HYDROGEN BONDS INVOLVING THE C-H LINKAGE*

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Rodebush and Latimer[1] in 1920 proposed the secondary valence of hydrogen or "hydrogen bond" to explain the abnormal properties of certain associated liquids. The hydrogen bond is a type of semi-polar bond capable of being formed between an unshared pair of electrons on an oxygen, nitrogen or fluorine atom and a hydrogen atom linked to another atom by a sufficiently ionic link. Such a bond is illustrated by the ether-chloroform complex, I. The atom supplying the elec-

R
:O: ⟶ $HCCl_3$
R

I

tron pair is called a "donor" atom and that containing the hydrogen atom with which the bond is formed is called an "acceptor" atom.

In the chloroform-ether complex, the presence of the strongly electron-attracting halogen atoms on the carbon atom loosens the hydrogen and makes it somewhat ionic thus making it available for coordination to the oxygen atom.

This concept of intermolecular hydrogen bonding has proved very helpful in explaining and predicting abnormally high solubility, high heat of mixing, and other deviations from "ideal" admixture laws of certain types of organic solvent-solute combinations.

Copley, Zellhoefer and Marvel[2] have studied the solubility of partially and completely halogenated methanes and ethanes in a vast array of organic solvents. The results obtained were readily explainable by the hydrogen bond concept. It was found that where intermolecular hydrogen bonds between solvent and solute were possible high solubilities were observed; where the solute and solvent were unassociated and there was no possibility of intermolecular hydrogen bonding solubilities close to those calculated by Raoult's Law were observed; and where the solvent was strongly associated through hydrogen bonding considerably less than theoretical solubilities were observed.

The types of compounds which have been found to exhibit electron-pair donorability are in approximately decreasing order of ability: amines, dialkyl amides, ethers, esters, ketones, nitriles and nitro compounds.

In the present investigation the heats of mixing of a number of C-H contain-

* Contribution from the Noyes Chemical Laboratory, University of Illinois.

[1] Rodebush and Latimer, J. Am. Chem. Soc., 42, 1419 (1920).

[2] Copley, Zellhoefer and Marvel, J. Am. Chem. Soc., *60*, 1337, 2660, 2714 (1938); *61*, 3550 (1939); *62*, 227 (1940).

ing acceptor molecules with donor liquids have been studied calorimetrically. The heat of mixing in such cases has been shown to be produced chiefly by the formation of hydrogen bonds.

One of the problems studied was the effect of substitution on the activity of the acceptor hydrogen atom. The more electro-negative the substituent is the more ionic the C-H bond becomes and the strength of the hydrogen bond increases accordingly. In the haloforms and methylene halides one would expect the activity of the acceptor hydrogen to increase in the order of increasing electronegativity of the halogen substituent, i.e., Cl>Br>I. This conclusion is borne out by the heat of mixing data in Table I. It is seen that:

$$CHCl_3 > \text{or} = CHBr_3 \text{ and } CH_2Cl_2 > \text{or} = CH_2Br_2 > CH_2I_2$$

TABLE I.—HEAT OF MIXING IN CALORIES PER MOLE OF SOLUTION FOR EQUIMOLAR MIXTURES

	$CHCl_3$ at 3°	$CHBr_3$ at 10°
N, N-dimethyl acetamide	920	920
Ethyl ether	700[3]	520

	CH_2Cl_2 at 3°	CH_2Br_2 at 3°	CH_2I_2 at 7°
N, N-dimethyl acetamide	535	410	100
Ethyl ether	290	210	no heat

The effect on the activity of the hydrogen of chloroform as an acceptor on successive replacement of the halogen atoms by the less electronegative phenyl group was studied. The results shown in Table II indicate that: $CHCl_3 > C_6H_5CHCl_2 > (C_6H_5)_2CHCl$ as acceptor molecules.

Another compound studied was *sym*-tetrachloroethane. This compound should have two active hydrogen atoms but only one was indicated by the heat of mixing curves. This seems to indicate a steric effect of the same sort as that found by Copley and Zellhoefer[4] for the dimethyl ethers of polyethylene glycols.

TABLE II.—HEAT OF MIXING IN CALORIES PER MOLE OF SOLUTION FOR EQUIMOLAR MIXTURES

	$CHCl_3$ at 3°	$C_6H_5CHCl_2$ at 3°	$(C_6H_5)_2CHCl$ at 14°
N, N-dimethyl acetamide	920	525	210
Ethyl ether	700[3]	240	50
Acetone	520	220	----------

The bond formed between donor molecules and tetrachloroethane should be weaker than those formed with chloroform. Actually the heats of mixing are found to be about the same in both cases as shown in Table III.

TABLE III.—HEAT OF MIXING IN CALORIES PER MOLE OF SOLUTION AT 3° FOR EQUIMOLAR MIXTURES

	$CHCl_3$	$CHCl_2CHCl_2$
N, N-dimethyl acetamide	920	1,100
Ethyl ether	700[3]	570
Acetone	520	630

This may be due to the fact that formation of a hydrogen bond in liquid mixtures is an equilibrium reaction dependent on the concentration of acceptor hydrogen atoms present. In a mole of *sym*-tetrachloroethane there is twice the concentration of acceptor hydrogen atoms as in a mole of chloroform.

Summary.—The heat of mixing of acceptor molecules containing the C-H linkage with donor liquids has proved valuable in showing the presence of hydrogen bonds, in approximating the strength of bond, and in determining the molecular ratio of donor and acceptor in the complex formed.

[3] McLeod and Wilson, Trans. Faraday Soc. *31*, 596 (1935).
[4] Copley and Zellhoefer, J. Am. Chem. Soc., *60*, 1343 (1938).