PHYSICAL CHEMISTRY

A. V. IOGANSEN

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. V. IOGANSEN

DEPENDENCE BETWEEN THE ENERGY OF A HYDROGEN BOND AND THE INTENSITY OF INFRARED ABSORPTION

(Presented by Academician A. N. Terenin, 11 III 1965)

Association of molecules by means of a hydrogen bond, as is known, substantially increases the intensity of the infrared band of the $\nu_{\mathrm{A-H}}$ stretching vibration of the hydrogen atom (see (^{1}, ^{2})), and it is precisely the enhancement of the band, and not the shift of its frequency, that may be regarded as the principal, most fundamental of the spectral indicators of the formation of the complex A—H ... B (^{3}). It is then more natural to compare its energy (ΔH) not with the position, as is generally accepted, but with the strength of the $\nu_{\mathrm{A-H}}$ band.

Becker (^{4}) correlated ΔH with the intensity $A = (cl)^{-1} \int \ln(I^0/I)\, d\nu$ and found that the correlation with A is better than with the frequency shift $\Delta\nu$. However, the energies of H-bonds should be compared not with the intensity itself, but with the increment of the quantity $A^{1/2}$ upon formation of an H-complex. This is suggested by the concepts (^{3}, ^{5}) that the growth of A is determined by the additive contribution of the H-bond proper to the transition dipole moment, the square of which is proportional to A. Since the quantity A, moreover, is proportional to the frequency ν, and it is different for different A—H and for "free" molecules and complexes, it is better to operate with the quantity Γ

$$\Gamma = (cl)^{-1} \int \ln(I^0/I)\, d\ln\nu \approx A/\nu.$$

Guided by the above considerations, we compared the quantities ΔH and $\Delta\Gamma^{1/2}$ for a number of systems with intermolecular hydrogen bonding. The correlation between $\Delta\Gamma^{1/2}$ and ΔH is presented in Fig. 1, where it is compared with the usual Becker—Bauer correlation for the same systems. The correlation leads to a linear dependence

$$\Delta H = 5.3\Delta\Gamma^{1/2}, \tag{1}$$

where $\Delta\Gamma^{1/2} = \Gamma_m^{1/2} - \Gamma_n^{1/2}$ is the difference for two states m and n (as a rule, m and n are the complex and the "free" molecule in CCl_4); Γ is expressed in

Fig. 1

Figure 1: Fig. 1

10^4 cm^2/mol and calculated per one A—H bond; ΔH is the enthalpy difference of the same states in kcal/mol per one H-bond.

Dependence (1), apparently incompatible with the idea of an electrostatic character of the H-bond, is explained with the aid of concepts of donor-acceptor interaction ([1], [2]). (However, quantum-mechanical calculations of the H-bond did not predict it.) We start from the additive model ([3]) of two independent bonds A—H and H ... B, in which $\mu'_{\mathrm{H}} = (\partial\mu_{\mathrm{H}}/\partial r_{\mathrm{H}})_R = (\partial\mu_{\mathrm{H}}/\partial R)_r$ ($R = r + r_{\mathrm{H}}$; r, μ and r_{H}, μ_{H} are the length in angstroms and the moment in debyes, respectively, of A—H and H ... B). For a harmonic oscillator (under the condition $\partial\mu/\partial r = \mathrm{const}$) $\mu'_{\mathrm{H}} = -2.7\Delta\Gamma^{1/2}$.

Assuming, in accordance with the experimental fact of the short range of H-forces, that $\Delta\Gamma^{1/2}(R)$ is exponential and relying on the value $R = 2.73$ in the formic-acid dimer and on the vanishingly small interaction at $R > 3.2$ ([1]), we obtain $\Delta\Gamma^{1/2} = \exp[-4.5(R - 2.8)]$. This gives the dependence $\mu_{\mathrm{H}}(R)$ and permits

calculate the moment of the H-bond:

$$\mu_H = \int_{\infty}^{R} \mu'_H \, dR = 0.6\, \Delta\Gamma^{1/2}. \tag{2}$$

Let us note that (2) and the expression following from its combination with (1),

$$\mu_H = 0.1\Delta H \tag{2a}$$

predict H-bond moments that agree with the observed increments of dipole moments in H-complexes ([1]).

