(\Delta H)^2 \quad \text{(in gauss)} \qquad (1)$$

where ΔH is the shift of the resonance field, for a given total spin state, which would occur if a cation were transferred from one site to the other. The ΔH value for the terephthalonitrile anion is given by:

$$\Delta H = (a_{H_1} - a_{H_2})(M_{H_1} - M_{H_2}) + (a_{N_1} - a_{N_2})(M_{N_1} - M_{N_2}) \qquad (2)$$

where M_{H_1} is the sum of nuclear magnetic quantum numbers of the pair protons whose coupling constants are a_{H_1} (see Table 1), and so on. M_H and M_N are equal to $M_{H_1}+M_{H_2}$ and $M_{N1}+M_{N2}$ respectively. The fact that the alternating line widths are observed only with the lines for different M_H values leads to the relations, $t \approx |\gamma(a_{H_1}-a_{H_2})|^{-1}$ and $t \ll |\gamma(a_{N_1}-a_{N_2})|^{-1}$. These relations may, in fact, be seen to hold by substituting appropriate numerical values into a's:

$$a_{H_1} - a_{H_2}(1.66\ \text{gauss}) \gg a_{N_1} - a_{N_2}\ (0.25\ \text{gauss}).$$

Thus, the second term in Eq. (2) being neglected for the DME or THF solution at 20°C, Eq. (1) becomes:

$$\Delta T_2^{-1} = \frac{1}{8} t\gamma(a_{H_1} - a_{H_2})^2(M_{H1} - M_{H_2})^2 \quad \text{(in gauss)} \qquad (3)$$

One may see from Eq. (3) that, when $M_N = \pm 1$, the line widths for four of the six degenerated spin states with $M_N = 0$ are unaffected by the transfer rate, and that the ΔT_2^{-1} values for the other two are equal to $4J$, where $J = \frac{1}{8} t\gamma(a_{H_1} - a_{H_2})^2$. The ΔT_2^{-1} values for all the four states with $M_H = \pm 1$ are equal to J. The line width for a spin state with $M_H = \pm 2$ is unaffected by the transfer rate. When $t \approx |\gamma(a_{H_1} - a_{H_2})|^{-1}$, the value of J is considerably greater than T_2^{-1}, a value free from the influence of the hopping of the lithium ion. Thus, the complete collapse of all lines for $M_H =$

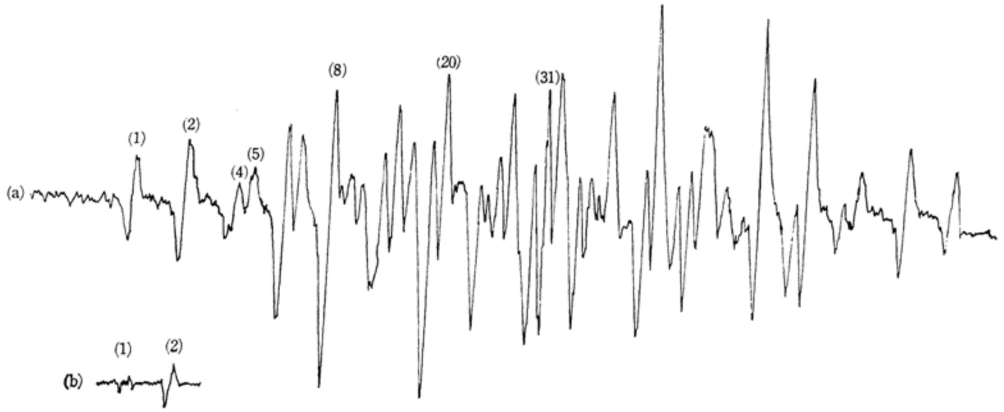

Fig. 7. (a) ESR spectrum of the ion pair with lithium in MeTHF at 20°C.
(b) The further splitting of the $(\bar{1}.\bar{1}.1.1)$ line due to lithium nucleus on dilution of (a).

