Ion Pairing in Alkali-metal Salts of 1,3-Diphenylalkenes. Part II.[1] The Determination of Equilibrium Constants from Absorption Spectra

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The existence of contact ion pairs (C) and solvent-separated ion pairs (SS) is well established in solutions of alkali-metal salts of carbanions. We present results for the alkali-metal salts of 1,3-diphenylpropene and 1,3-diphenylbut-1-ene which indicate that two kinds of contact ion pair exist in these systems: a poorly solvated contact ion pair (C_1) and a more highly solvated contact ion pair (C_2). The thermodynamic parameters ΔH° and ΔS° have been determined, in appropriate cases, for the processes $C_1 \rightarrow C_2$ and $C_2 \rightarrow SS$.

THE visible spectra of solutions of the alkali-metal salts of 1,3-diphenylbut-1-ene (DPB^-M^+) in ethers present evidence for the existence of ion pairs in three distinct solvation states,[1] *viz.*, the solvent-separated ion pair (SS) and two contact ion pairs (C_1 and C_2) differing in their degree of solvation. The relevant solvation processes can be represented by equilibria (1)—(3),

$$DPB^-,M^+ + nS \rightleftharpoons DPB^-M^+,S_n \qquad (1)$$

$$DPB^-M^+,S_n + xS \rightleftharpoons DPB^-||M^+ \qquad (2)$$

$$DPB^-M^+ + mS \rightleftharpoons DPB^-||M^+ \qquad (3)$$

where DPB^-,M^+ represents the poorly solvated ion pair (C_1), $DPB^-M,^+S_n$ the more highly solvated contact ion pair (C_2), and $DPB^-||M^+$ the solvent separated ion pair (SS).

We have extended our earlier work to the alkali-metal salts of 1,3-diphenylpropene (DPP^-M^+), the results for which present even clearer evidence for reactions (1)—(3).

EXPERIMENTAL

1,3-Diphenylpropene[2] (DPP) and 1,3-diphenylbut-1-ene[1] (DPB) were prepared and purified as described previously. All the solvents utilised in the present study were commercial except for *cis*- and *trans*-2,5-dimethyltetrahydrofuran. These were separated from an approximately equimolar mixture of the two isomers (Fluka) by the use of a spinning-band fractionating column. Although preparative-scale separation of the isomers by g.l.c. proved unsuccessful on any of the several columns tried, analytical-scale g.l.c. did afford sufficient resolution to permit the determination of the isomeric composition. The purified isomers were identified by i.r. spectroscopy[3] and analysis by g.l.c. showed that their purity was better than 98%.

All solvents were purified and dried by stirring over sodium–potassium alloy under high vacuum. Solutions of the required hydrocarbon were reduced by the appropriate metal in a Pyrex vessel attached to a quartz cell of 0·01 cm pathlength. Typically, a concentration of about 3×10^{-3}M was used.

Visible absorption spectra were recorded on a Perkin-Elmer 137 spectrophotometer. The spectroscopic cell was placed in a partially silvered quartz Dewar vessel which was filled with ethanol and the temperature was lowered by the addition of small pieces of solid carbon dioxide. For studies at temperatures above ambient, the Dewar vessel was filled with warm water. A copper–constantan thermocouple, located within a few millimetres of the cell, was used to determine the temperature. During the recording of a spectrum in the range studied (+60 to −70 °C) the temperature remained constant to better than ±0·5 °C.

Spectra arising from mixtures of ion pairs were analysed by Vierordt's method, which allows for the overlap of the two bands. It was first necessary to determine the band shapes and extinction coefficients for each type of ion pair. In a previous paper[1] we reported the extinction coefficient for the solvent-separated ion pair of DPB^-M^+ to be $5{\cdot}5 \times 10^4$ and that of the contact ion pair to be $3{\cdot}3 \times 10^4$ l mol^{-1} cm^{-1}. In the present work we use the latter value for both contact ion pairs (C_1 and C_2) and we have assumed that the extinction coefficients for the species derived from diphenylpropene are the same as those of the corresponding species from diphenylbutene. The errors introduced by these assumptions are likely to be small.

