Molecular Orbital Study on the H_2O-HCl System

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The hydrogen bonded system of H_2O–HCl was studied by the CNDO/2 method. Calculation of the potential energy for the system showed that the complex of H_2O–HCl is considerably stable. The equilibrium structure of the complex and its charge distribution were also investigated.

A number of studies by molecular orbital calculations on simple hydrogen bonded systems have been reported since Clementi carried out a detailed study on ammonium chloride.[1] One of us (S.S.) determined experimentally the molecular structure of NH_4Cl in gaseous phase.[2] Structure determination of the H_2O–HCl system was undertaken for studying simple hydrogen bonded systems. Electron diffraction study was also carried out on the system in gas state. The result confirmed the existence of the molecular complex of H_3OCl. A theoretical study was made in order to see whether the H_2O–HCl molecular complex is actually stable and, if so, to confirm its geometrical structure.

According to Murthy and Rao[3] who carried out many molecular orbital calculations on various hydrogen bonded systems showed that the CNDO/2 procedure[4] can yield satisfactory results for potential energies of hydrogen bonds. Kollman and Allen,[5] and Rao and Murthy[6] recently carried out calculations for the H_2O–HF and NH_3–HF systems, respectively. However, there have been no CNDO/2 studies on hydrogen bonds containing a chlorine atom. It is well-known that the CNDO/2 method is also applicable to the system in which d orbitals contribute.[7] Thus CNDO/2 calculation was carried out on the H_2O–HCl system.

Procedure

Most calculations were performed with the use of a spd set as a basis, and some of them with a sp set. The values of the parameters used in these calculations were the same as those given by Santry and Segal[7] except for the empirical parameter K which is defined by the following relation of the resonance integral:

$$\beta_{AB} = K(\beta_A+\beta_B)/2$$

Santry and Segal suggested the use of 0.75 for K. However, this seems to be somewhat ambiguous, and other values were also used.

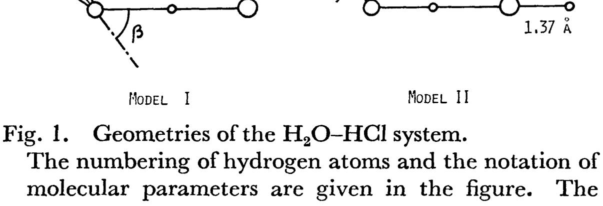

Fig. 1. Geometries of the H_2O–HCl system.
The numbering of hydrogen atoms and the notation of molecular parameters are given in the figure. The listed values of the molecular parameters were assumed in the CNDO/2 caculations.

With respect to geometries of the H_2O–HCl complex two structures, shown in Fig. 1, were taken into consideration. Both were inferred from the gas electron diffraction study. The O–Cl distance, denoted by R_1, and the H(3)–Cl distance (H(2)–Cl distance in model II), by R_2, were varied at intervals of 0.3 and 0.1 Å, respectively. In the neighbourhood of minimum of potential energy R_1 was varied at an interval of 0.1 Å. The angle H(1)OH(2), denoted by α, and the O–H distance were also varied. In the first stage of calculations α was assumed to be 105° from the experimental data for water[8] and the O–H distance was fixed as 1.05 Å obtained from the calculation where other parameters were kept in most probable values. In model I the angle between the H(1)OH(2) plane and the OH(3)Cl line, denoted by β, was also varied preserving the C_s symmetry of the complex. A planar structure was assumed for model II. In both models the hydrogen bonds of O–H–Cl were assumed to be linear. All the calculations were carried out with a FACOM 230-60 computor at Nagoya University Computing Center.

Results and Discussion

For model I, the potential energies of the system, shown in Fig. 2, were calculated as a function of R_1 with the fixed R_2. The calculations were carried out by using K=0.75, spd set, R(O–H)=1.05 Å and α= 105°. A potential energy minimum was found at R_1= 2.8 Å, independent of R_2. Calculations using the sp basis set also gave nearly the same equilibrium distances

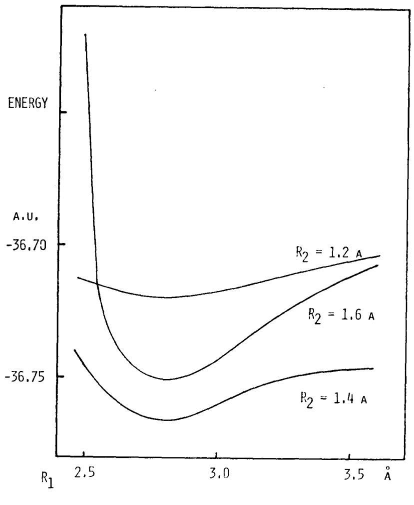

Fig. 2. The energy of the H_2O–HCl system (the model I) as a function of the O–Cl distance, R_1.

as those for the spd basis set though the total energies were considerably different. The distance of 2.8 Å seems to be reasonable in comparison with the O–Cl distance of 2.95 Å found experimentally in crystalline hydrogen chloride monohydrate H_2O–HCl.[9)]

The potential curve shows no energy barrier for formation of the complex $H_2O \cdot HCl$. The dissociation energy of the complex was found to be 16 kcal/mol (Table 1). This value also seems to be reasonable in compaison with the calculated value of 10.7 kcal/mol for the H_2O–HF system.[3)]

Table 1. Dissociation energies for the H_2O–HCl systems (kcal/mol)

K	Model I		Model II	
	spd	sp	spd	sp
0.75	16	19	8	−14
0.875	8		19	
1.0	5	6	40	−18

Fixed as R(O–H) = 1.03 Å, α = 104°.