The quantity μ_H can be interpreted as a measure of the "delocalization" of the electrons of the base or, alternatively, μ_H/μ_T as the contribution of the structure $\overset{-}{\mathrm{A}}\ \mathrm{H}-\overset{+}{\mathrm{B}}$ with moment $\mu_T = eR = 13$. Then dependence (1) means that the energy

Fig. 1. **A** —correlation of the quantities $\Delta\Gamma^{1/2}$ and ΔH; **B** —correlation of the quantities $\Delta\nu/\nu$ and ΔH in systems with intermolecular hydrogen bonding. Presented in order of decreasing ΔH are complexes: a) phenol—triethylamine ([6]); pyridine ([6,7]); hexamethylenetetramine ([1]); di-*n*-butyl ether; butanone-2; diphenyl ether; benzene ([8]) (the intensity, besides the second and third systems, was measured by us); b) alcohols (average for methanol, ethanol, and tert-butanol)—pyridine; dimethylformamide; dioxane; acetone; benzophenone; ethyl

acetate (4); c) acetylenes (average for acetylene and 1-alkynes) hexamethylphosphoramide; N-methylpyrrolidone; dimethylformamide; cyclohexanone, acetone; dioxane (9,3); d) associates on saturated carboxylic acids (1,10), methanol (1,11); water (1,12); N-methylacetamide (1,13).
1 –phenol + base; 2 –R–OH + base; 3 –R–C C–H + base; 4 –dimers and polymers.

of the H-interaction is proportional to the "delocalization" of the electrons of the base or to the weight of the structure with charge transfer. If, for estimating D_H (see below), the energy of the $\overset{+}{\mathrm{O}}-\mathrm{H}$ bond is taken equal to the energy of an ordinary OH bond, then from (2) we obtain unexpectedly exact agreement with the experimental relation (1), namely

$$D_H = 100\,\mu_H/\mu_T = 4.6\Delta\Gamma^{1/2}.$$

It would be more interesting to measure the dependence $\Delta\Gamma^{1/2}(R)$ in crystals with an H-bond, which, in combination with (1), would give the dependence $D_H(R)$ and, perhaps, refine the model of the H-bond.

Let us discuss the discovered dependence (1). Its most striking feature is its generality. As Fig. 1 shows, complexes of various "acids" and diverse "bases," and different associates of identical molecules, fit the common straight line equally well; moreover, comp–

hydrogen-bonded associates (water, alcohol) are no exception. The latter should also follow from the validity of (1) for binary complexes. Indeed, in the presence of a distribution over states (not explicitly taken into account), formula (1) in fact gives an average value, since the measured quantity $(\langle\Gamma\rangle)^{1/2}$ differs little from the required ratio (1) $\langle\Gamma^{1/2}\rangle$. Only for complexes with pyridine is the intensity greater, and for them their own straight line is indicated (the dotted line through the points P in Fig. 1A)*.

The set of systems presented in Fig. 1 covers a wide range of H-bond energies, 1–9 kcal/mol, from very "weak" to "strong." It is possible that dependence (1) is not limited by the value 9 kcal/mol, but there are no data on stronger bonds. The study of such bonds appears very interesting. Downward, (1) extends also to weaker H-interactions, down to very small ones. Thus, the transition from gas to solution in "inert" CCl_4 is accompanied by an increase in Γ, corresponding to H-bond energies from ~ 2 kcal/mol for HCl to ≤ 0.05 kcal/mol per C–H bond for saturated hydrocarbons (15). Expression (1) gives a reasonable agreement with experiment for the heats of mixing of chloroform with solvents, the energies of H-complexes of HCl with argon, etc.

Also noteworthy is the substantial difference in the accuracy of relation (1) from the approximate (and nonlinear) correlation with the frequency shift (Fig. 1B). The deviations of all points from the straight lines in Fig. 1A do not exceed the possible errors in measuring the quantities ΔH and $\Delta\Gamma^{1/2}$; in this connection we may speak rather of dependence (1) than of a correlation between ΔH and $\Delta\Gamma^{1/2}$. Clarification of the limits of accuracy of dependence (1) apparently requires, and deserves, a more detailed investigation.