RESULTS AND DISCUSSION

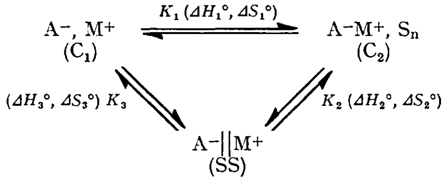
The visible spectra of the alkali-metal salts of 1,3-diphenylbut-1-ene are very sensitive to cation, solvent, and temperature and are most appropriately interpreted in terms of ion pairs in three distinct solvation states. Conductivity studies have proved that concentrated solutions (>10^{-3}M) contain much less than 1% of free

[1] Part I, J. W. Burley and R. N. Young, *J. Chem. Soc.* (*B*), 1971, 1018.

[2] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735.

[3] M. Lj. Mihailovic, R. J. Mamuzic, Lj. Zigic-Mamuzic, J. Bosnjak and Z. Cekovic, *Tetrahedron*, 1967, **23**, 215.

ions and the equilibria can therefore be represented as shown in the Scheme.



$A^- \equiv DPP^-, DPB^-$
$M^+ \equiv Li^+, Na^+, K^+, Rb^+, Cs^+$

SCHEME

The results of spectroscopic examination of a number of solutions of DPP^-M^+ are summarised in Table 1. That the expected anion had in fact been produced was verified by exchanging the solvent for 1,2-dimethoxyethane whereupon the absorption maximum shifted to 537 nm and the spectrum became identical with that produced upon direct reduction of diphenylpropene by potassium in dimethoxyethane. In hexane, no reaction occurred between diphenylpropene and Na–K alloy, which suggests that benzene has some slight solvating ability.

Comparison of Table 1 with Table 2 (which summarises our results for DPB^-M^+) shows that there is a general similarity between these allylic anions and it is accordingly of interest to examine these in detail.

Effect of the Methyl Substituent.—Both DPP^-Li^+ and DPB^-Li^+ exist in tetrahydrofuran as solvent-separated ion pairs and their absorption maxima are both located at 565 nm. The methyl substituent in DPB^- therefore appears to have no effect upon the absorption spectrum of the solvent separated ion pair. In contrast, however, the absorption maximum of DPP^-Li^+ in *trans*-2,5-dimethyltetrahydrofuran is at 481 nm whereas that of DPB^-Li^+ in the same solvent is at 488 nm. Similarly, DPP^-Li^+ in diethyl ether has $\lambda_{max.}$ at 476 nm whereas DPB^-Li^+ in Et_2O has $\lambda_{max.} = 484$ nm. In weakly

TABLE 1

$\lambda_{max.}$ and the ratio of the concentration of solvent-separated ion pairs [SS] to that of all contact ion pairs $\Sigma[C_i]$ for DPP^-M^+

		20 °C			−50 °C			
Cation	Solvent	$\lambda_{max.}$/nm [a]		$[SS]/\Sigma[C_i]$	$\lambda_{max.}$/nm [a]			$[SS]/\Sigma[C_i]$
Li^+	n-Hexane	450		<0·01				
Li^+	Diethyl ether	476		<0·01				
Li^+	*trans*-2,5-Dimethyltetrahydrofuran	481		<0·01	489	520	561	0·11
Li^+	*cis*-2,5-Dimethyltetrahydrofuran	483	561	0·06		520	561	0·32
Li^+	Tetrahydrofuran		564	>50			564	>50
Na^+	3,4-Dihydropyran	505		<0·01		520		<0·01
Na^+	Tetrahydropyran	518		<0·01		523		<0·01
Na^+	2-Methyltetrahydrofuran	516		<0·01		524	565	0·4
Na^+	Tetrahydrofuran	523	564	0·11		535	564	2·6
K^+	Benzene	514		<0·01				
K^+	Tetrahydrofuran	537		<0·01		537	563	2·4
K^+	Dimethoxyethane	537	563	0·7			563	>50

[a] Accurate to ±2 nm.

