A Theoretical Consideration of the ^{13}C NMR Chemical Shift of Protonated Systems. I. The Acetone–Sulfuric Acid System

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A quantum-chemical method has been developed using a point-charge model to calculate the ^{13}C chemical shift for protonation in an acidic solution. This method has been applied to the acetone–sulfuric acid system; the gross tendencies between the observed and calculated results agree.

The NMR parameter, the chemical shift, is closely associated with the electronic structure of a molecule. In solution, the electronic structure of the molecule is affected by the surrounding molecules; thus, the chemical shift is solvent-dependent. The nature of the solvent effects may be mainly classified into the following two categories:

(i) The molecule considered forms a loose bonding with a solvent, such as hydrogen bonding or protonation.

(ii) Without such a bonding, the molecule is affected by intermolecular interaction with the surrounding molecules.

For Case (ii), we have successfully interpreted the observation of the solvent effect of the ^{13}C chemical shift[1,2] and the long-range chemical shift by magnetic anisotropy[3] in some organic compounds, acetone, acetonitrile and other compounds, by the application of Klopman's solvaton model[4] to the MINDO/2[5] and CNDO/2 methods.[6] It is the purpose of this work to treat quantum-chemically the protonation in Case (i) and use it in interpreting the behavior of the ^{13}C chemical shift of the protonated acetone molecule which occurs in a strongly acidic solution such as a sulfuric acid solution.

A study of the effect of protonation on the ^{13}C chemical shift of acetone was first done by de Jue[7] using the average-excitation-energy approximation. However, this approximation is too gross to enable us to discuss exactly the nature of the ^{13}C chemical shifts of the molecule being considered. We will, therefore, discuss the behavior of the ^{13}C chemical shifts of the protonated acetone using our proposed model for protonation without the average-excitation-energy approximation.

Theoretical

As a model of protonation we assume that a positive point charge approaches and loosely bonds to the oxygen atom in the carbonyl group of acetone. In order to formulate this model generally, we consider a molecular system with M electrons and N nuclei, adding a point charge. On the basis of this model, the Hamiltonian, H, of the specified molecular system consists of the inherent term, H_{inh}, and the protonation term, H_{prot}, and is given as (in atomic units)

$$H = H_{\mathrm{inh}} + H_{\mathrm{prot}}, \tag{1}$$

$$H_{\mathrm{inh}} = \sum_{i=1}^{M}\left[\left(-\frac{1}{2}\nabla_i^2 - \sum_{n=1}^{N}\frac{Z_n}{r_n}\right) + \frac{1}{2}\sum_{j=1}^{M}\frac{1}{r_{ij}}\right] + \frac{1}{2}\sum_{m=1}^{N}\sum_{n=1}^{N}\frac{Z_m Z_n}{r_{mn}}, \tag{2}$$

$$H_{\mathrm{prot}} = -\sum_{i=1}^{M}\frac{Q_{\mathrm{a}}}{r_{\mathrm{a}i}} + \sum_{n=1}^{N}\frac{Q_{\mathrm{a}}Z_n}{r_{\mathrm{a}n}}, \tag{3}$$

where Q_{a} is the magnitude of the point charge, $r_{\mathrm{a}i}$ and $r_{\mathrm{a}n}$ are the point charge-electron and the point charge-nucleus distances respectively, and Z_n is the charge on the nucleus, n. In these calculations, two additional assumptions were made for Eq. 3; (1) if the electron and the point charge are associated with the same atomic center, the point charge-electron distance, $r_{\mathrm{a}i}$, is taken to be the van der Waals radius of the oxygen atom, and (ii) if the electron and the point charge are associated with different atomic centers, the point charge is assumed to be centered on the atomic center associated with Q_{a}, and then the point charge-electron distance, $r_{\mathrm{a}i}$, is evaluated as the distance between their atomic centers.

Using the Roothaan's matrix notation, the total energy, E_{T}, of the system is given as

$$E_{\mathrm{T}} = 2\sum_{i}^{\mathrm{occ}}\boldsymbol{C}_i{}^*\boldsymbol{H}\boldsymbol{C}_i + \sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{occ}}\boldsymbol{C}_i{}^*(2\boldsymbol{J}_j - \boldsymbol{K}_j)\boldsymbol{C}_i + \frac{1}{2}\sum_{m}^{N}\sum_{n}^{N}\frac{Z_m Z_n}{r_{mn}} + \left[2\sum_{i}^{\mathrm{occ}}\boldsymbol{C}_i{}^*\boldsymbol{D}\boldsymbol{C}_i + \sum_{n}^{N}\frac{Q_{\mathrm{a}}Z_n}{r_{\mathrm{a}n}}\right]. \tag{4}$$

The fourth term is due to the contribution of the protonation, where the elements of D are given as

$$D_{ij} = \int \phi_i{}^*(1)\left(-\frac{Q_{\mathrm{a}}}{r_{\mathrm{a}1}}\right)\phi_j(1)\mathrm{d}\tau(1) \tag{5}$$

D_{ij} are estimated according to similar procedures developed by Germer.[8]

The integral:

$$D_{\mathrm{ss}} = D_{\mathrm{A}} \tag{6}$$

is calculated for each atomic center, A, using the S orbitals of the atom. The $D_{\mu\nu}$ is approximated as

$$D_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(D_{\mathrm{A}} + D_{\mathrm{B}}), \tag{7}$$

where $S_{\nu\mu}$ is the overlap integral, μ and ν being valence orbitals on the A and B atoms respectively. This approximation was incorporated into the MINDO/2 MO method.

