Extrathermodynamic Relationships for Ion-pair Equilibria in Media of Low Dielectric Constant

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The enthalpy and entropy changes for the interconversion both of the tight and loose ion-pairs of a wide variety of carbanions are related by the equation $\Delta H = \alpha\Delta S + \beta$ where α and β are constants characteristic of the solvent and the cation. A simple electrostatic treatment gives a qualitative explanation of this effect.

THE thermodynamics of the interconversion both of the tight and loose ion-pairs of the alkali-metal salts of 1,3-diphenylpropene and several of its derivatives have been investigated for a wide variety of ether solvents.[1–3] It was observed that the mole fraction of the loose ion-pair was increased by lowering the temperature, by substituting a lighter alkali-metal cation, and by employing an ether whose oxygen atom is less sterically hindered. The influence of substitution of the anion can be interpreted qualitatively in terms of a combination of conformational, steric, and inductive effects. These systems based on the diphenylallyl structure appear to conform to the relationship $\Delta H = \alpha\Delta S + \beta$. A survey of the literature has shown that ion-pairs of a wide variety of other unrelated carbanions also obey this relationship.

EXPERIMENTAL

Tetrahydrofuran (THF), *cis*-2,5-dimethyltetrahydrofuran (DMTHF), and an equimolar mixture of *cis*- and *trans*-DMTHF were rigorously dried under high vacuum over sodium–potassium alloy. The capacitances of a cell containing a parallel-plate condenser were determined when filled with these solvents, using a Wayne–Kerr B642 Universal Bridge. A Townson and Mercer Minus 70 bath was used to thermostat the cell. For THF the capacitances were plotted against the dielectric constants obtained by Szwarc [4] for the temperature range 22 to −49 °C. A linear equation was obtained, correlating cell capacitance with the dielectric constant of the solvent. This enabled the experimental capacitances to be converted into dielectric constants for all three solvents, with an error of ± 0.02 (Table 1). Graphs of $\ln D$ against $\ln T$ were plotted to determine values of $\mathrm{d}\ln D/\mathrm{d}\ln T$ at 250 K. The temperature dependence of dielectric constant can be represented by the equation $D = m/T + c$, where m and c are constants, also given in Table 1.

RESULTS

Extensive data on the thermodynamics of the interconversion both of tight and loose ion-pairs exists in the litera-

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[1] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 835.

[2] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1006.

[3] G. C. Greenacre and R. N. Young, *J.C.S. Perkin II*, 1975, 1661.

[4] C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 1965, **86**, 5548.

ture only for the solvents THF and 2-methyltetrahydrofuran (MTHF). Plots of ΔH *versus* ΔS are shown in the Figure [(a) and (b), respectively]. Similarly, (c) in the Figure represents data in DMTHF. The least-mean-square line is drawn on (a) in the Figure for the sodium salts only; in (b) separate least-mean-square lines are drawn for the lithium and sodium salts. The results plotted in these diagrams were obtained by a variety of physical techniques, and in most cases the authors did not quantify their errors. In our experience, using visible absorption spectrophotometry, the errors were usually ±8%. This is approximately the scatter of points about these lines. In (b) it is clear that the sodium and lithium salts must be represented by different straight lines, the lithium line being the steeper. There is some suggestion that the points in (a) may behave similarly.

