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^{14}N Nuclear Quadrupole Resonance of the Molecular Complexes of Urea

Hisao Negita,* Tsuneo Kubo, and Hitoshi Kato

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730

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The ^{14}N nuclear quadrupole resonance (NQR) was studied in four kinds of molecular complexes of urea, such as urea-nitric acid, urea-phosphoric acid, urea-oxalic acid, and urea-ammonium chloride. The ^{14}N quadrupole coupling constants and asymmetry parameters at liquid nitrogen temperature are as follows: $|e^2Qq/h|=3.157$ MHz and $\eta=0.475$ for the HNO_3 complex; $|e^2Qq/h|=3.277$ MHz and $\eta=0.414$ for the H_3PO_4 complex; $|e^2Qq/h|=3.456$ MHz and $\eta=0.363$ for the $(COOH)_2$ complex; and $|e^2Qq/h|=3.544$ MHz and $\eta=0.298$ for the NH_4Cl complex. From the temperature dependence of the resonance lines in these complexes, the strength of hydrogen bonds are discussed. The differences of the electron densities at the nitrogen atoms between urea and its complexes were derived from the corresponding NQR parameters, and the bond characters in these complexes are discussed.

It is well known that urea forms molecular complexes with a number of compounds, being held together by hydrogen bonding. These hydrogen bonds have been investigated by various spectroscopic methods.[1,2] It is interesting to study the hydrogen bonds in these complexes by means of the nuclear quadrupole resonance (NQR) of nitrogen-14. The molecular complexes of urea examined are urea–nitric acid (1 : 1) (HNO_3 complex), urea–phosphoric acid (1 : 1) (H_3PO_4 complex), urea–oxalic acid (2 : 1) ($(COOH)_2$ complex), and urea–ammonium chloride (1 : 1) (NH_4Cl complex). On the basis of the ^{14}N NQR results, the strength of the hydrogen bonds and the charge distributions at nitrogen atoms were compared with those in urea itself.

Experimental

^{14}N NQR measurements were carried out using a pulse spectrometer described previously.[3] The resonance lines were observed by the spin-echo signals using a 90—180° pulse sequence series. The pulse width of a 90° pulse was about 50 μs. The spin-echo signal was averaged in a Nicolet Instrument Model 527 signal averager. The temperature was controlled by the method of Abe.[4] The temperature was measured by the use of a copper-constantan thermocouple and stabilized within ±0.1 K. The frequency was checked by means of a frequency counter, TR-5104, from Takeda Riken Co.

The sample of the HNO_3 complex was prepared by crystallization at 0 °C from an aqueous solution containing an equimolar amount of urea and nitric acid, and was purified by recrystallization from methanol.[5] Found: C, 9.95; H, 4.13; N, 34.42%. Calcd for $CH_5N_3O_4$: C, 9.76; H, 4.10; N, 34.14%. The sample of the H_3PO_4 complex was obtained by slowly evaporating an equimolar solution of urea and phosphoric acid.[6] Found: C, 7.60; H, 4.54; N, 17.63%. Calcd for $CH_7N_2O_5P$: C, 7.60; H, 4.46; N, 17.72%. The sample of the $(COOH)_2$ complex was obtained from an aqueous solution of urea and oxalic acid in the stoichiometric ratio.[7] Found: C, 22.91; H, 4.84; N, 26.51%. Calcd for $C_3H_6N_2O_5$: C, 22.86; H, 4.80; N, 26.66%. The sample of the NH_4Cl complex was prepared by slowly evaporating a solution containing urea and ammonium chloride in a molar ratio of 1 : 1.[8] Found: C, 10.69; H, 7.17; N, 36.78; Cl, 30.8%. Calcd for CH_8ClN_3O: C, 10.58; H, 7.10; N, 37.01; Cl, 31.2%. All the samples were ground into powder after drying, and about 20 g of the samples were used for the measurements.

Results and Discussion

For the case of nitrogen-14 one observes in general a spectrum consisting of two NQR absorption lines ν_- and ν_+:

$$\nu_\pm = \frac{|e^2Qq|}{4h}(3\pm\eta), \tag{1}$$

where $|e^2Qq/h|$ and η are the quadrupole coupling constant and asymmetry parameter, respectively. In the cases of the HNO_3 complex, the H_3PO_4 complex, and the $(COOH)_2$ complex, two pairs of resonance lines were observed at liquid nitrogen temperature. On the other hand, three closely spaced pairs of resonance lines were observed in the NH_4Cl complex. These lines could not be paired because the third possible resonance line $\nu_d=\nu_+-\nu_-$ could not be observed on account of its very low frequency. Accordingly, the quadrupole coupling constants and the asymmetry parameters in these complexes were derived from the average values of ν_- and ν_+; they are listed in Table 1.

