

Studies of the Hydrogen Bond

IV. Theoretical Determination of Electronic Polarization Energies

INGA FISCHER-HJALMARS
and RAGNAR GRAHN

*Institute of Theoretical Physics, University
of Stockholm, Stockholm, Sweden*

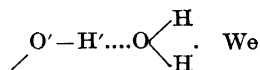
The problem why some molecules associate by aid of hydrogen bonds (H bonds) while others seem to have no disposition for the formation of such bonds has been thoroughly discussed for many years but has not yet been solved in a completely satisfactory way. The main factors, which cooperate in the formation of an H bond, are supposed to be: 1) electrostatic interaction, 2) covalent binding, 3) polarization. In many investigations of the H bond only the two first factors have been taken into consideration. The factor 3) seems, however, to be of the same importance as the other two. It has been discussed previously by, *e.g.*, Bauer and Magat¹ and by Ehrenberg and Fischer^{2,3} (Studies of the Hydrogen Bond I, II, III). Bauer and Magat¹ have calculated the energy of an H bond between water molecules with due consideration to polarization effects. This calculation was carried out in a classical way by use of the experimental value of the polarizability of the whole molecule. Ehrenberg and Fischer^{2,3} have pointed out that certain organic compounds with a less polarizable hetero-atom are less soluble in water than others with a more polarizable hetero-atom. They proposed quantum mechanical calculations to clarify the rôle of polarization for H bond formation, and a very rough calculation of this kind was carried out⁴.

The influence from the above-mentioned three factors upon an H bond cannot be strictly separated. It would therefore have been desirable to make a complete, quantum mechanical calculation of the total energy of H-bonded systems. Because of the complexity of such systems we have chosen to investigate primarily the electronic polarization effects and less rigorously the other two factors. Even this simplified programme must be further reduced to make the computational work tolerable.

Hitherto we have studied the association of H₂O, where there is a strong H bond,

and of H₂S, where there is no H bond. Calculations on the association of HF and of HCl are going on but will not be reported here. They will be published later by one of us (R.G.) together with a more detailed description of the calculations on H₂O and H₂S.

In the study of the H bond between H₂O molecules we have considered the

following system:  We

have used the intermolecular distances given by the ice-structure, proposed by Bernal and Fowler⁵. For the description of the electron distribution of a free H₂O molecule we have used the molecular orbitals (MO's), calculated by Ellison and Shull⁶. Our investigation includes a study of i) the strengthening of the H bond, caused by the electronic polarization of the whole H₂O in the field from the net positive charge on H' and ii) the strengthening of the H bond, caused by the polarization of H' in the field from the adjacent H₂O.

The energy gain from the effect i) has been obtained from a computation of the change of the original MO's of H₂O, caused by the potential from H'. Now, the O atom of the free H₂O has two filled lone-pair MO's. When expressing the electron distribution by aid of equivalent orbitals, it is seen that already in the free H₂O these MO's are almost completely localized at the "back" of the O atom. Thus, the computed electron density at the back of the O atom cannot increase as a result of the H' potential, unless excited atomic orbitals (AO's) are included in the changed MO's. However, for computational reasons, we have assumed the changed MO's to be linear combinations of the same AO's as the original MO's. Consequently, our calculation can only take into account that part of the effect from H', which consists in moving the electrons of the O—H bonds closer towards the O atom. The energy gain from this movement is found to be comparatively small, only 0.2 kcal/mole. However, the sign of this energy change indicates that the effect i) would give a much larger energy gain, if excited AO's of the O atom were included.

The effect ii) has been computed by replacing the 1s AO of H' by a hybrid of the three AO's 1s, 2p_σ and 2p_π. The coefficients of this hybrid have been determined by a variation method. The energy

gain from this polarization of H' has been found to be about 1.5 kcal/mole.

Summing up, the total computed energy gain from polarization effects is $0.2 + 1.5 = 1.7$ kcal/mole. This value is, however, not very definite. There are several factors, which could modify it in one direction or the other. One factor, which would increase it, is the fact that 0.2 and 1.5 kcal/mole should be considered as lower limits of the effects i) and ii). Another, which would diminish it, is the fact that the effect ii) should cause a slight weakening of the O'—H' bond. Although the value 1.7 kcal/mole is rather approximate, it is interesting to compare it with the purely electrostatic interaction energy. Using the point charge model, discussed by Bauer and Magat¹, this energy is computed to 5.1 kcal/mole. Thus, it is seen that the polarization energy is not a negligible part of the total H bond energy.

For comparison with H₂O we have also studied the association of H₂S, which has an electronic structure similar to that of H₂O. H₂S solidifies at -82.9°C , but it does not seem to have a definite crystalline form. We have studied the interaction of

two H₂S molecules, $\diagdown\text{S}'-\text{H}'\dots\text{S}\begin{matrix} \text{H} \\ \diagup \\ \text{H} \end{matrix}$, assuming

the atoms S'H'S to be on a straight line. In the case of H₂S we have only computed the above-mentioned polarization effect ii). We have found a small energy gain, about 0.05 kcal/mole. Since the effect ii) is giving the main contribution to the polarization energy in the H₂O case, it is reasonable to assume the total polarization energy in the association of H₂S to be of the order of magnitude of 0.05 kcal/mole. The purely electrostatic interaction energy is in this case computed to be 0.25 kcal/mole, when a point charge model is used.

The numerical results of the present investigation are collected in Table 1.

Table 1. Effects contributing to H bond formation. Energies in kcal/mole.

Molecule	Polarization energy			Electrostatic energy	Exptl. H bond energy
	i)	ii)	total		
H ₂ O	0.2	1.5	1.7	5.1	5.8
H ₂ S	—	0.05	~0.05	0.25	—

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From Table 1 it is seen that the polarization effects are important for the H bond formation in the H₂O case, whereas they cannot have any influence in the H₂S case.

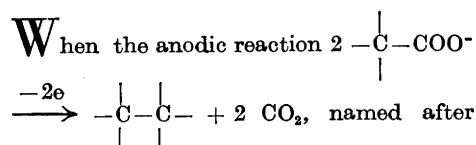
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Some Advantages of Using a Mercury Cathode in the Kolbe Electro-synthesis

NGUYEN DINH-NGUYEN

Department of Medical Biochemistry, University of Gothenburg, Sweden



Hermann Kolbe¹, is used for the preparation of alkali-sensitive substances such as esters, present practice usually avoids hydrolysis by electrolyzing free carboxylic acids in the presence of only a few per cent of their sodium salts, the reaction being stopped when the electrolyte turns neutral. The solvent is generally methanol and the electrodes smooth platinum sheets.

In an attempt to prepare dimethyl adipate from methyl hydrogen succinate using this technique, a yield of only 38 % was obtained, in contrast to the 70 % reported by Bouveault². He electrolysed equivalent amounts of succinic anhydride and sodium in methanol, using a water-cooled platinum-tube anode and a mercury cathode. New runs were therefore made with mercury as cathode at the bottom of a beaker, and a platinum-sheet anode