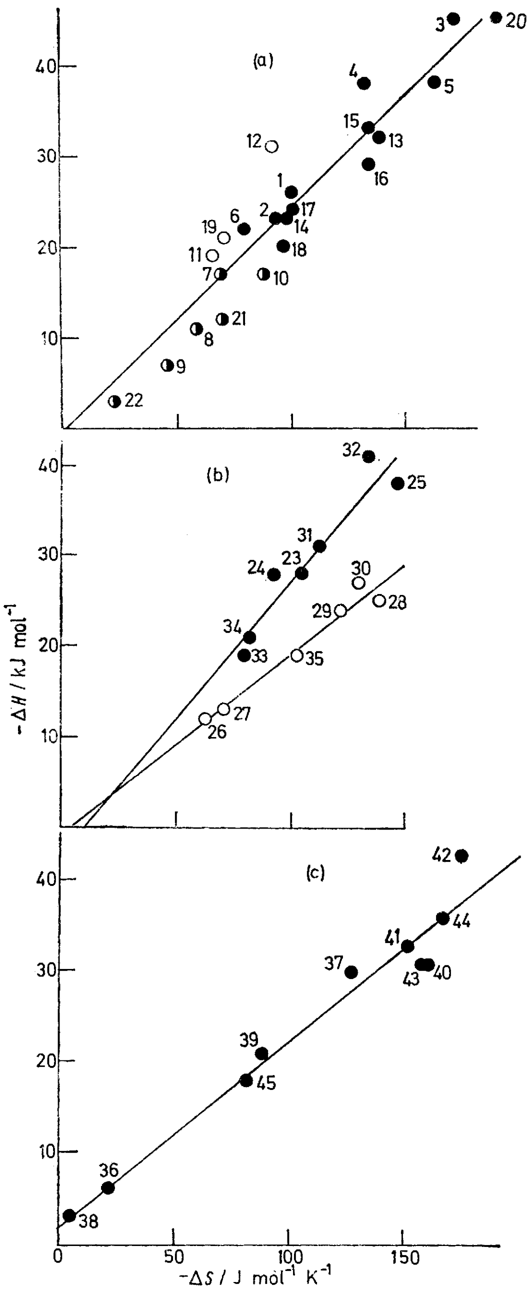

TABLE 1

Temperature [a] dependence of dielectric constant [b]

THF

T/K	295.2	288.4	283.7	279.2	269.0	262.7	256.2
D	7.52	7.70	7.84	8.01	8.32	8.62	8.85
T/K	250.7	245.7	238.7	233.7	228.7	224.2	
D	9.11	9.32	9.65	9.88	10.11	10.35	

$D = 2\,700/T - 1.676$ $\quad$ $\mathrm{dln}\,D/\mathrm{dln}\,T = -1.183$

Equimolar *cis*- and *trans*-DMTHF

T/K	296.5	284.0	277.2	272.2	268.2	262.2	253.2
D	5.39	5.71	5.92	6.05	6.17	6.37	6.68
T/K	244.0	233.7	224.2				
D	6.99	7.41	7.81				

$D = 2\,220/T - 2.100$ $\quad$ $\mathrm{dln}\,D/\mathrm{dln}\,T = -1.302$

cis-DMTHF

T/K	302.2	296.2	295.7	288.2	282.9	277.2	271.7
D	4.94	5.03	5.06	5.21	5.30	5.43	5.62
T/K	265.2	256.0	250.2	245.2	243.2	233.2	226.7
D	5.75	6.03	6.21	6.37	6.54	6.79	7.07
T/K	221.2	215.2	207.7				
D	7.30	7.52	7.90				

$D = 2\,020/T - 1.875$ $\quad$ $\mathrm{dln}\,D/\mathrm{dln}\,T = -1.279$

[a] Temperatures recorded to ±0.2K. [b] Dielectric constant determined to ±0.02.

Caption and references to Figure :—

(a) Plot of thermodynamic parameters for ion-pairs in THF: ○ Li salts, ● Na salts, and ◑ salts of other cations. Point 1 = Na 1,3-diphenylallyl,[1] 2 = Na 1,3-diphenylallyl,[1] 3 = Na 2-methyl-1,3-diphenylallyl,[3] 4 = Na 1,3-diphenyl-2-t-butylallyl,[3] 5 = Na 2-methyl-1,3-di-*p*-tolylallyl,[3] 6 = Na 1,2,3-triphenylallyl,[3] 7 = K 1,3-diphenylallyl,[1] 8 = K 1,3-diphenylbutenyl,[1] 9 = Sr 1,3-diphenylallyl,[3] 10 = Ba 1,3-diphenylallyl,[3] 11 = Li 1,1-diphenylhexyl,[5] 12 = Li fluorenyl,[6] 13 = Na fluorenyl,[6] 14 = Na acenaphthylene,[7] 15 = Na biphenyl,[8] 16 = Na naphthalene,[8] 17 = Na naphthalene,[9] 18 = Na 1,5-di-t-butylnaphthalene,[10] 19 = Li methylenephenanthrene,[11] 20 = Na methylenephenanthrene,[11] 21 = K methylenephenanthrene,[11] 22 = Cs methylenephenanthrene.[11]

