Medium effects on rotational equilibria. Part III. The theory for any number of dipoles and its application to 1,1,2-trichloroethane

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Medium Effects on Rotational Equilibria. Part III.[1] The Theory for Any Number of Dipoles and its Application to 1,1,2-Trichloroethane

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An electrostatic theory of the effect of the medium on the energy differences between rotational isomers, previously given only for very simple molecules, is generalised to apply to any solute molecule. The theory is applied to 1,1,2-trichloroethane and shown to give good agreement with the experimental values of the energy difference between the rotational isomers in the liquid and vapour states. The proton coupling constants of the rotational isomers can be obtained by use of the theory from the solvent-dependence of the observed coupling constant and are 2·2 and 6·38 c./sec., respectively, for the *gauche* and *trans* isomers. Certain exceptional solvents are considered as either preferentially associating with one isomer or preferentially solvating the solute with polar groups in the solvent.

DESPITE numerous investigations of medium effects in rotational and conformational equilibria,[2] a quantitative theory of such effects is lacking. In simple molecules such as substituted ethanes the effect of different media on the energy difference between two rotational isomers can be estimated by calculating the energy of the electric field of the solute dipole in the medium. This is only of qualitative use but is the basis of the useful generalisation that the isomer of higher dipole moment is more stable in polar media.[3] In conformational work the corresponding energy difference is often calculated as the energy of interaction of the two dipolar groups in the molecule, the formula for the electrostatic interaction between two point dipoles being used. However, the dielectric constant which is used in these calculations is neither that of the solute nor that of the solvent but some semi-empirical value between the two.[4]

An investigation of the proton–proton coupling constants in 1,2-disubstituted ethanes (Part I [5]) led to the development of a theory which evaluated the energy difference between the rotational isomers of a 1,2-disubstituted ethane as a function of the dielectric constant of the medium (Part II [1]). The theoretical calculations were considerably simplified by considering these molecules ($RCH_2 \cdot CH_2R'$; R = F, Cl, or Br) as possessing two equal C–X dipoles. However, in order to apply the theory to more complex molecules such as $CH_2X \cdot CH_2Y$ where X and Y are very dissimilar groups, or to tri- and tetra-substituted ethanes it is necessary to formulate the theory in general terms. This is given below and the theory is then applied to the results for 1,1,2-trichloroethane.

Calculation of the Energy Difference between the Rotational Isomers.—We use subscripts to denote the rotamer, *i.e.*, A, B, *gauche* (g) and *trans* (t), and superscripts to denote the state, *i.e.*, vapour (v), solution (s), or pure liquid (l). We wish to calculate the energy difference $\Delta E = E_A - E_B$ between two rotational isomers A and B as a function of the medium. For this it is necessary to calculate the energy of each isomer as a function of the medium, *i.e.*, $E_A^v - E_A^s$. This is

calculated here on the basis of the classical electrostatic theory of dielectrics.[6] On this theory a molecule is stabilised when placed in a medium by the energy of the molecular electric field in that medium. For a spherical polarisable molecule of radius a and dipole moment μ the energy of the dipolar field in a medium of dielectric constant ε is [6]

$$E_n = E^v - E^s = -\frac{\mu^2}{a^3}\frac{x}{1-lx} \qquad (1)$$

where x equals $(\varepsilon - 1)/(2\varepsilon + 1)$ and l equals $2(N_D^2 - 1)/(N_D^2 + 2)$, N_D being the solute refractive index. The molecular electric field, in the general case, will consist of the dipole field plus higher-order terms (the quadrupole, octupole fields, etc.).

Following the principles laid down in ref. 6, we calculate the energy of the quadrupole field as

$$E_n = \frac{3x}{5-x} \cdot \frac{3}{2a^5} \cdot \sum_{i,j=x,y,z}^{i \neq j} [4q_{ii}^2 + 3(q_{ij} + q_{ji})^2 - 4q_{ii} \cdot q_{jj}] \qquad (2)$$

where $q_{ij} = \mu_i \times j$ and $\mu_{x,y,z}$, and x, y, z are the components and co-ordinates of the bond dipole moment μ.