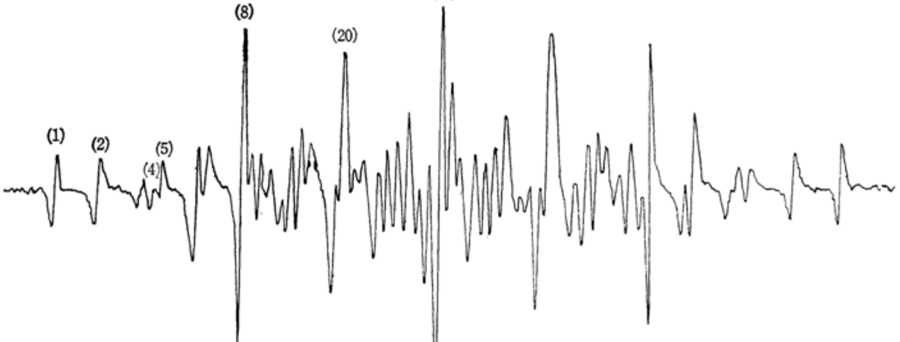

Fig. 8. ESR spectrum of the ion pair with lithium in THP at 20°C.

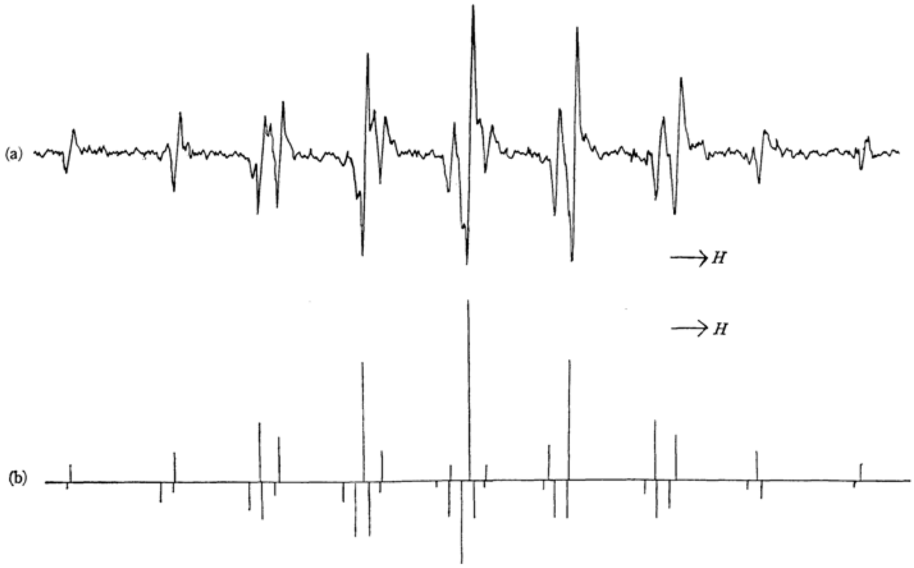

Fig. 9. (a) A superposition of the ESR spectrum of the free terephthalonitrile anion (the relative intensity 1) and that of its sodium ion pair (the relative intensity 3), in THF at −40°C.
(b) The reconstruction corresponding to (a).
The upper part : The ion-pair. the lower part : the free anion.

±1 and the partial collapse (two out of six) of the lines for $M=0$ is understandable.

Although the spectra of the THP and MeTHF solutions shown in Figs. 7(a) and 8 may be explained in terms of the coupling constants of two sets of pair protons and of two non-equivalent nitrogens, as has been done for the spectrum of the ethyl ether solution, there are some differences among these three spectra, as will be explained below. The value of $a_{H_1}-a_{H_2}$ remained unchanged through these spectra, while the apparent value of $a_{N_1}-a_{N_2}$, which is measured by the spacing between the lines 4 and 5 in Figs. 7 and 8, is reduced in the order: ethyl ether>MeTHF>THP (*cf.* Table 2). Furthermore, with a lowering of the temperature, the apparent value of $a_{N_1}-a_{N_2}$ in THP is increased, while that in ethyl ether seems to be independent of the temperature. Such apparent variations in $a_{N_1}-a_{N_2}$ are related to the change in the transfer rate arising from the solvent and temperature variations. The transfer rate in an ethyl ether solution will be slow enough to obtain an exact value of $a_{N_1}-a_{N_2}$. On the other hand, the rate in the THP or the MeTHF solution is rather fast, $t\approx(\gamma w)^{-1}$, resulting in the partial collapse of the split lines to a single line; this also leads to the relatively low intensity of lines which should disappear within the limit of the fast transfer rate of the lithium ion, as may be seen from the amplitude ratio of the $(\bar{1}.0.1.1)$ line to the $(\bar{1}.\bar{1}.1.1)$ line in Table 2 (see the footnote to Fig. 5).