Calculations were carried out varying β from 0 to 60°. The planar structure ($\beta=0°$) was found to be most stable. The energy difference between the planar structure and the structure with $\beta=60°$ was estimated to be 4 kcal/mol. This is contrary to the expectation that the hydrogen bond would be formed toward the direction of the lone pair sp^3 hybrid orbitals of the oxygen atom. It would be understandable from the view point of dipole-dipole interaction.[10)]

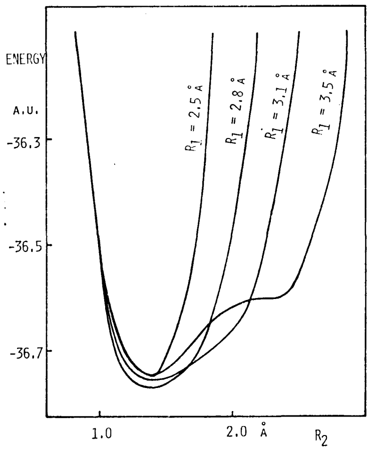

Fig. 3. The energy of the H_2O–HCl system (the model I) as a function of the H(3)–Cl distance.

Figure 3 shows potential energy calculated as a function of R_2 with the fixed R_1, using K=0.75 and spd set. The minimum of the potential energy was found at R_2=1.4 Å, nearly independent of R_1. The H(3)–Cl equilibrium distance of 1.4 Å is considerably greater than 1.27 Å found experimentally for free hydrogen chloride.[11)] However, the HCl equilibrium distance calculated by the CNDO/2 method is 1.37 Å. Thus the net increment of H–Cl distance in the complex formation seems to be fairly small. On the other hand, the O–H(3) distance of 1.4 Å is much greater than the O–H(1) distance of 1.03 Å, which is the value calculated for water molecule by the CNDO/2 method. Thus the H_2O–HCl complex can be considered essentially as H_2O hydrogen bonded to HCl. It can be seen from Fig. 3 that transfer of the hydrogen atom of HCl to H_2O is very difficult.

When R_1 is smaller than 2.8 Å, there is no evidence for a double minimum potential. The potential is close to the NH_3–HF potential calculated by Rao and Murthy,[6)] differing slightly from the NH_3–HCl potential calculated by Mazur and Ratajczak[12)] by means of the Extended Hückel method. As R_1 becomes larger, the potential curve appears asymmetric around the minimum. For R_1=3.5 Å, which is unreasonably long, a new minimum was found around R_2=2.3 Å. In this configuration an ionic structure can be predominant because excess electronic charge on the chlorine atom is 0.67. The complex can thus be considered as hydronium chloride, $H_3O^+Cl^-$.

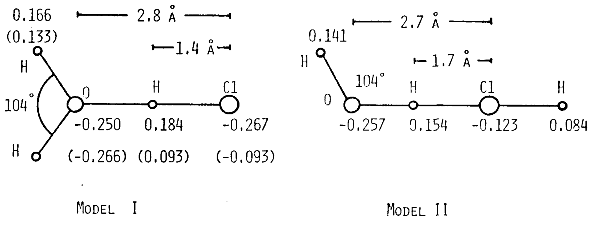

Fig. 4. The equilibrium structures and the atomic populations for the two models.

Figure 4 shows equilibrium structures and their charge distributions calculated by the use of K=0.75 and spd set. Numbers in parentheses are the charge distributions in free H_2O and HCl molecules. In the formation of the complex, H_2O donates electron to HCl, especially to the chlorine atom. However, the total amount of electrons donated to HCl is 0.08. The amount of charge transfer is almost the same as in the case of NH_3–HF system where it was estimated to be 0.05.[6)] When the spd basis set was used with K=1 in the CNDO/2 calculations, the equilibrium structure and the charge distribution obtained were the same as those from K=0.75, but the dissociation energy of the complex decreased to about 5 kcal/mol.

For model II, the calculations were carried out by use of the spd basis set with K=0.75 in order to estimate the dissociation energy as well as the equilibrium structure. The dissociation energy was 8 kcal/mol (Table 1), which leads to the conclusion that model I is preferable to model II in agreement with the result for H_2O–HF system by Kollman and Allen.[5)] On the other hand the use of the sp basis set showed that model II was unstable itself. From the calculation using the spd set with K=1, however, the dissociation energy was estimated to be 40 kcal/mol, which seems large as compared with the calculated value of 100 kcal/mol (experimental value of 37—58 kcal/mol) for the very strong hydrogen bonds such as HF_2^-.[13)] This calculation also gives a large population in d_σ orbital of the chlorine atom, 0.2. This is caused mainly by a large overlap between d_σ orbital of the chlorine atom and 1s orbitals of the H(2) and H(3) atoms. The use of the spd set with $K=1$ may not be correct since it gives rise to an excessive contribution of the d orbital. Santry and Segal found that good agreement of calculation with experiment is obtained for $K=0.75$.[7] These results lead us to prefer model I for the structure of the H_2O–HCl complex. However, a definite conclusion cannot be made since the stabilities of the two models are essentially dependent on the choice of the K value.

Conclusion

The CNDO/2 procedure gave the conclusion that the H_2O–HCl complex is stable in the planar structure with the equilibrium O–Cl distance of 2.8 Å. The complex can be considered to be H_2O hydrogen bonded to HCl than H_3O^+ bonded to Cl^-. The results, however, could not exclude the other structure of HOH–ClH with the O–Cl distance 2.7 Å.

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