The required energy is thus the sum of equations (1) and (2). For a molecule with a number of dipolar bonds, the required dipole and quadrupole moments are merely the sums of the individual moments, *e.g.*, for two dipoles the term $q_{xx} = \mu_{x_1} \times x_1 + \mu_{x_2} \times x_2$. It is convenient to combine equations (1) and (2) to give the required energy difference between the two rotational isomers A and B in any solvent s as [1]

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

where $\Delta E^s = E_A^s - E_B^s$, $\Delta E^v = E_A^v - E_B^v$, k is the dipole-moment term equal to $(\mu_A^2 - \mu_B^2)a^3$ and h is the quadrupole term which may be written as $3(q_B - q_A)/2a^5$ where q_A and q_B represent the summation in equation (2) for isomers A and B, respectively. Equation (6) thus gives the required energy difference ΔE^s in terms of the dipole and quadrupole moments of the individual rotamers A and B.

[1] Part II, R. J. Abraham, K. G. R. Pachler, and L. Cavalli, *Mol. Phys.*, 1966, **11**, 471.
[2] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, " Conformational Analysis," Interscience, New York, 1965.
[3] N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 288.
[4] Ref. 2, ch. 7.
[5] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 1964, **7**, 165.
[6] C. J. F. Böttcher, " Theory of Electric Polarisation," Elsevier, Amsterdam, 1952.

Application of the Theory to 1,1,2-*Trichloroethane.*— The most stringent test of the theory is to see whether it can reproduce the observed energy differences between the rotational isomers in the pure liquid and vapour states. There are two distinct rotational isomers of 1,1,2-trichloroethane, the *trans* (t) which exists in two mirror-image forms and the *gauche* (g) (Figure 1).
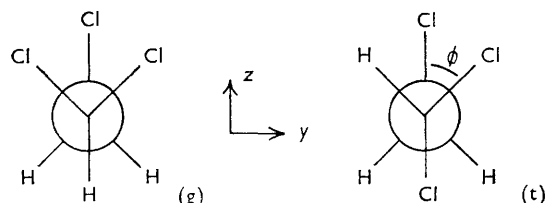

FIGURE 1

The calculation of the dipole and quadrupole moments of the isomers assumes point dipoles at the mid-points of each C–Cl bond pointed along the bond. Normal bond lengths [1] and tetrahedral angles were used with ϕ (Figure 1) equal to 70°.[7] As previously,[1] the dipole moments were taken from the corresponding ethyl compounds [8,9] giving dipole moments of 1·79 and 2·03 D for C–Cl bonds in the $CHCl_2$ and CH_2Cl groups, respectively.

The value of the quadrupole moment depends on the origin chosen, which should be the centre of the molecule. In the case of the *trans* isomer, the quadrupole moment was virtually independent of the co-ordinate axes and in the *gauche* isomer the very nearly spherical shape of the molecule (from Courtauld models) enabled the the centre of the molecule to be estimated as 0·7 Å along the *z* axis (see Figure 1; the *x* axis is perpendicular to the plane of the paper). The value of the molecular radius was obtained from the molecular volume, *i.e.*,

$$4/3 \, \pi \, a^3 = M/N\rho$$

where M is the molecular weight, N Avogadro's number, and ρ the density of the pure liquid (1·4357 g./ml.).

These values gave, for the *gauche* isomer, k_g and h_g 5·18 and 1·18 kcal./mole, respectively and for the *trans* isomer $k_t = 1\cdot03$ and $h_t = 4\cdot00$ kcal./mole. Thus equation (6) becomes for this compound

$$\Delta E^s = E_g{}^s - E_t{}^s = \Delta E^v - 4\cdot15x/$$
$$(1 - 0\cdot560x) + 8\cdot46x/(5 - x) \quad (7)$$

This gives the required ΔE^s for any medium in terms of the dielectric constant of the medium and ΔE^v, the energy difference in the gas. However, before we can compare the calculated value of $\Delta E^v - \Delta E^l$ with the observed values it is necessary to correct for the temperature dependence of ΔE^l itself. This arises because the value of ΔE^l depends on the dielectric constant of the

liquid, which is itself temperature-dependent, whereas the "observed" values of ΔE^l (which we call $\Delta E_o{}^l$) assume a temperature-independent ΔE. It is easy to show that [1]

writing $\qquad \Delta E^l = \Delta E^v - H$

then $\qquad \Delta E_o{}^l = \Delta E^l + T(\mathrm{d}H/\mathrm{d}T)$

i.e., $\qquad \Delta E^v - \Delta E_o{}^l = H - T(\mathrm{d}H/\mathrm{d}T)$

where T is the temperature of measurement.