As the effective van der Waals radius of the oxygen atom, 1.4 Å is used.[9]

According to Pople, the ^{13}C chemical shift, σ^{T}, is estimated by the sum of the diamagnetic and paramagnetic contributions. These contributions were calculated according to Pople's GIAO-MO theory[10] without the average-excitation-energy approximation.

The bond lengths and bond angles used are standard values proposed by Pople and Gordon.[11] All the calculation were carried out with the HITAC-8800 computer of the Computer Center of the University of Tokyo.

Experimental

High-resolution pulsed FT ^{13}C NMR spectra were obtained at 25.15 MHz using a JEOL PS-100 spectrometer equipped with a PFT-100 Fourier transform system, a JEC-6 spectrum computer, a ^{2}D field-frequency lock, and a noise-modulated proton-decoupling system. The observed free induction decay after a 90° pulse was sampled at 8192 data points. A deuteron signal of benzene-d_6 sealed in a capillary inserted into an 8 mm o.d. tube was employed for the lock signal, where ^{13}C-enriched tetramethylsilane(20%) dissolved in benzene-d_6 was used as the reference. The ^{13}C chemical shift was corrected for bulk magnetic susceptibility.[12] The bulk magnetic susceptibility for a solution, χ_{soln}, is given as

$$\chi_{\text{soln}} = \sum_{i}^{n} \phi_i \chi_i, \tag{8}$$

where χ_i and ϕ_i are the bulk magnetic susceptibility and the volume fraction of the i-th component molecule in solution respectively.

In a strongly acidic solution, the protonation of the acetone molecule may occur. The concentration of acetone is 2 mol % in various sulfuric acid–water concentration ratios. The sulfuric acid concentration varies from 0 to 25 mol % in the total solution.

Results and Discussion

In Fig.1 the ^{13}C chemical shifts of the carbonyl and methyl carbons are shown for 2 mol % acetone in various sulfuric acid–water concentration ratios. The carbonyl carbon chemical shift moves to a much lower field with an increase in the concentration of sulfuric acid. On the other hand, the methyl carbon chemical shift moves to an appreciably lower field upon protonation. These trends agree with de Jue's results,[7] although the concentrations of acetone are different in the two cases.

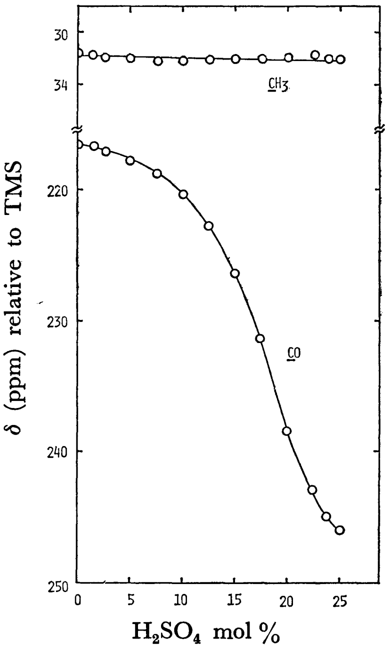

Fig. 1. Observed ^{13}C chemical shifts for 2 mol % acetone in various concentration ratios of sulfuric acid-water.

Let us analyze this behavior upon protonation on the basis of our calculations. The values of the excess charges on the carbon and oxygen atoms in acetone molecules are plotted against the magnitude of the charge, Q_a, associated with the oxygen atom in the carbonyl group in Fig. 2. The electron densities on the oxygen and carbon atoms in the carbonyl group increase with an increase in Q_a, while, on the other hand, that on the methyl carbon decreases. In this molecule, the electrons are drawn to the oxygen atom and the distribution of electrons is polarized by an inductive $-\mathrm{I}^-$ type effect, $\mathrm{O^-{=}C^+{-}C^-}$. However, its effect decreases by the association with the charge, Q_a. The electron densities on the carbonyl oxygen and carbon atoms increase, and that on the methyl carbon atom decreases, with an increase in Q_a. Then, the charge on the methyl carbon atom becomes positive.

