BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1767—1768 (1969)

An Application of Mulliken's Theory of the Charge-transfer Complex to the Hydrogen-bonding Mechanism

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(Received October 28, 1968)

Recently several authors[1-4] have emphasized the importance of the charge-transfer mechanism of hydrogen bonding. Therefore, we may expect the appearance of charge-transfer bands in hydrogen-bonding systems as well as in molecular complexes. However, the present author could not find any certified charge-transfer bands for hydrogen-bonding systems except for the C. T. band of the hydrogen maleate anion found by Nagakura and his co-workers.[3] Regarding hydrogen-bonding systems, the relations between the shift of the X–H stretching vibration; the enthalpy of formation of the complex, ΔH; the excess dipole moment for the complex over the sum of the ingredients, $\Delta\mu$; the equilibrium constant of the complex, K, and the coefficients of Mulliken's theory, a and b, will be discussed here, and the C. T. band of the formic acid dimer will be estimated.

Mulliken[5] has written the wave functions for the ground and first excited states of the complex as:

$$\Psi_{\mathrm{N}} = a\psi_0 + b\psi_1, \qquad \Psi_{\mathrm{E}} = a^*\psi_1 - b^*\psi_0$$

In the approximation of the variation method, the following relation[6] holds:

$$aW_0 + bH_{01} = W_{\mathrm{N}}(a + bS). \tag{1}$$

Here,

$$W_0 \equiv H_{00} = \int\psi_0 H\psi_0 \mathrm{d}\tau,\ H_{01} = \int\psi_0 H\psi_1 \mathrm{d}\tau,$$

$$S = \int\psi_0\psi_1 \mathrm{d}\tau,$$

$$\Delta H \approx W_{\mathrm{N}} = \int\psi_{\mathrm{N}} H\psi_{\mathrm{N}} \mathrm{d}\tau / \psi_{\mathrm{N}}{}^2 \mathrm{d}\tau.$$

H is the exact Hamiltonian operator for the entire set of nuclei and electrons. In weak complexes, $a \approx 1$, and bS is a sufficiently small number compared with a. Therefore, Eq. (1) may be reduced to:

$$W_0 + b\beta_0 = \Delta H.$$

Here, $\beta_{01} = H_{01} - W_0 S$; then, for weak complexes, $\beta_0 \approx H_{01}$ will hold. If we suppose W_0 and β_0 to be approximately constant for given complexes, there is a direct relation between b and ΔH. However, there is no theoretical reason to expect W_0 and β_0 to remain constant for weak complexes, even with the same donor. On the other hand, as is well known, ΔH is given by:

$$\Delta H = -\boldsymbol{R}T \ln K + \text{constant}$$

Here $\boldsymbol{R}$ and T are the gas constant and the absolute temperature respectively. According to Mulliken,[5] for weak complexes the excess dipole moment for the complex over the sum of the acceptor and the donor, $\Delta\mu$, is given approximately by:

$$\Delta\mu \equiv \mu_{\mathrm{M}} = \mu_1(b^2 + abS) \approx b^2\mu_1 \tag{2}$$

The value of μ_1, the dipole moment of the dative structure, will be quite large due to the high charge separation in the dative structure, and it will be approximately constant for weak complexes. Therefore, the following direct relation will hold:

$$\sqrt{\Delta\mu} \propto \log K$$

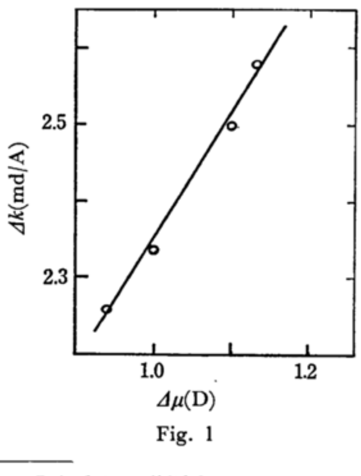

Fig. 1

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[1] R. S. Mulliken, *J. chim. phys.*, **1963**, 20.

[2] H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).

[3] S. Nagakura, *J. chim. phys.*, **1964**, 217.

[4] S. Bratož, "Advance in Quantum Chemistry," Vol. III, ed. by P. O. Löwdin, Academic Press, New York, N. Y. (1967), p. 221.

[5] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[6] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin (1961), p. 11, Eq. (II, 16).

[7] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco (1960), p. 25.

TABLE 1

	Free OH str. (cm^{-1})	k_0* (md/A)	Bonded OH str.[a] (cm^{-1})	k_n* (md/A)	Δk (md/A)	$\Delta\mu$ (D)
HCOOH	3700	7.59	3077	5.25	2.34	1.00[b]
CH_3COOH	3700	7.59	3100	5.33	2.26	0.94[c]
C_6H_5COOH	3700	7.59	3007	5.01	2.58	1.13[c]
CCl_3COOH	3700	7.59	3030	5.09	2.50	1.1[d]

* Force constants are estimated approximately for OH molecule.

a) S. Bratož, D. Hadži and N. Sheppard, *Spectrochim. Acta*, **8**, 249 (1956).

b) C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931). See also McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company (1963), p. 41.

c) H. A. Pohl, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941). See also Ref. 7, p. 24.

d) R. J. W. Le Févre and H. Vine, *J. Chem. Soc.*, **1938**, 1795. See also McClellan's Tables, p. 52.

Pimental and McClellan[7] find a proportionality between $\sqrt{\Delta\mu}$ and $\log K$ in the triethylamine-phenols and carboxylic acid dimers.

Person and Friedrich[2] have given the following equation:

$$(k_0-k_n)/k_0 \equiv \Delta k/k_0 = (1-k_1/k_0)(b^2+abS) \qquad (3)$$

If Eq. (2) is inserted into Eq. (3), the relation between Δk and $\Delta\mu$ is found to be:

$$\Delta k = [(k_0-k_1)/\mu_1]\Delta\mu$$

Here k_n, k_0, and k_1 are the X–H stretching force constants in the bonded X–H, free X–H, and $(X\text{–}H)^-$ molecules respectively. If k_0, k_1, and μ_1 are supposed to be approximately constant, there is a proportionality between Δk and $\Delta\mu$. Empirically there is a direct relation, as is shown in Fig. 1, between Δk and $\Delta\mu$ in a series of carboxylic acid dimers. The k_0, k_1, and $\Delta\mu$ values of carboxylic acid dimers are summarized in Table 1. Nakamoto *et al.*[8] have selected a constant frequency for each type of X–H stretching band; they concluded that each type of hydrogen bond shows a distinct relationship between the shift of the X–H band and the distance of the hydrogen bond. They selected 3700 cm^{-1} as the value of the free OH stretching band, so it seems reasonable to suppose that k_0 and k_1 are approximately constant.

Thereby, Mulliken's theory for the C.T. complex can be applied to hydrogen bonding systems. We may estimate 150 mμ as the approximate value for the charge transfer band characteristic of the interaction between the electron donor and acceptor in a formic acid dimer by using the following equation[9]:

$$\Delta H \approx h\nu_{CT}(b^2/a^2)$$

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[8] K. Nakamoto, M. Margoshes and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).

[9] See Ref. 7, p. 22, Eq. (IV, 10).