(b) Plot of thermodynamic parameters for ion-pairs in MTHF: ● Li salts and ○ Na salts. Point 23 = Li 2-methyl-1,3-diphenylallyl,[3] 24 = Li 1,3-diphenyl-2-t-butylallyl,[3] 25 = Li 2-methyl-1,3-di-*p*-tolylallyl,[3] 26 = Na 1,3-diphenylallyl,[1] 27 = Na 1,3-diphenylbutenyl,[1] 28 = Na 2-methyl-1,3-diphenylallyl,[3] 29 = Na 1,3-diphenyl-2-t-butylallyl,[3] 30 = Na 1,2,3-triphenylallyl,[3] 31 = Li fluorenyl,[6] 32 = Li 9-hexylfluorenyl,[12] 33 = Li methylenephenanthrene,[11] 34 = Li biphenyl-2-ylmethyl,[13] 35 = Na anthracene.[10]

(c) Plot of thermodynamic parameters for ion-pairs in DMTHF: Point 36 = Li 1,3-diphenylallyl,[1] 37 = Li 1,3-diphenylallyl,[1] 38 [a] = Li 1,3-diphenylbutenyl,[1] 39 = Li 1,3-diphenylbutenyl,[1] 40 = Li 2-methyl-1,3-diphenylallyl,[3] 41 = Li 1,3-diphenyl-2-t-butylallyl,[3] 42 = Li 1,2,3-triphenylallyl,[3] 43 = Li 1,3-diphenylallyl,[1] 44 = Li 1,3-diphenylbutenyl,[1] and 45 = Li biphenyl-4-ylmethyl,[13]

[a] Interconversion of two different tight ion-pairs

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[13] Unpublished results from this laboratory.

DISCUSSION

The association of ions to form ion-pairs was first proposed by Bjerrum,[14] but a satisfactory mathematical treatment was not produced until later. One of the more successful treatments is that due to Denison and Ramsey.[15] By considering the solvent as a continuous dielectric they deduced the formula

$$\Delta G_{\mathrm{dis}} = \Delta G^{\circ}_{\mathrm{dis}} + Le^2/4\pi\varepsilon_0 Da \qquad (1)$$

where L is Avogadro's constant, D the dielectric constant, a the interionic separation, $\Delta G^{\circ}_{\mathrm{dis}}$ the non-electrostatic free-energy for dissociation of the ion-pair, and ε_0 is the permittivity of a vacuum.

Recognising that ion-pairs exist in both tight and loose forms, and designating the free energies of dissociation respectively as ΔG_{t} and ΔG_{l}, the free energy for the conversion from tight to loose ion-pairs, $\Delta G_{\mathrm{t/l}}$ is given by $(\Delta G_{\mathrm{l}} - \Delta G_{\mathrm{t}})$. If the interionic separation of a tight ion-pair is a_{t} and that of a loose ion-pair a_{l} then substitution in equation (1) yields $\Delta G_{\mathrm{t/l}} = \Delta G' + p/D$ where $p = (Le^2/4\pi\varepsilon_0)(1/a_{\mathrm{l}} - 1/a_{\mathrm{t}})$ and $\Delta G' = (\Delta G_{\mathrm{l}}^{\circ} - \Delta G_{\mathrm{t}}^{\circ})$. Letting $\Delta H'$ and $\Delta S'$ be the non-electrostatic enthalpy and entropy, it follows that

$$\Delta H_{\mathrm{t/l}} = (p/D)(1 + \mathrm{dln}\, D/\mathrm{dln}\, T) + \Delta H'$$

and

$$\Delta S_{\mathrm{t/l}} = (p/DT)(\mathrm{dln}\, D/\mathrm{dln}\, T) + \Delta S'$$

Using the relationship $D = m/T + c$ (where m and c are constants) then

$$\Delta H_{\mathrm{t/l}} = pc/D^2 + \Delta H' \qquad (2)$$

$$\Delta S_{\mathrm{tl/}} = -pm/D^2T^2 + \Delta S' \qquad (3)$$

Denison and Ramsey studied the dissociation of several perchlorate salts in ethylene chloride and concluded that it was not necessary to include a non-electrostatic contribution to the entropy and that the non-electrostatic enthalpy was only some 10% of the observed enthalpy change. In the case of ion-pair equilibria it is instructive to consider two hypothetical limiting cases: (a) $\Delta H' = 0$ and (b) $\Delta S' = 0$. Four systems were selected whose points lay close to the least-mean-square lines of Figures (a), (b), and (c). Using the experimental enthalpies, entropies, and a mean temperature (250 K) equations (2) and (3) were solved for p and $\Delta S'$ for case (a) and for p and $\Delta H'$ for case (b). The resulting values are summarised in Table 2.

