128. *Solvent Effects in Association Equilibria.*

By Albert Wassermann.

This paper deals with the thermal equilibrium between the free radical β-benzoyl-αα-diphenylhydrazyl and its dimeride dibenzoyltetraphenyltetrazan. The equilibrium constant, K, has been measured by Goldschmidt and Bader in four solvents in all of which it can be represented by $K = B\text{e}^{-\Delta H/RT}$, where B is a measure of the statistical weight of the dimeride and ΔH is the heat of reaction. It is now shown that the solvent effects consist in changes of both parameters log B and ΔH, the numerical results of the measurements suggesting a linear functional relationship between these two quantities. This is explained with the aid of correlations between the equilibrium constants and the solubilities and between entropies and heats of solution.

The experiments here discussed deal with solvent effects in the following thermal dimerisation of a free radical:

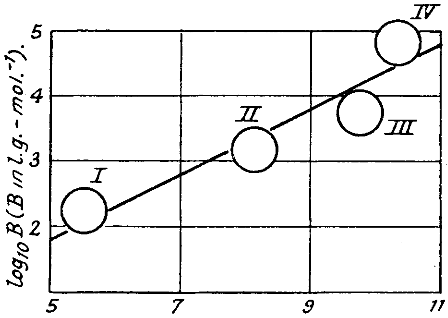
$$2NPh_2\cdot NBz\cdot = NPh_2\cdot NBz\cdot NBz\cdot NPh_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equilibrium constants, K, of this reaction were measured by Goldschmidt and Bader (*Annalen*, 1929, **473,** 137) and can be represented by

$$K = [c]/[a]^2 = B\text{e}^{-\Delta H/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where [*a*] and [*c*] are volume concentrations relating respectively to the free radical and to its dimeride, B is a measure of the statistical weight of the dimeride, and ΔH is the heat change. So far as the author is aware, these results proved for the first time that solvent effects in an association equilibrium involving electroneutral participants can be sufficiently large to produce changes in ΔH which are considerably larger than the corresponding changes in $\log K$.* It is now shown that this experimental fact is consistent with the assumption that there is a functional linear relationship between $\log B$ and ΔH which can be explained with the help of correlations between the equilibrium constant and solubilities (van't Hoff, " Lectures on Theoretical and Physical Chemistry," 1898, Vol. 1, p. 221; Dimroth, *Annalen*, 1910, **377**, 134) and between entropies and heats of solutions (Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1335; 1937, **33**, 166; cf. also Bell, *ibid.*, 1937, **33**, 496; Butler, *ibid.*, p. 229; Barclay and Butler, *ibid.*, 1938, **34**, 1445).

Functional relationship between the parameters of the equilibrium constant.



I, *Chloroform* ; II, *acetone* ; III, *ether* ; IV, *toluene.*

The heat changes have been computed by using

$$-\Delta H = \boldsymbol{R}T^2(\partial \ln K/\partial T)_p - \boldsymbol{R}T^2\varepsilon \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ε is the coefficient of thermal expansion of the solvent, the B factors being obtained by substituting in (2) the ΔH values and the most reliable equilibrium constants. Experiments were carried out between −50° and −18°, and within this range it can be assumed that both B and ΔH are not measurably altered by the temperature change. Numerical values of $\log K$ and of the two parameters of equation (2) are in the accompanying table. The suggested relationship between the figures in the last two columns is graphically represented in the figure, the magnitude of the experimental errors being indicated by the diameter of the various circles; it should be noted that the slope of the graph is about 10^{-4} cals.$^{-1}$.

Equilibrium constants, heat changes, and non-exponential B *factors relating to the thermal association of* β-*benzoyl-αα-diphenylhydrazyl.* (Both K and B are expressed in terms of l./g.-mol.)