TABLE 2

$\lambda_{max.}$ and the ratio of the concentration of solvent separated ion pairs [SS] to that of all contact ion pairs $\Sigma[C_i]$ for DPB^-M^+

		20 °C			−50 °C			
Cation	Solvent	$\lambda_{max.}$/nm [a]		$[SS]/\Sigma[C_i]$	$\lambda_{max.}$/nm [a]			$[SS]/\Sigma[C_i]$
Li^+	n-Hexane	445		<0·01				
Li^+	Diethyl ether	484		<0·01				
Li^+	*trans*-2,5-Dimethyltetrahydrofuran	488		<0·01	492	525	560	0·59
Li^+	*cis*-2,5-Dimethyltetrahydrofuran	497	561	0·6		520	561	2·7
Li^+	3,4-Dihydropyran	502		<0·01		519	565	0·8
Li^+	Tetrahydrofuran		565	>50			565	>50
Na^+	Tetrahydropyran	520		<0·01		523		<0·01
Na^+	2-Methyltetrahydrofuran	519		<0·01		528	565	0·48
Na^+	Tetrahydrofuran	525	565	0·19		532	565	3·3
K^+	Benzene	520		<0·01				
K^+	Diethyl ether	525		<0·01		529		<0·01
K^+	Tetrahydrofuran	535		<0·01		535	564	2·9
K^+	Dimethoxyethane	537	563	1·2			563	>50

[a] Accurate to ±2 nm.

Hexane solutions of 1,3-diphenylpropene did not react with lithium metal and DPP^-Li^+ was therefore prepared in this solvent by abstracting a proton from diphenylpropene by reaction with butyl-lithium. (Addition of butyl-lithium to the olefinic double bond competed with this reaction[4] and gave rise to an additional peak at 335 nm.) Benzene solutions of diphenylpropene were reduced by Na–K alloy to give DPP^-K^+ which had an absorption maximum at 514 nm. The reaction was very slow but was facilitated by the large surface area of metal created by vigorous shaking. That the ex-

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[4] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*C*), 1971, 3780.

solvating ethers, where contact ion pairs predominate, the methyl substituent appears to have a much greater effect than in strong ethers. Waack and Doran [5] have explained why methyl substitution causes a bathochromic shift of the absorption maxima of carbanions, on the basis of hyperconjugation and the inductive effect. The present results, however, show that this effect is considerably modified by ion pairing. One result of association into ion pairs is the transfer of some of the electron density from within the anion to lie between the cation and anion: experimentally, this is manifested as a down-field shift of the ^1H n.m.r. spectrum for ion pairs relative to that of the free anion.[6] It therefore seems likely that the inductive effect will be increased in a contact ion pair relative to the free anion or solvent-separated ion pairs. In accordance with this view, DPP^-Na^+ and DPB^-Na^+, which are less tightly bound contact ion pairs (because of the larger ionic radius of Na^+) have absorption maxima which differ by only 3 nm (solutions in 2-methyltetrahydrofuran).

At 20 °C the spectra of the contact ion pairs of most DPB^-M^+ salts are sharp and exhibit only one maximum (see Figures 2 and 3 of ref. 1). In certain cases, the presence of a $C_1 \rightleftharpoons C_2$ equilibrium is manifested by a bathochromic shift of the absorption maximum upon lowering the temperature: for example DPB^-Na^+ in methyltetrahydrofuran and DPB^-K^+ in Et_2O (Table 2). In the case of DPP^-M^+, the absorption maxima of C_1 and C_2 are more nearly resolved and, for DPP^-Na^+ in tetrahydropyran and 3,4-dihydropyran, the spectra are broad and asymmetric. Lowering the temperature of these samples causes a change in the shape of the absorption curve, coincident with the bathochromic shift of the absorption maximum. The behaviour of DPP^-Na^+ in tetrahydropyran is shown in Figure 1: the displacement of the $C_1 \rightleftharpoons C_2$ equilibrium to the right as the temperature was lowered is clearly evident. No solvent-separated ion pair was observed in this system, even at −50 °C. The spectrum of DPB^-Na^+ in tetrahydropyran at 20 °C is included in Figure 1 for comparison. The electronic transition responsible for the absorption spectrum of the diphenylallyl carbanions is the excitation of an electron from the non-bonding orbital (n) to the lowest antibonding orbital (π^*). The magnitude of this transition energy is modified by the association of the anion with a cation, since this stabilises the ground-state energy level more than the excited state (Figure 2).[7,8] The contact ion pairs accordingly absorb at shorter wavelengths than the solvent-separated ion pair, the latter having an absorption maximum nearly identical to that of the free anion. If the perturbation of the energy levels of the anion is particularly sensitive to the interionic separation, cation–solvent interactions will cause the position of the contact ion pair absorption maximum to vary with solvent.