Table 2 shows that the assumption $\Delta H' = 0$ is unrealistic as the resulting values of ΔS_{el} and $\Delta S'$ are impossibly high. In addition, the mean value of p is 1.4 MJ mol^{-1} which would require a_{t} to be less than 1 Å. In contrast, case (b) yields values of ΔH_{el} and $\Delta H'$ which *are* physically attainable, together with a mean value of p of 0.14 MJ mol^{-1} corresponding to interionic separations in the range 2—7 Å. The relative magnitudes of $\Delta H'$ and ΔH_{el} contrast sharply with the corresponding parameters obtained for dissociation by Denison and Ramsey. One difference is that the present systems all contain an anion which cannot truly be regarded as spherical. However, ion-pair equilibria provide a much more severe test of the simple electrostatic treatment since large variations in the thermodynamic parameters are generated from small changes in small interionic separations. It is clear that the greatest weakness of this treatment is the assumption that the solvent behaves as a continuous dielectric medium. The electrostatic model does not allow for specific solvation effects. In the case of the bulky ions which form the phenyltrimethylammonium perchlorate ion-pair studied in chloroalkanes by Denison and Ramsey, such specific effects are likely to be much less significant than in the cases of ion-pairs of the small and highly polarising alkali-metal cations in ethereal solvents.

TABLE 2

Comparison of experimental and calculated thermodynamic parameters *

Experimental values		case (a) calculation		case (b) calculation	
$-\Delta H_{\mathrm{expt}}$	$-\Delta S_{\mathrm{expt}}$	$-\Delta S_{\mathrm{el}}$	$-\Delta S'$	$-\Delta H_{\mathrm{el}}$	$-\Delta H'$
26	100	671	−571	4	22
28	105	865	−760	3	25
12	63	371	−308	2	10
30	127	517	−390	7	23

$\Delta H_{\mathrm{el}} = pc/D^2$ and $\Delta S_{\mathrm{el}} = -pm/D^2T^2$

* Units of enthalpy kJ mol^{-1} and entropy J mol^{-1} K^{-1}. In case (a) $\Delta H'$ was assumed to be zero allowing the calculation of p and hence ΔS_{el}. In case (b) $\Delta S'$ was assumed to be zero allowing the calculation of p and hence ΔH_{el}.

Differentiation of equation (2) yields

$$\frac{\mathrm{d}\Delta H_{\mathrm{t/l}}}{\mathrm{d}T} = \frac{-2pc}{D^3} \cdot \frac{\mathrm{d}D}{\mathrm{d}T} + \frac{\mathrm{d}\Delta H'}{\mathrm{d}T} = \frac{2pcm}{T^2D^3} + \Delta C'_{\mathrm{p}} \qquad (4)$$

Similarly, from equation (3)

$$\frac{\mathrm{d}\Delta S_{\mathrm{t/l}}}{\mathrm{d}T} = \frac{2pcm}{T^3D^3} + \frac{\Delta C'_{\mathrm{p}}}{T} \qquad (5)$$

Dividing (4) by (5),

$$\frac{\mathrm{d}\Delta H_{\mathrm{t/l}}}{\mathrm{d}\Delta S_{\mathrm{t/l}}} = T \qquad (6)$$

The wide range of systems shown in Figures (a), (b), and (c) conform, within experimental error, to the equation $\Delta H = \alpha\Delta S + \beta$ where α and β are constants whose values are listed in Table 3. Subject to the ultimate adequacy of the equation $D = m/T + c$ the mean experimental temperature [equation (6)] can be identified with α.

TABLE 3

Least-mean-square experimental values of α and β

		α/K	β/kJ mol^{-1}
THF	Na	248	0.4
MTHF	Na	198	0.7
	Li	301	3.0
DMTHF	Li	206	−1.7

In accordance with this, α reflects the ease of the conversion of tight to loose ion-pairs, those systems requiring the lowest temperatures to effect this change having the smallest values of α.

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