Solvent.	$\log_{10} K$ at −18°.	$-\Delta H$ (kg.-cals.).	$-\log_{10} B$.	Solvent.	$\log_{10} K$ at −18°.	$-\Delta H$ (kg.-cals.).	$-\log_{10} B$.
$CHCl_3$	2·627	5·6 ± 0·6	2·2 ± 0·4	OEt_2	4·561	9·8 ± 0·7	3·8 ± 0·5
$COMe_2$	3·830	8·2 ± 0·6	3·2 ± 0·4	PhMe	3·943	10·4 ± 0·6	4·9 ± 0·4

In attempting to give a theoretical explanation for a relationship between the parameters of (2), the equation connecting the equilibrium constant, K, with the solubilities, σ, of the participants of the equilibrium is written in the form (cf. van't Hoff, Dimroth, *locc. cit.*) :

$$K^m/K^n = (\sigma_a^m)^2\sigma_c^n/\sigma_c^m(\sigma_a^n)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here and below, the superscripts indicate that the relevant quantity refers to solvents m and n, and the subscripts relate respectively to β-benzoyl-αα-diphenylhydrazyl and its dimeride. The solubilities can be represented by

$$\sigma_a = e^{\Delta S_a/\boldsymbol{R}}e^{-\lambda_a/\boldsymbol{R}T} = C_a e^{-\lambda_a/\boldsymbol{R}T} \text{ and } \sigma_c = e^{\Delta S_c/\boldsymbol{R}}e^{-\lambda_c/\boldsymbol{R}T} = C_c e^{-\lambda_c/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad (5)$$

where ΔS and λ are respectively the entropies and heats of solution. If the equilibrium constants and the solubilities in (4) are substituted by products of non-exponential and exponential factors, an equation of the following form can be deduced

$$\alpha + \beta/\boldsymbol{R}T = \gamma + \delta/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where α, β, γ, and δ respectively are abbreviations for $\log B^m - \log B^n$, $\Delta H^m - \Delta H^n$, $\log C_c^n + 2 \log C_a^m - \log C_c^m - 2 \log C_a^n$, and $\lambda_c^n + 2\lambda_a^m - \lambda_c^m - 2\lambda_a^n$. The parameters B, ΔH, C, and λ are assumed to be not measurably affected by small temperature changes and, therefore, (6) can only be valid at different temperatures if

$$\log B^m - \log B^n = \log C_c^n + 2 \log C_a^m - \log C_c^m - 2 \log C_a^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\Delta H^m - \Delta H^n = \lambda_c^n + 2\lambda_a^m - \lambda_c^m - 2\lambda_a^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The empirical correlation between entropies and heats of solution, to which reference has been made above, can be written as follows :

$$\log C_a^m - \log C_a^n = r(\lambda_a^m - \lambda_a^n) + q_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\log C_c^m - \log C_c^n = r(\lambda_c^m - \lambda_c^n) + q_c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Evans and Polanyi (*loc. cit.*) found that such equations, with $r \sim 10^{-4}$ cals., hold true in the case of many solute and solvent molecules of widely different chemical constitution, and it is assumed, therefore, that (9) and (10)

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* It is of interest that (1) is not the only dimerisation equilibrium which has been studied in different solvents. Ziegler and Ewald (*Annalen*, 1929, **473**, 163) measured the temperature dependence of the K values relating to the association of triphenylmethyl in nine solvents, and found that the variations of ΔH and B are smaller than the experimental errors.

will also apply to the participants of the chemical equilibria the constants of which appear in equation (4). It follows that the terms on the right-hand side of (9) and (10) can be substituted for those on the right-hand side of (7). This leads to

$$\log B^{\mathrm{m}} - \log B^{\mathrm{n}} = r(2\lambda_a^{\mathrm{m}} - 2\lambda_a^{\mathrm{n}}) - r(\lambda_c^{\mathrm{m}} - \lambda_c^{\mathrm{n}}) + (2q_a - q_c) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

When (8) is taken into account it follows that

$$\log B^{\mathrm{m}} - \log B^{\mathrm{n}} = r(\Delta H^{\mathrm{n}} - \Delta H^{\mathrm{m}}) + (2q_a - q_c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the suggested functional relationship between the logarithm of the non-exponential B factor and the heat of association of the hydrazyl.

Further experiments will perhaps show that also in some other reactions log B increases linearly with ΔH, but it is not believed that the various assumptions leading to an equation of the type of (12) can always be valid. It is possible, therefore, that certain equilibria will be discovered in which a marked solvent effect obtains but in which a simple functional relationship between log B and ΔH is not apparent. Deviations from (12) are likely to occur in ionic equilibria, for in those reactions it is less justifiable to assume that the heat and entropy changes are independent of temperature than it is in associations involving electroneutral species.

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