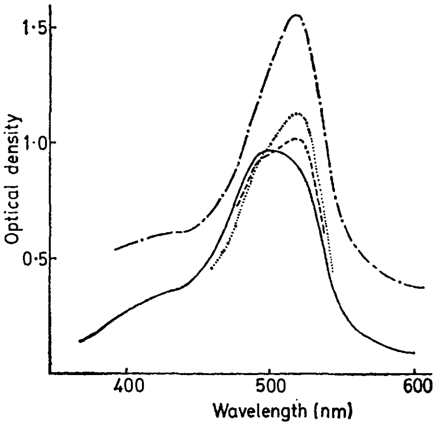

FIGURE 1 The visible absorption spectrum of DPP^-Na^+ in tetrahydropyran; ——, at 48 °C; – – – –, at −8 °C; · · · ·, at −45 °C; —·—·—, the absorption spectrum of DPB^-Na^+ in tetrahydropyran at 20°

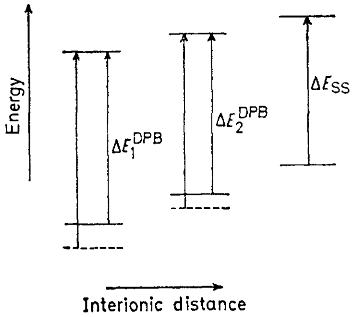

FIGURE 2 Schematic energy-level diagram for the ion pairs of DPP^-M^+ and DPB^-M^+. In the cases of the contact ion pairs C_1 and C_2, the ground-state levels of DPB^- are represented by solid lines and those for DPP^- by broken lines

Since methyl substitution has little effect upon the transition energy of the solvent separated ion pair, ΔE_{SS} (Figure 2) represents this quantity for both $DPP^-||M^+$ and $DPB^-||M^+$. Methyl substitution does however modify the transition energy of the contact ion pairs, producing the larger effect upon the tighter C_1.

Accordingly, ΔE_1 and ΔE_2, the excitation energies of C_1 and C_2, differ more for diphenylpropene than for diphenylbutene, *i.e.*, relation (4). For graphical simplicity, Figure 2 assumes that only the ground-state energy levels are perturbed by the methyl group; without doubt the excited states are in reality also perturbed.

$$(\Delta E_1^{\mathrm{DPP}} - \Delta E_2^{\mathrm{DPP}}) > (\Delta E_1^{\mathrm{DPB}} - \Delta E_2^{\mathrm{DPB}}) \qquad (4)$$

Effect of Temperature.—When solutions of DPP^-M^+ and DPB^-M^+ are cooled, their spectra undergo changes which represent a change in the average solvation state of the species present. Tables 1 and 2 summarise the

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[5] R. Waack and M. A. Doran, *J. Phys. Chem.*, 1964, **68**, 1148.

[6] J. W. Burley, R. Ife, and R. N. Young, *Chem. Comm.*, 1970, 1256.

[7] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1965, **69**, 2466.

[8] K. H. J. Buschow and G. J. Hoytink, *J. Chem. Phys.*, 1964, **40**, 2501.

results obtained at 20 and −50 °C. The spectrum of DPB$^-$Na$^+$ in tetrahydrofuran [Figure 3(b)] indicates that at 20 °C, the predominant species are contact ion pairs ($\lambda_{max.}$ 525 nm). As the temperature is lowered, solvent-separated ion pairs are formed ($\lambda_{max.}$ 565 nm) and the absorption maximum of the contact ion pairs shows an apparent bathochromic shift to 535 nm at −42 °C. A genuine shift would indicate a displacement of the $C_1 \rightleftharpoons C_2$ equilibrium to the right, but in this case it is not possible to state categorically that the shift is not an artefact arising from overlap of the contact ion pair absorption band with that of the solvent separated ion pair. However, there is no doubt that poorly solvated contact ion pairs (C_1) are indeed present in solutions of DPP$^-$Na$^+$ in tetrahydrofuran. In the spectrum [Figure 3(a)] recorded at 17 °C, there is a clearly defined shoulder on the short-wavelength side of the contact ion pair absorption band. At −64 °C the spectrum is sharp and the absorption maximum of the contact ion pair has shifted from 523 to 530 nm. Similarly, the absorption maximum of DPB$^-$Na$^+$ in 2-methyltetrahydrofuran varies from 519 nm at 20 °C to 528 nm at −50 °C, again indicating the production of a more highly solvated contact ion pair at low temperature. Solvent-separated ion pairs are also produced when the temperature is lowered (see Figure 3 of ref. 1). In contrast, solutions of DPB$^-$K$^+$ in tetrahydrofuran and in dimethoxyethane and of DPB$^-$Rb$^+$ in dimethoxyethane give spectra which indicate the presence of only two species (C_2 and SS) over the temperature range 20 to −60 °C.