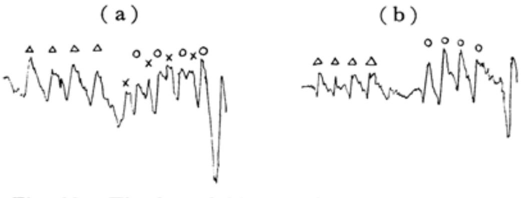

Fig. 10. The low field end of ESR spectrum of the ion-pair with sodium in THF.
(a) At 20°C (b) At −40°C
△: $(\bar{2}.2)$ line ×: $(\bar{1}.2)$ line ○: $(\bar{2}.1)$ line

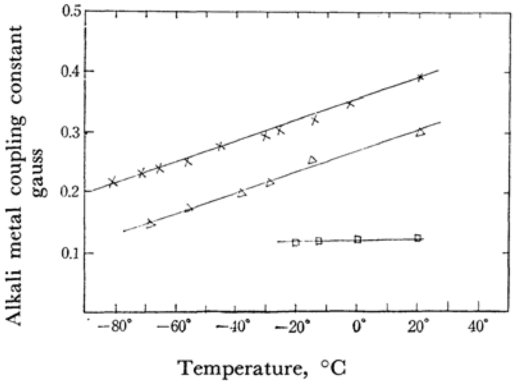

Fig. 11. The temperature dependence of alkali metal splittings.
×: Sodium splitting in THF
△: Sodium splitting in DME
□: Potassium splitting in THP

We shall now discuss briefly the results obtained for the sodium and potassium ion pairs. While the spectrum within the limits of the slow transfer rate was not obtained, the one exhibiting the alternating line widths was observed with the