Dependence (1), its generality, breadth, and accuracy compel one to accept that, in the majority of systems with a hydrogen bond, the quantities ΔH are mainly or completely determined by forces of one nature, which simultaneously determine the growth of the intensity of $\nu_{\mathrm{A-H}}$. Understanding by D_{H} the energy of H-bonds due only to these forces, defining it by the relation

$$D_{\mathrm{H}} = 5.3\Delta\Gamma^{1/2} \tag{1a}$$

and comparing D_{H} and ΔH, we can in the remaining cases distinguish the H-bond from other interactions and estimate their contributions. For example, in the series studied by Kuhn (^{16}), $CH_3O(CH_2)_{\mathrm{nOH}}$, $n = 4, 3, 2$, with intramolecular hydrogen bonds, $\Delta H = 2.7;$ 2.1 and 2.2, $D_{\mathrm{H}} \approx 2.9;$ 1.1 and 0.3 kcal/mol. As can be seen, at $n = 4$ an intramolecular H-bond is indeed formed, which does not differ from intermolecular ones, and it completely determines the stability of the cyclic structure. On the contrary, at $n = 2$, where a linear O—H···O bond is impossible, the contribution of the H-bond to the energy difference of rotational isomers is very small. In *o*-chlorophenol—the usual example of an intramolecular hydrogen bond—or in β-chlorospirits, according to (1a), there is no O—H···Cl H-bond at all, and the stabilization of rotational isomers is determined entirely by other forces, possibly electrostatic ones**.

It is thought that the discovered dependence may find a number of applications for structural diagnostics, and also for determining H-bond energies in various macromolecules, in matrices frozen in, and in other nonequilibrium systems where thermodynamic methods are impossible, etc. Judging from the limited data, $\Delta\Gamma^{1/2}$ values of different acids with the same series of bases may turn out to be linearly interrelated. Together with (1a) this would mean that D_H can be represented as $D_H = F_A F_B$, where F_A and F_B characterize the participants of the H-complex separately. F_A, the acceptor (acid) factor, is approximately parallel to the electronegativity of atom A; F_B, the donor (base) factor, depends more complexly on the structure of the molecule and is not reducible to a property of the atom.

* The probable reason is the "conjugation effect" (^{14}): the electron displacement during the vibration $\nu_{\mathrm{A-H}}$ is not localized, as usual, in A—H···B, but extends over the pyridine ring with a hydrogen atom, creating an additional moment. The same should also apply to other aromatic N-heterocycles. Conversely, the usual intensity for complexes with benzene may be regarded as evidence that the H-bond with π-electrons is normal to the plane of the benzene ring.

** It is strange to suppose that hydrogen binds to the chlorine atom of its own molecule located on the A side, but is indifferent to the same chlorine of the surrounding solvent molecules—carbon tetrachloride.

State Scientific Research
and Design Institute of the Nitrogen Industry
and Products of Organic Synthesis

Received
3 III 1965

REFERENCES

1. J. Pimentel, O. McClellan, *The Hydrogen Bond*, Moscow, 1964.
2. N. D. Sokolov, in: *Hydrogen Bond*, Moscow, 1964.
3. A. V. Iogansen, G. A. Kurkchi, *Optics and Spectroscopy*, **13**, 480 (1962).
4. E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).
5. H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).
6. M. D. Joesten, R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).
7. N. Fuson, P. Pineau, M. L. Josien, *J. Chim. Phys.*, **55**, 454 (1958).
8. R. West et al., *J. Am. Chem. Soc.*, **86**, 3227 (1964); D. L. Powell, R. West, *Spectrochim. Acta*, **20**, 983 (1964).
9. G. A. Kurkchi, Dissertation, Moscow State University, 1964.
10. J. Wenograd, R. A. Spurr, *J. Am. Chem. Soc.*, **79**, 5844 (1957).
11. U. Liddel, E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).
12. Th. Ackermann, *Zs. phys. Chem.*, **27**, 253 (1961).
13. R. L. Jones, *Spectrochim. Acta*, **20**, 1879 (1964).
14. A. V. Iogansen, G. D. Litovchenko, *DAN*, **153**, 1367 (1963).
15. A. V. Iogansen, E. V. Broun, G. D. Litovchenko, *Optics and Spectroscopy*, **18**, 38 (1965).
16. L. P. Kuhn, R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

Note: Figure translations are in progress. See original paper for figures.