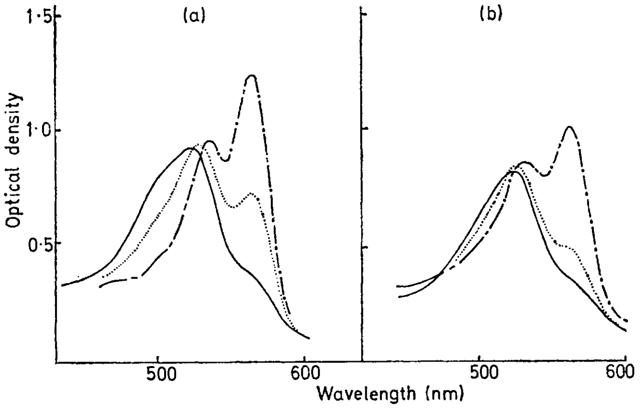

FIGURE 3 (a) The absorption spectrum of DPP$^-$Na$^+$ in tetrahydrofuran; ——, at 17 °C; · · · ·, at −14 °C; —·—·—, at −64 °C. (b) The absorption spectrum of DPB$^-$Na$^+$ in tetrahydrofuran; ——, at 20 °C; · · · ·, at 0 °C; —·—·—, at −31 °C

Figure 4 shows the effect of temperature upon the spectrum of DPB$^-$Li$^+$ in *trans*-2,5-dimethyltetrahydrofuran. At 20 °C the spectrum consists of a single maximum at 488 nm, corresponding to contact ion pairs in the lower solvation state C_1. As the temperature is lowered, this peak is replaced by two others, at 525 and 560 nm, corresponding to the more highly solvated contact ion pair C_2 and the solvent separated ion pair respectively. The spectra show an approximate isosbestic point, suggesting that two species predominate *viz.*, C_1 and SS. The spectrum of DPP$^-$Li$^+$ in the same solvent undergoes an essentially similar change except that the fraction of solvent-separated ion pairs at any given temperature is somewhat smaller. Figure 5 shows the effect of temperature upon the spectrum of DPP$^-$Li$^+$ in *cis*-2,5-dimethyltetrahydrofuran. At 20 °C the spectrum is very similar to that of DPP$^-$Li$^+$ in *trans*-2,5-dimethyltetrahydrofuran. However, as the temperature is lowered, the absorption band due to the contact ion pair broadens and the maximum shifts to longer wavelength. At −26 °C the breadth of the band reaches a maximum and it is clearly evident that two species are present, C_1 and C_2. Simultaneous with this change is the formation of solvent-separated ion pairs. As the temperature is further reduced, the contact ion pair absorption band progressively sharpens to a maximum at 520 nm, corresponding to the presence of only one kind of ion pair (C_2). In contrast to those in *trans*-2,5-dimethyltetrahydrofuran, spectra in the *cis*-solvent do not exhibit an isosbestic point and the con-

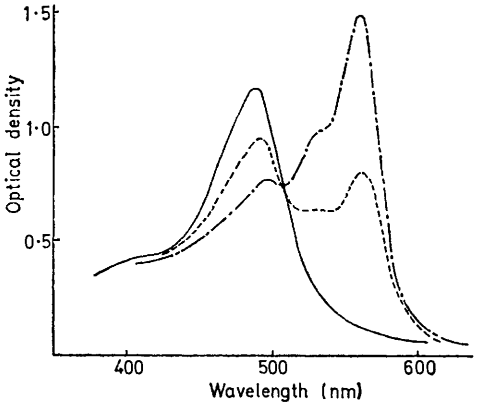

FIGURE 4 The absorption spectrum of DPB$^-$Li$^+$ in *trans*-2,5-dimethyltetrahydrofuran; ——, at 20 °C; – – – –, at −41 °C; —·—·—, at −60 °C