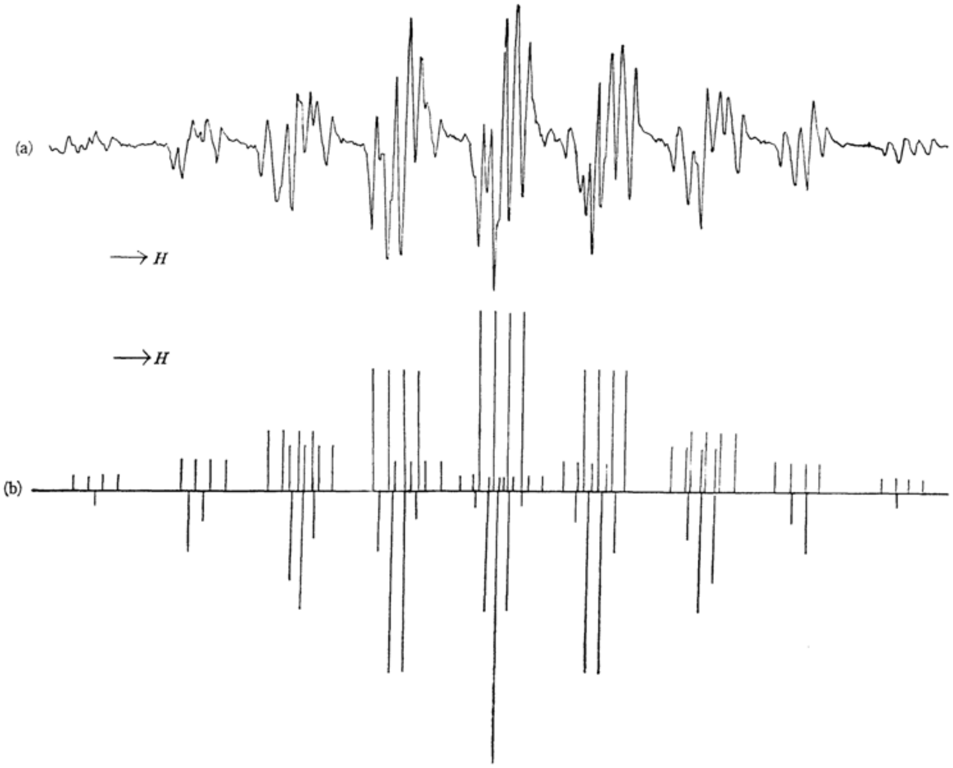

Fig. 12. (a) A superposition of the ESR spectrum of the free terephthalonitrile anion (the relative intensity 1) and that of its ion pair with sodium (the relative intensity 4), in THF at −60°C.
(b) The reconstruction corresponding to (a).
The upper part: the ion pair. The lower part: the free anion.

TABLE 2. THE APPARENT Δa_N AND THE AMPLITUDE RATIOS OF $(\bar{1}.0.1.1)$ LINE TO $(\bar{1}.\bar{1}.1.1)$ LINE IN THE SPECTRA OF THE LITHIUM ION PAIRS

Solvent	Temp °C	Δa_N gauss	R	t, sec	w gauss
Ethyl ether	20	0.25	*	$>1\times10^{-5}$	0.08
MeTHF	20	0.21	1.62	6×10^{-6}	0.16**
THP	20	0.11	0.82	5×10^{-7}	0.09
	−45	0.18	1.5	1×10^{-6}	0.12

R The amplitude ratio of the $(\bar{1}.0.1.1)$ line to the $(\bar{1}.\bar{1}.1.1)$ line (see Figs. 5, 7 and 8).
t The life time of a cation at a cyano group.
w A peak-to-peak line-width, in which the additional broadening due to the transfer is excluded.
Δa_N $a_{N_1}-a_{N_2}$.
* A weak intensity of the spectrum prevents the estimation.
** The large line-width is due to an unresolved lithium splitting.

TABLE 3. DATA ON THE ALTERNATING LINE-WIDTHS AND THE LIFE-TIMES OF METAL CATIONS AT A CYANO GROUP

Metal	Solvent	R*	t, sec**	Temp °C
Lithium	DME, THF	0	$3-8\times10^{-8}$	20
Sodium	DME	2	$<10^{-9}$	20
	THF	1	6.5×10^{-9}	20
	THF	0.5	1.4×10^{-8}	−3
	THF	0.24	2.8×10^{-8}	−20
Potassium	THP, MeTHF	1.1	3.5×10^{-9}	20
	THP	0.82	5×10^{-9}	0
	THP	0.5	1×10^{-8}	−23

* The amplitude ratio of the $(\bar{2}.1)$ line, to the $(\bar{1}.2)$ line, where figures in parentheses represent the sums of the nuclear magnetic quantum numbers of protons and nitrogen nuclei in that order (see Fig. 3).
** A peak-to-peak line-width w, 0.1—0.09 gauss *for the sodium and lithium ion-pairs and* 0.07 *gauss for the potassium ion pair, was used in* Eq. (4) to derive t.

sodium ion pair in THF, THP, or MeTHF, and with the potassium ion pair in THP or MeTHF. The spectra of the sodium ion pair in DME and of the potassium ion pair in DME or THF are free from the influence of the transfer rate. Examples of the spectra exhibiting the alternating