As the change in dielectric constant with temperature is known for pure liquid 1,1,2-trichloroethane,[10] $T(\mathrm{d}H/\mathrm{d}T)$ can immediately be calculated. From equation (7) we obtain $H = 1\cdot41$ kcal./mole and $T(\mathrm{d}H/\mathrm{d}T) = -0\cdot6$ kcal./mole. Thus $\Delta E^v - \Delta E_o{}^l$ is calculated to be 2·0 kcal./mole. The observed value of $\Delta E_o{}^l$ is 0·3 kcal./mole,[3] but there is some disagreement about the value of ΔE^v. Kuratani *et al.* quote 2·9 kcal./mole from infra-red results [11] whilst Harrison and Kobe [12] quote 2·3 from thermodynamic results. The latter value gives $\Delta E^v - \Delta E_o{}^l = 2\cdot0$ kcal./mole, in exact agreement with our calculations, and is also supported by our solvent results. In any case, the theory has reproduced the value of $\Delta E^v - \Delta E_o{}^l$ to within the accuracy of the experimental determinations. A similar calculation for 1,1,2,2-tetrachloroethane also gave very good agreement with the experimental values.[13]

The very good agreement of the calculated and observed values for this most severe test of the theory (the energy differences between the liquid and vapour are much larger than between different solvents) is encouraging. Before the solution results are considered there is one point of note. The $T(\mathrm{d}H/\mathrm{d}T)$ term is the difference between the true value of ΔE^l and the value obtained by variable-temperature studies which assume a constant energy difference ($\Delta E_o{}^l$). In 1,1,2-trichloroethane this term is considerable (0·6 kcal./mole). Thus the true value of ΔE^l is 0·9 kcal./mole whereas the value of $\Delta E_o{}^l$ is only 0·3 kcal./mole. This illustrates the error which can occur in the "constant energy difference approximation."

In our previous work [1] the variation of the density with temperature was included in calculating the $\mathrm{d}H/\mathrm{d}T$ term. However, this has not been considered here, as on the basis of the the classical model of a solute cavity in a medium of continuous dielectric constant the variations in the density of the medium with temperature (which may be considered as arising from the formation of holes in the liquid as a result of the molecular motion) are included in the change in the dielectric constant. Furthermore, the resulting equations became much more complex, introducing a $\rho^{5/3}$ function in h.

The calculations for the $CH_2X \cdot CH_2Y$ compounds [1] remain virtually unchanged, as the density variation

[7] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, 1958, **28**, 175.
[8] " Handbook of Chemistry and Physics," 45th edn., Chemical Rubber Co., Cleveland, 1965.
[9] A. L. McClellan, " Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, 1963.

[10] Landholt-Börnstein, Physical-Chemistry tables.
[11] K. Kuratani and S. Mizushima, *J. Chem. Phys.*, 1954, **22**, 1403.
[12] R. H. Harrison and K. A. Kobe, *J. Chem. Phys.*, 1957, **26**, 1411.
[13] R. J. Abraham and M. A. Cooper, *Chem. Comm.*, 1966, **588**.

changes the $T(dH/dT)$ term by only *ca.* 0·1—0·2 kcal./mole, well within experimental error.