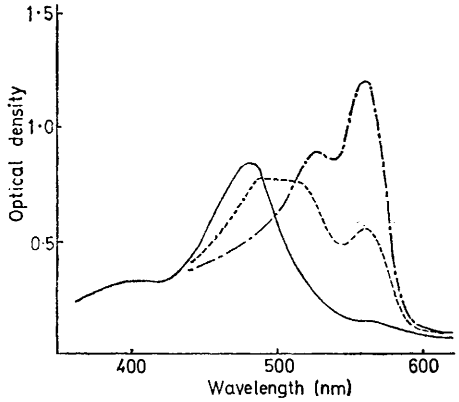

FIGURE 5 The absorption spectrum of DPP$^-$Li$^+$ in *cis*-2,5-dimethyltetrahydrofuran; ——, at 20 °C; – – – –, at −26 °C; —·—·—, at −65 °C

centration of solvent-separated ion pairs only exceeds that of contact ion pairs below −50 °C.

Thermodynamic Parameters.—In order to obtain the thermodynamic parameters (ΔH° and ΔS°) of a solvation process it is first necessary to determine the equilibrium constant K_{eq} as a function of temperature. Where two species having overlapping absorption bands are present, Vierordt's method can be employed to analyse the spectrum. In applying this technique, the spectrum of DPB^-Li^+ in Et_2O was used as a model for the spectrum of any contact ion pair (C_1 or C_2) and that of DPB^-Li^+ in tetrahydrofuran for any solvent-separated ion pair.

A study of DPP^-Na^+ in tetrahydropyran and in 3,4-dihydropyran yielded thermodynamic parameters for the step $C_1 \longrightarrow C_2$ (Table 3). Although a spectrum of pure C_1 was not obtainable, the absorption maximum was estimated to be at 490 nm from a study of the spectra of DPP^-Na^+ in tetrahydropyran and 3,4-dihydropyran at high temperatures (+60 °C) where the fraction of C_2 was very small. The absorption maximum for C_2 was taken to be at 525 nm from a study of the spectra at very low temperature and by comparison with that of DPB^-Na^+ in tetrahydrofuran in which the contact band has no shoulder. Similar analyses, at the appropriate wavelengths, gave parameters for the second solvation step $C_2 \longrightarrow SS$ for the systems DPP^-Na^+, DPB^-Na^+, and DPB^-K^+ in tetrahydrofuran and for DPB^-K^+ and DPB^-Rb^+ in dimethoxyethane. In the case of DPP^-Na^+ in tetrahydrofuran there was a slight shoulder on the C_2 absorption band at ambient temperature, corresponding to the presence of some C_1. Analysis of the spectrum showed that C_1 constituted only 5% of the total contact ion pair concentration at 17 °C: since this figure diminished with decreasing temperature, equilibrium constants were calculated on the assumption that all the contact ion pairs were of type C_2. A good linear plot was obtained of $\log K_2$ against the reciprocal temperature, vindicating this assumption.

TABLE 3

Thermodynamic parameters for DPP^-M^+ and DPB^-M^+

Salt	Solvent	$\frac{-\Delta H_1^\circ}{kJ\ mol^{-1}}$	$\frac{-\Delta S_1^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{-\Delta H_2^\circ}{kJ\ mol^{-1}}$	$\frac{\Delta S_2^\circ}{J\ K^{-1}\ mol^{-1}}$
DPP^-Na^+	Tetrahydropyran	12·2	31·4		
DPP^-Na^+	3,4-Dihydropyran	9·6	24·3		
DPP^-Na^+	Tetrahydrofuran			26·0	107
DPB^-Na^+	Tetrahydrofuran			23·4	94
DPB^-Na^+	2-Methyltetrahydrofuran			13·0	70·7
DPB^-K^+	Tetrahydrofuran			11·3	58·6
DPB^-K^+	Dimethoxyethane			29·3	103
DPB^-Rb^+	Dimethoxyethane			26·0	113
DPP^-Li^+	*cis*-2,5-Dimethyltetrahydrofuran	30·2	127	6·3	22·2
DPB^-Li^+	*cis*-2,5-Dimethyltetrahydrofuran	20·5	89	2·9	4·6
DPP^-Li^+	*trans*-2,5-Dimethyltetrahydrofuran	ΔH_3° −31·4 kJ mol^{-1}; ΔS_3° −159 J K^{-1} mol^{-1}			
DPB^-Li^+	*trans*-2,5-Dimethyltetrahydrofuran	ΔH_3° −36·0 kJ mol^{-1}; ΔS_3° −167 J K^{-1} mol^{-1}			