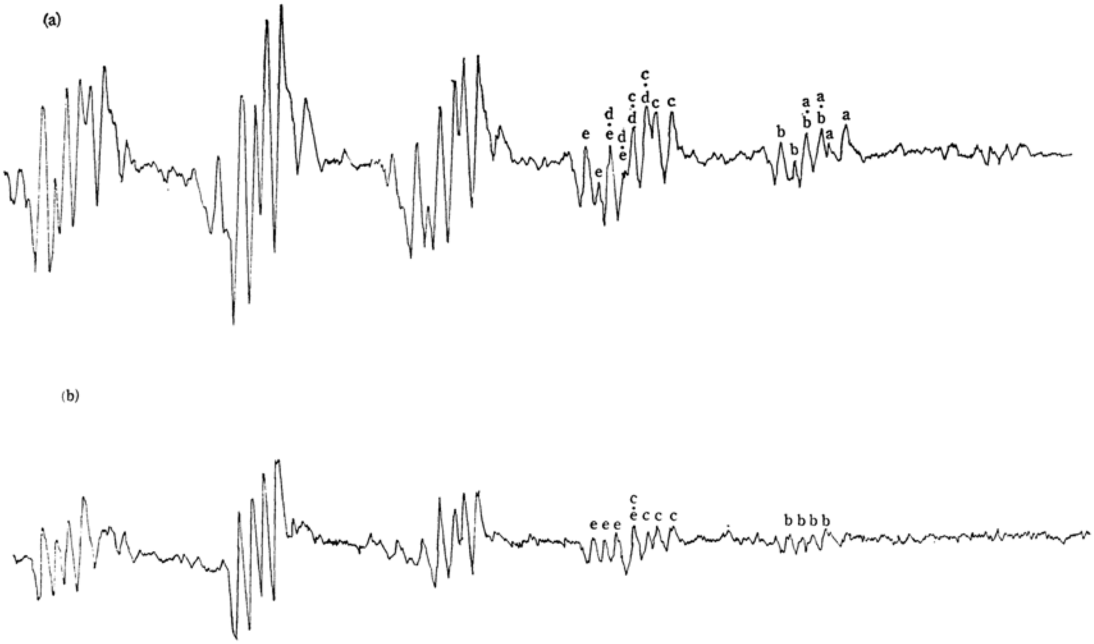

Fig. 13. The high field halves of ESR spectra of the ion-pair with potassium in THP.
(a) At 20°C (b) At −23°C
a: (1.$\bar{2}$) line b: (2.$\bar{1}$) line c: (0.$\bar{2}$) line d: (1.$\bar{1}$) line e: (2.0) line

line-widths are presented; the spectra of the sodium ion pair in THF at 20°C and −40°C in Figs. 10(a) and (b), and the spectra of the potassium in THP at 20°C and −23°C in Figs. 13(a) and (b). From Figs. 10(a) and (b), one may see the partial collapse of the lines for $M_H = \pm 1$ at 20°C and the complete collapse of the same lines at −40°C.

The Life Time of Alkali Metals at a Cyano Group. Tables 2 and 3 list the life time, which is equal to the invesrse of the transfer rate, of lithium, sodium, and potassium ions at a cyano group in several solvents, together with the amplitude ratios and the spacings between some characteristic lines. The life-times were estimated in the following way:

1) *The Life-time of the Lithium Ion in THP or MeTHF.* Gutowsky *et al.* treated the case in which the life-time, *t*, is in such a range as to influence the spacing between the two lines, which collapse into a single line within the limits of fast transfer and the T_2^{-1} value of which is of the same order of magnitude as the spacing between two lines.[14] They gave a schematic representation expressing the relationship among *t*, T_2, and the spacing between two lines. The use of this representation and of $a_{N_1} - a_{N_2}$ in Table 2 for the spacing allows us to estimate *t* for these cases.

2) *The Life-time of the Potassium in THP or MeTHF, or of the Sodium Ion in THF.* By assuming a Lorentzian shape of the spectral line and by using Eq. (1), the life-time, *t*, is given by:

$$t = 4\sqrt{3}\,\frac{w_1}{\gamma(\Delta H)^2}\cdot\frac{1-\sqrt{u}}{\sqrt{u}} \qquad (4)$$