EXPERIMENTAL AND RESULTS

Commercial-1,1,2-trichloroethane, dried ($CaCl_2$) and re-distilled, had b. p. 113°. The proton–proton coupling constant was measured using Varian A-60 and HA-100 spectrometers on 10% (w/w) solutions of the trichloro-ethane in a variety of solvents, with 1% tetramethylsilane as internal reference. The solvents were all dried and redistilled before use. The spectrum was of the first order and thus the coupling could be measured directly to an accuracy of ±0·03 c./sec. The dielectric constants of the
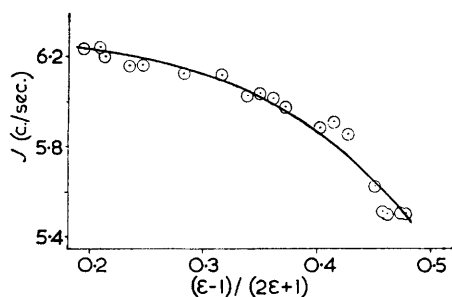

FIGURE 2

solutions were measured on a G.E. capacity bridge, pre-viously calibrated with standard liquids. The coupling constants and dielectric constants of the solutions are given in the Table.

Proton coupling constant (c./sec.) of $CHCl_2 \cdot CH_2Cl$ in various solvents and dielectric constant at 30°

Solvent	J	ε	Solvent	J	ε
n-Hexane *	6·24	1·95	n-Heptyl bromide	5·99	5·38
n-Pentane	6·25	2·07	Neat liquid	5·90	7·15
n-Hexane	6·21	2·10	CH_2Cl_2	5·93	8·25
Decalin	6·17	2·32	$CH_2Cl \cdot CH_2Cl$	5·87	9·75
CCl_4	6·17	2·45	Mesityl oxide	5·64	15·0
CS_2	6·13	2·95	$CH_3CO \cdot Et$	5·53	17·3
$CCl_2:CHCl$	6·13	3·55	Acetone	5·52	19·2
Pr^i_2O	6·04	4·10	CH_3CN	5·52	32·0
Et_2O	6·05	4·50	CH_3CN *	5·52	34·4
$CHCl_3$	6·03	4·90			

* 5% Solutions.

Solvent Dependence of the Coupling Constants.—The ob-served value of the coupling constant (J) is the weighted mean of the couplings in the *trans* (J_t) and *gauche* (J_g) isomers, *i.e.*,

$$J = n_t J_t + n_g J_g$$

where $\quad n_t + n_g = 1$

and $\quad n_g/n_t = \frac{1}{2} \exp(-E^s/\boldsymbol{R}T)$

Elimination of n_g and n_t gives

$$J = J_t - (J_t - J_g)/[1 + 2 \exp (\Delta E/^s\boldsymbol{R}T)] \quad (8)$$

Combination of equations (7) and (8) gives the observed variation of the coupling constant J with ε in terms of the three unknowns J_t, J_g, and ΔE^v. Use of a computer pro-gramme to obtain the best-fit values of these parameters gave $\Delta E^v = 2 \cdot 2 \pm 0 \cdot 2$ kcal./mole, J_t 6·83 ± 0·05 c./sec., and J_g 2·18 ± 0·2 c./sec. The observed points are shown

together with the calculated curve in Figure 2. Agreement is very good. As a further check on these values, the temperature-dependence of the coupling constant can be calculated completely using these values. These give values of 5·89 c./sec., at 30° and 5·86 at 90° whereas the observed values are 5·93 and 5·87 ± 0·02 c./sec. Again the agreement is very reasonable. Note that the errors in the values of J_t and J_g are not equal, because there is only a minor amount of the *gauche* form present even in solutions of very high dielectric constant. [For $\varepsilon = \infty$, $x = 0 \cdot 5$, and equation (7) predicts $\Delta E^s = 0 \cdot 26$, thus there is only *ca.* 25% of the *gauche* form present in the most polar media.]

DISCUSSION

ΔE^v obtained from the solution results, which has been obtained without any assumptions about the values of ΔE^v or ΔE^s [except that their difference must be given by equation (7)] is virtually identical with that obtained by Harrison and Kobe.[12] This supports this value (2·3 ± 0·1 kcal./mole) against the higher value of Kuratani and Mizushima.[11] There are considerable experimental difficulties in determining large ΔE values from infrared data, as the variation in intensity with temperature of very weak bands must be measured. In this case, only one band due to the *gauche* isomer was separated sufficiently from those of the predominant *trans* isomer to be measured. The agreement obtained between the solution method and the other methods of measuring ΔE^v does suggest that the solution method can give accurate values of ΔE^v in favourable cases.

