The Effect of Solvent on Rotational Isomeric Equilibria

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A QUANTITATIVE theory of the effect of solvent on the energy difference between rotational or conformational isomers has been sought for some time, present theories being either somewhat ambiguous,[1] or else of little quantitative use.[2] We report that we have developed an electrostatic theory of the solvent reaction field which gives excellent agreement with experiment. Preliminary accounts of the theory for the particularly simple case of the 1,2-disubstituted ethanes have appeared elsewhere.[3]

On this theory, the energy difference, $\Delta E^{\mathrm{s}} = E_{\mathrm{A}} - E_{\mathrm{B}}$, between two rotational isomers A and B in any solvent, S, of dielectric constant ϵ is given in terms of the energy difference in the gas, ΔE^{v}, by:—

$$\Delta E^{\mathrm{s}} = \Delta E^{\mathrm{v}} - kx/(1 - lx) + 3hx/(5 - x) \quad (1)$$

where $x = (\epsilon - 1)/(2\epsilon + 1)$, and $l = 2(n_{\mathrm{D}}^2 - 1)/(n_{\mathrm{D}}^2 + 2)$, n_{D} being the solute refractive index. k and h are given by $(\mu_{\mathrm{A}}^2 - \mu_{\mathrm{B}}^2)/a^3$ and $(q_{\mathrm{B}}^2 - q_{\mathrm{A}}^2)/a^5$ respectively, $\mu_{\mathrm{A,B}}$ and $q_{\mathrm{A,B}}$ being the dipole and quadrupole moments of isomers A and B, and a being the molecular radius. These moments are calculated by assuming point dipoles at the centres of the dipolar bonds. Thus the theory gives $\Delta E^{\mathrm{v}} - \Delta E^{\mathrm{s}}$ in terms of known or easily calculable parameters. The theory was tested by calculating the energy difference $\Delta E^{\mathrm{v}} - \Delta E^{\mathrm{l}} = H$, ΔE^{l} being the energy difference for the pure liquid, between the *gauche*- and *trans*-isomers of 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane These values are shown in the Table (col. 2). ΔE^{l} is temperature-dependent as the reaction field term H depends on the dielectric constant of the medium which varies with temperature. Experimental determinations of the energy difference assume that ΔE^{l} is independent of temperature and thus these experiments measure another quantity ($\Delta E_0{}^{\mathrm{l}}$) which is related to the true energy difference by the addition of the term $T\mathrm{d}H/\mathrm{d}T$. Hence the experimental values of $\Delta E^{\mathrm{v}} - \Delta E_0{}^{\mathrm{l}}$ must be compared with the calculated value of $H - T\mathrm{d}H/\mathrm{d}T$. The agreement between observed and calculated values (see Table) is well within the combined limits of error of the experimental and theoretical values. Two important results follow from this agreement.

The difference between the real and apparent ΔE^{l} values may be quite large (in 1,1,2-trichloroethane it is as much as 0·6 kcal./mole). Thus the evaluation of the energy differences between rotational isomers from variable-temperature measurements can give erroneous results if a constant ΔE^{l} is assumed. Furthermore, any other parameters which are obtained by the same assumption may be in error. For example, from the measurement of the proton–proton coupling constant in liquid 1,1,2,2-tetrachloroethane, Gutowsky *et al.*[4] derived, on the basis of a constant ΔE^{l}, $J_{\mathrm{trans}}^{\mathrm{HH}}$ 16·35 c./sec., $J_{\mathrm{gauche}}^{\mathrm{HH}}$ 2·01 c./sec., and ΔE^{v} — 1·1 kcal./mole. On the basis of equation 1, calculating ΔE^{l} at each temperature from the

TABLE

Molecule	Energy Differences (kcal./mole)					
	Calculated			Observed[a]		
	$H(\Delta E^{\mathrm{v}} - \Delta E^{\mathrm{l}})$	$-T\mathrm{d}H^{*}/\mathrm{d}T$	$H - T\mathrm{d}H/\mathrm{d}T$ $(\Delta E^{\mathrm{v}} - \Delta E_0^{\mathrm{l}})$	ΔE^{v}	ΔE_0^{l}	$\Delta E^{\mathrm{v}} - \Delta E_0^{\mathrm{l}}$
$CH_2Cl{\cdot}CH_2Cl$	0·98	0·3	1·3	1·2	0·0	1·2
$CH_2Cl{\cdot}CHCl_2$	1·41	0·6	2·0	2·9	0·3	2·6
				2·3[a]	0·3	2·0
$CHCl{\cdot}_2CHCl_2$	0·95	0·35	1·3	0·0	−1·1[b]	1·1

[a] Values quoted in ref. 6.

[b] R. H. Harrison and K. A. Kobe, *J. Chem. Phys.*, 1957, **26**, 1411.

* The variation of the density with temperature need not be considered (ref. 3).

known values of the dielectric constant, the same experimental results give $J^{\mathrm{HH}}_{\mathrm{trans}}$ 10·4 c./sec., $J^{\mathrm{HH}}_{\mathrm{gauche}}$ 2·2 c./sec., and ΔE^{v} 0·1 kcal./mole. The value of J_{trans} in particular is in much better agreement with the values found in rigid systems[5] than is Gutowsky's value.

Equation 1 can also be used to deduce the variation of ΔE^{l} with solvent, and thus from the measurement of any molecular parameter as a function of solvent, the value of ΔE^{v} and the extrapolated parameter values for the individual isomers can be obtained. For instance, we have measured the H–H coupling constant in 1,1,2-trichloroethane in dilute solution in nineteen different solvents. The variation in coupling (from 6·25 c./sec. in n-pentane solution to 5·52 c./sec. in acetonitrile) can be fitted using equation 1 to calculate ΔE^{s}, and hence the proportions of the isomers in any solvent. A computer fit of the data gives the couplings in the two isomers as 6·38 ± 0·10 c./sec. for the *trans*-isomer and 2·2 ± 0·5 c./sec. for the *gauche*-isomer. These parameters also gave good agreement with the variable-temperature measurements of *J*. These values are in good agreement with the somewhat less accurate results obtained by a different method.[7]

This method is in principle applicable to any system in which the dipole and quadrupole moments of the interconverting isomers differ appreciably. Thus it may be of considerable use in the general study of rotational and conformational equilibria.

We are grateful to Dr. K. Pachler for much stimulating discussion.

(*Received, July 20th,* 1966; *Com.* 523.)

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[1] *cf.*, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", John Wiley, Interscience, New York, 1965, p. 460.

[2] *cf.*, N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 295.

[3] R. J. Abraham, L. Cavalli, and K. G. R. Pachler, "N.M.R. in Chemistry", Academic Press, New York, 1965, p. 111; also *Mol. Phys.*, in the press.

[4] H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, 1962, **36**, 3353.

[5] *e.g.*, J. Musher, *J. Chem. Phys.*, 1961, **34**, 594; R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.

[6] Ref. 2, pp. 296—297.

[7] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, 1959, *A*, **252**, 506—519.