The charges of this distribution of the electron density with an increase in the Q_a in this system cannot explain the observed results. For example, the increase in the electron density on carbonyl carbon with an increase in the Q_a cannot explain the observed low-field shift with an increase in the concentration of sulfuric acid. This suggests that the change in the excitation energy may play an important role in the observation of the chemical shift. Some typical examples of the calculated diamagnetic, ρ^d, paramagnetic, ρ^p, and total chemical shifts are shown against the value of Q_a in Table 1. The calculated chemical shifts are also plotted in Fig. 2. The major part of the Q_a dependence of the chemical shift arises from variations in σ^p. The chemical shifts of the carbonyl and methyl carbons shift to a lower field with an increase in the value of Q_a, and the change in the former is larger than that in the latter. These tendencies agree with the observed ones, but the change in the methyl carbon is too large.

The observed chemical shift of carbonyl carbon

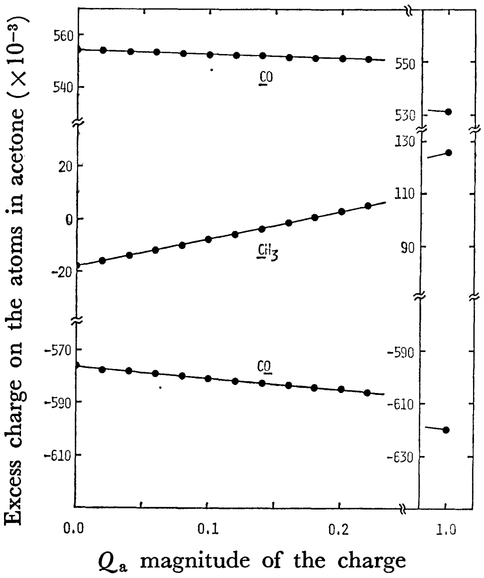

Fig. 2. Dependence of excess charge on carbon and oxygen atoms in acetone upon the magnitude of the charge Q.

TABLE 1. DEPENDENCE OF THE CALCULATED CHEMICAL SHIFTS OF METHYL AND CARBONYL CARBONS IN ACETONE UPON THE MAGNITUDE OF THE CHARGE, Q_a

Q_a		Calculated chemical shift (ppm)		
		Diamagnetic contribution σ^d	Paramagnetic contribution σ^p	Total contribution σ^T
0.0	CH_3	57.99	−211.55	−153.56
	CO	52.81	−352.58	−299.76
0.01	CH_3	57.99	−212.26	−154.27
	CO	52.81	−354.41	−301.59
0.02	CH_3	57.98	−212.98	−154.99
	CO	52.82	−356.25	−303.43
0.05	CH_3	57.96	−215.14	−157.19
	CO	52.82	−361.94	−309.12
0.10	CH_3	57.91	−218.86	−160.95
	CO	52.83	−371.90	−319.08
0.20	CH_3	57.83	−226.62	−168.79
	CO	52.84	−393.96	−341.11
0.50	CH_3	57.52	−253.95	−196.44
	CO	52.91	−479.29	−426.38
1.00	CH_3	56.30	−320.44	−263.64
	CO	53.04	−738.67	−685.63

moves to a lower field by about 30 ppm for the concentration variation of sulfuric acid from 0 to 25 mol %. This value corresponds to the one calculated when the value of Q_a is about 0.15. When the value of Q_a is 1.0, the calculated value shifts to considerably a lower field. According to these results, if the protonation is complete, dose such a low-field shift arise? This may be interesting problem.

Reviewing our results from the viewpoint of the exchange between free and protonated molecules, the finding that the value of Q_a is about 0.15, considerably smaller than 1, is not surprising. Although, in this work, we have chosen a simple system in applying our developed procedure to the protonation, we should apply a more complicated system to ascertain the applicability of our model.

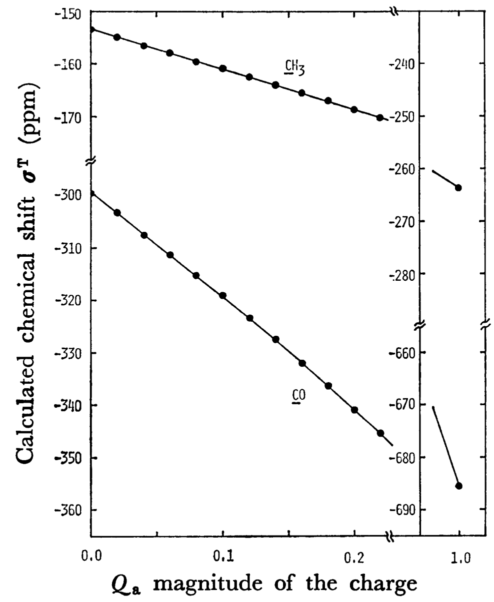

Fig. 3. Dependence of calculated ^{13}C chemical shifts of methyl and carbonyl carbons in acetone upon the magnitude of the charge Q.

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