The values of the coupling constants of the individual rotamers are also in complete agreement with previous results derived by a direct infrared measurement of the proportions of the isomers in different solvents [14] (J_t 10·5 ± 3·0 c./sec.; J_g 3·0 ± 1·5 c./sec.). It is a pity that the most accurate value (J_t) is the average coupling constant in the *trans* isomer, *i.e.*, $\frac{1}{2}(J_{trans} + J_{gauche})$ (cf. Figure 1). The values obtained are not surprising; the noteworthy point is the fact that the similar values of J_{gauche} in trichloroethane and 1,1,2,2,-tetrachloroethane (both 2·2 c./sec.) [13] do add support to the idea that the substituent effect on J_{gauche} is largely determined by the substituents *trans* to the coupling nuclei.[1,15]

Because of the overall good agreement of the theory with experiment, it is instructive to consider the basic assumptions of the theory in terms of the intermolecular forces in solution. The theory is based on classical electrostatics and specifically excludes any chemical bonding between solvent and solute and in addition the solvent is regarded as a medium of uniform di-electric constant. In addition, merely for convenience in simplifying the calculations, we assume spherical solute molecules and neglect the quadrupole polaris-ability and octupoles and higher moments. However, in principle these could be included, which differentiates

[14] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, 1959, *A*, **252**, 506.
[15] H. Booth, *Tetrahedron Letters*, 1965, 411.

these from the basic assumptions above, which are of more interest.

Certain solvents do not obey this theory and the reasons are obvious. Non-polar aromatic solvents form complexes with practically any polar solute and this gives rise to the well known specific chemical shifts of compounds dissolved in them.[16] These interactions have been studied extensively and are of *ca.* 1—2 kcal./mole energy.[17] On this basis it would be expected that benzene would complex preferentially with the more polar *gauche* isomer of trichloroethane and this is clearly demonstrated in the low value of the coupling constant (5·94 c./sec. for a dielectric constant of 2·60). Although polar aromatic solvents tend to behave more normally, [16] we have excluded aromatic solvents from the solvent studies on these grounds. Also as might have been expected hydroxylic solvents behave somewhat abnormally. Obviously chemical bonding between the solvent molecules must be considered here, as the solute has to break solvent–solvent bonds to dissolve.

A more novel exception occurs when the second of the basic assumptions is not valid, *i.e.*, when the dielectric constant at the solute molecule is not the same as in the bulk medium. This occurs with solvents which contain strongly polar groups plus a large hydrocarbon segment. In this case preferential solvation of the polar groups in the solvent would be expected to occur. Thus the dielectric constant around the solute is now higher than the solvent bulk dielectric constant, which produces low values of the coupling constant (*e.g.*, in cyclohexanone $J = 5\cdot46$ c./sec. and ε 15·6). This is *not* the same as a chemical complex but merely the result of an increase

in the energy of the solute electric field (which gives a decreased energy of the system) in more polar media. Further, this preferential solvation will occur in all solvent mixtures in which one of the solvents is polar and one non-polar. Thus solvent mixtures cannot be used in our investigations, and indeed show pronounced deviations from the curve. This phenomenon has not been considered in some recent investigations of the behaviour of polar solutes in solvent mixtures,[18] and may be the cause of the anomalous behaviour reported. The prospect is envisaged of using the coupling constant of trichloroethane (or any other suitable molecule) as a probe to measure the effective dielectric constant around a polar solute in such media. Further work on these lines is in progress.

Apart from these obvious exceptions, almost any solvent may be used for this work, and the overall agreement strikingly indicates the extent to which interactions in solution can be represented by this simple classical theory. Presumably one of the major reasons for this good agreement is that the theory is only concerned with energy differences between rotamers. Thus any solvent–solute interaction which affects both isomers equally will not affect ΔE. Even so the extent of the agreement in the calculations of $\Delta E^{\mathrm{v}} - \Delta E^{\mathrm{l}}$ suggests that the theory could be used to give reasonable estimates of energies of solvation for simple molecules.

[16] N. S. Bhacca and D. H. Williams, " Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, 1964, ch. 7.

[17] R. J. Abraham, *Mol. Phys.*, 1961, **4**, 369.
[18] P. Laszlo and J. I. Musher, *J. Chem. Phys.*, 1964, **41**, 3906.