Analysis of systems containing three species is more complex since the observed spectrum is now the resultant envelope of three overlapping spectra. In principle, Vierordt's method can be extended for the interpretation of such spectra by making measurements at three wavelengths. However, this technique proved to be hopelessly inaccurate for the analysis of the spectra of DPB^-Li^+ in *cis*-2,5-dimethyltetrahydrofuran; the sum of the concentrations of C_1, C_2, and SS recorded at different temperature appearing to vary by 50%. The following alternative procedure was therefore devised for the analysis of the spectra of DPB^-Li^+ and DPP^-Li^+ in *cis*- and *trans*-2,5-dimethyltetrahydrofuran.

In all but one case (DPB^-Li^+ in *cis*-2,5-dimethyltetrahydrofuran) the spectrum obtained at ambient temperature corresponded to the presence of C_1 alone, from which the total concentration of organolithium compound [T] could be found. At low temperature C_2 and SS are formed, resulting in absorption at longer wavelengths. The concentration of SS present at any temperature was determined by analysis at a single wavelength, 570 nm. Typically, this is some 9—10 nm to longer wavelength than the absorption maximum of SS and was chosen so as simultaneously to maximise sensitivity and to minimise overlap with the spectra of C_1 and C_2. Such neglect of overlap is justified since the extinction coefficient of C_2 ($\lambda_{max.}$ 520 nm) at 570 nm is only 0·035 of its extinction coefficient at its absorption maximum and the extinction of C_1 is even smaller. Since $[C_1] + [C_2] + [SS] = [T]$ is known, and [SS] can be determined at any temperature, it is convenient to define a contact ion pair–solvent separated ion pair equilibrium constant K^* by equation (5). A plot of

$$K^* = [SS]/([C_1] + [C_2]) = [SS]/([T] - [SS]) \quad (5)$$

ln K^* against the reciprocal of temperature should yield a curve, the slope of which at any point yields $\Delta H^{*\circ}$. At low temperatures the fraction of C_1 present in solution will decrease; hence the curvature of the plot. K^* is related to K_1 ($= [C_2]/[C_1]$) and K_2 ($= [SS]/[C_2]$) by equation (6). Differentiation with respect to the

$$K^* = K_1K_2(1 + K_1)^{-1} \quad (6)$$

inverse temperature yields equation (7). When K_1 is

$$\Delta H^{*\circ} = \Delta H_1^\circ(1 + K_1)^{-1} + \Delta H_2^\circ \quad (7)$$

small, we obtain equation (8), and when it is large, (9).

$$\Delta H^{*\circ} \simeq \Delta H_1^\circ + \Delta H_2^\circ = \Delta H_3^\circ \quad (8)$$

$$\Delta H^{*\circ} \simeq \Delta H_2^\circ \quad (9)$$

That is, in the plot of ln K^* against reciprocal temperature, the limiting values of the slope at high and low temperatures will yield values for $\Delta H_3°$ and $\Delta H_2°$ respectively. (Values for the entropies can be calculated in the same manner.) Figure 6 represents the plot obtained for DPP$^-$Li$^+$ in *cis*-2,5-dimethyltetrahydrofuran. A similar type of plot was obtained for DPB$^-$Li$^+$ in the same solvent, but the results (Table 3) are likely to be somewhat less accurate since in this case [T] was determined from a spectrum which indicated the presence of some C_2 and SS. When this procedure was applied to DPP$^-$Li$^+$ in *trans*-2,5-dimethyltetrahydrofuran, a linear plot was obtained over the entire temperature range studied (Figure 6) indicating that the concentration of C_2 was small throughout. The plot for DPB$^-$Li$^+$ in *trans*-2,5-dimethyltetrahydrofuran was also linear over a wide temperature range, but did show distinct curvature at low temperature, *i.e.*, the fraction of C_2 is very small, except at low temperatures.