where $u = h_2 s_1/h_1 s_2 = (w_1/w_2)^2$; *w*, the peak-to-peak line width; *s*, the statistical weight, and *h*, the amplitude. The 1 suffix denotes the line 1, whose line-width is independent of the transfer rate, while the suffix 2 denotes line 2, whose line width is increased by $\frac{1}{8}t\,\gamma(\Delta H)^2$ (in gauss) as a result of the transfer rate. Using the ($\bar{2}$.1) line as the line 1 and the ($\bar{1}$.2) line as the line 2, *u* is estimated from the figures in the third column of Table 3. The ΔH value for the ($\bar{1}$.2) line is equal to $a_{H_1} - a_{H_2}$, being obtainable only from the lithium ion pair data. Hence, the use of $a_{H_1} - a_{H_2}$ of the lithium ion pair in place of that of the sodium or potassium ion pair will insert some uncertainty into the present estimation. The application of the Arrhenius-type equation, $k = 1/t = \nu \exp(-E/\boldsymbol{R}T)$, to the data in Table 3 leads to the activation enthalpy, *E*, for the hopping; the values of *E* obtained are 5.5±1 kcal/mol for the sodium ion pair in THF and 3.7±1 kcal/mol for the potassium ion pair in THP.

The results presented so far may be summarized as follows: The transfer rates of alkali metal ions in the same solvent increase with increasing cationic size, *viz.*, in the sequence; lithium< sodium<potassium. When the solvent is altered, the transfer rate of the cation is increased with an

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14) H. S. Gutowsky and G. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

increase in the solvating power for the cation, *viz.*, in the sequence; ethyl ether$<$MeTHF$<$THP$<$THF$<$DME.

The Dissociations of the Ion-Pairs and the Alkali Metal Splittings. The lithium ion-pair in DME or THF tends to dissociate on dilution, and also with a lowering of the temperature.

TABLE 4. THE ALKALI METAL SPLITTINGS AT 20°C

Metal	Solvent	Coupling constant gauss
Lithium	MeTHF	0.055
Lithium	DME, THF, THP, Ethyl ether	<0.03*
Sodium	DME	0.30
Sodium	THF	0.38
Sodium	THP	0.43
Sodium	MeTHF	0.44
Potassium	THP	0.12
Potassium	MeTHF	0.12

* Unresolved

The ion pair and the free anion are slightly different not only in proton and nitrogen coupling constants, but also in *g* value, as may be seen in Table 1. Therefore, as dissociation occurs to an appreciable extent, a complex and unsymmetrical spectrum is observed. An example is represented in Fig. 9(a), as well as the corresponding reconstruction. The spectrum of the free anion, which was obtained at an extreme dilution at a low temperature, was identical with that of Fig. 2. A similar dissociation of the sodium ion pair was observed in DME or THF, as is shown in Fig. 12. In the spectrum of the anion produced with potassium in DME or THF, the absences of both the potassium hyperfine splittings and the alternating line-widths makes it difficult to assign this spectrum to either the ion-pair or the free anion. Because both the lithium and the sodium ion pair dissociate rather readily in THF or DME, however, there is a good possibility for the potassium ion pair to dissociate completely in these solutions, even at 20°C. Dissociation was not observed in other solvents. In general, the readiness of an ion pair to dissociate seems to be accompanied by a rapid transfer of the cation between the two cyano groups.

Sodium hyperfine splittings were observed in all the solvents used; potassium splittings, in THP and MeTHF, and lithium splitting, only in MeTHF. The solvent effects of these splittings are listed in Table 4. With a lowering of the temperature, the alkali metal splittings are reduced, as is illustrated in Fig. 11.

From the observations described so far, the mechanism of the transfer and the dissociation may be inferred to be as follows: Existing in close proximity to a cyano group, a cation is considered to be enclosed within a shell consisting of the anion and several solvent molecules. Such a shell is constantly demolished and reconstructed in many different ways, with a characteristic time constant of the order of the relaxation time or a few collision intervals. The cation may still be found in the proximity of the same cyano group, or it may have moved to the other cyano group (that is, a transfer has occurred), or it may have become surrounded only by solvent molecules (dissociation). In the transition state of either the transfer or the dissociation, the cation will be enclosed whithin an unstable shell and be more solvated than when it forms an ion-pair, but less solvated than in its free state. Thus, the large transfer rate of the cation may be associated with the readiness of the ion pair to dissociate.

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