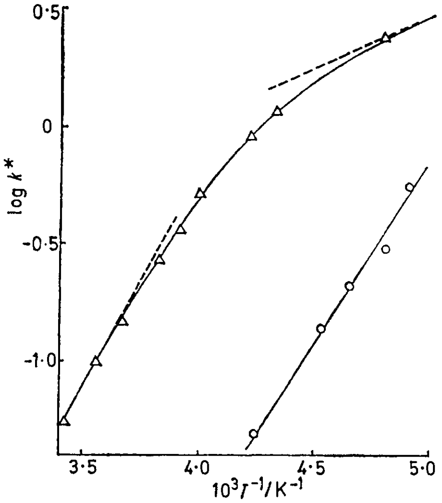

FIGURE 6 The variation of K^* with temperature; △, DPP$^-$Li$^+$ in *cis*-2,5-dimethyltetrahydrofuran; ○, DPP$^-$Li$^+$ in *trans*-2,5-dimethyltetrahydrofuran

The accuracy of this procedure was readily checked. According to equation (7) a plot of $\Delta H^{*°}$ against $(1 + K_1)^{-1}$ should be a straight line of slope $\Delta H_1°$ and intercept $\Delta H_2°$. From the values found for $\Delta H_1°$ and $\Delta S_1°$, the value of K_1 could be calculated at any temperature by means of the van't Hoff isochore. $\Delta H^{*°}$ was measured at several temperatures as described above. In the case of DPP$^-$Li$^+$ in *cis*-2,5-dimethyltetrahydrofuran a linear plot was obtained with slope $-31·4$ kJ mol^{-1} and intercept $-5·7$ kJ mol^{-1}. These values compare very favourably with $\Delta H_1°$ and $\Delta H_2°$ obtained from the extremities of the plot of ln K^* against reciprocal temperature (Table 3).

These results present conclusive evidence for the existence of contact ion pairs in two solvation states. Similarly, Hirota and his co-workers[9] concluded from e.s.r. studies that diethyl ether solutions of sodium naphthalene and sodium anthracene contained two types of ' tight ' (synonymous with contact) ion pair. They measured $\Delta H°$ and $\Delta S°$ for several systems and our results for the $C_1 \rightleftharpoons C_2$ and, $C_2 \rightleftharpoons$ SS equilibria present comparable data.

The solvation state of the contact ion pair of fluorenyllithium in dioxan has been found to be modified by the addition of hexamethylphosphoramide or ethylenediamine.[10] External solvation of the lithium ion of the contact ion pair was manifested by a bathochromic shift of the absorption maximum.

That $\Delta H_1°$ and $\Delta S_1°$ are much greater than $\Delta H_2°$ and $\Delta S_2°$ for DPP$^-$Li$^+$ and DPB$^-$Li$^+$ in *cis*-2,5-dimethyltetrahydrofuran indicates that initial localisation of solvent molecules around the lithium cation can play an important role in determining the thermodynamic parameters for contact–solvent separated ion-pair equilibria. It seems likely that the concept of two contact ion pairs should be quite widely applicable, some systems such as the fluorenyl anion, however, giving spectra which are relatively insensitive to this effect. In such cases the existence of such ion pairs may be revealed by curvature of the plots of ln K against reciprocal temperature.

Whilst the thermodynamic parameters $\Delta H_3°$ and $\Delta S_3°$ are comparable for DPP$^-$Li$^+$ in *cis*- and *trans*-2,5-dimethyltetrahydrofuran, the spectral behaviour and plots of ln K^* against reciprocal temperature for these systems are markedly different. This must therefore indicate differences in the relative contributions of $\Delta H_1°$ and $\Delta H_2°$ (and $\Delta S_1°$ and $\Delta S_2°$) in the two solvents. Since the basicities of the two ethers are likely to be almost identical, these differences must arise from steric factors.

[1/2274 *Received, 30th November*, 1971]

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