The average temperature coefficient $\langle\alpha\rangle$ was calculated by the following equation:

$$\langle\alpha\rangle = 2(\nu_1-\nu_2)/[(\nu_1+\nu_2)(T_1-T_2)], \tag{2}$$

where ν_1 and ν_2 are the resonance frequencies of the ν_+ lines at liquid nitrogen temperature (T_1) and about 275 K (T_2), respectively. These coefficients in the complexes are calculated as listed in Table 1, and decrease in the order of the $(COOH)_2$ complex, the HNO_3 complex, and the H_3PO_4 complex. Every coefficient is smaller than the value in urea, which is calculated from the reference[9] to be 13.43×10^{-5} deg^{-1}. This fact suggests that the vibrations of the nitrogen atoms in the urea molecules are suppressed in the order of urea, the $(COOH)_2$ complex, the HNO_3 complex, and the H_3PO_4 complex, that is, the strength of the hydrogen bonds, N–H···O, increases in this order. On the other hand, in the NH_4Cl complex, the temperature dependence of three ν_+ lines was nearly equal, and the resonance line ($\nu=2.9318$ MHz), the intensity of which was largest among in these lines, could be observed at about 200 K, whereas the other two lines were able to be observed at about 190 K. Therefore, the average temperature coefficient was calculated between liquid nitrogen temperature and about 200 K for the line ($\nu=2.9318$ MHz); the value

Table 1. NQR parameters and the average temperature coefficients in urea complexes

Complex	ν_- / MHz	ν_+ / MHz	$\lvert e^2Qq/h \rvert$ / MHz	η	$\langle\alpha\rangle$ / deg^{-1}
$OC(NH_2)_2 \cdot HNO_3$	2.0505 1.9347	2.7828 2.7015	3.157	0.475	8.37×10^{-5}
$OC(NH_2)_2 \cdot H_3PO_4$	2.1476 2.0901	2.8159 2.7783	3.277	0.414	4.95×10^{-5}
$OC(NH_2)_2 \cdot (COOH)_2$	2.3701 2.1863	2.9634 2.8484	3.456	0.363	11.24×10^{-5}
$OC(NH_2)_2 \cdot NH_4Cl$	2.4335 2.4006 2.3473	2.9488 2.9318 2.8853	3.544	0.298	14.97×10^{-5}

is listed in Table 1. The temperature coefficient in the NH_4Cl complex is larger than that in urea. This suggests that the hydrogen bond in this complex, N–H···Cl, is weaker than the bond in urea, N–H···O. This may be explained by the difference of the electronegativities between a chlorine atom and an oxygen atom.

According to the results of the neutral diffraction study of the HNO_3 complex⁵⁾ and the X-ray diffraction studies of the H_3PO_4 complex and the $(COOH)_2$ complex,⁶,⁷⁾ the geometry of the NH_2 groups in these complexes is nearly equal to that in urea; we thus assumed the nitrogen σ-bond orbitals to be sp^2-hybrids. In the case of the NH_4Cl complex, there are three crystallographically nonequivalent nitrogen atoms, and each nitrogen atom forms two weak hydrogen bonds with a chlorine ion of ammonium chloride, the length of which is in the range from 3.14 to 3.40 Å.⁸⁾ Therefore, the electronic state of nitrogen atom in the NH_2 group may be considered not to be largely different from that in urea; we thus assumed that the nitrogen σ-bond orbitals are sp^2-hybrids.

The electron densities at the nitrogen atoms in these complexes can be calculated by means of the following equations:¹⁰⁾

$$\alpha = |e^2Qq/e^2Qq_p| = n - (2/3)\sigma_{NH} - (1/3)\sigma_{NC}, \qquad \alpha\eta = \sigma_{NH} - \sigma_{NC}, \tag{3}$$

where n is the electron density in the lone-pair orbital; σ_{NH} and σ_{NC} are the σ-electron densities in the N–H and N–C bonds, respectively; and $|e^2Qq_p/h|$ is the quadrupole coupling constant due to one 2p-electron of a nitrogen atom. The α and $\alpha\eta$ values in urea and its complexes are denoted by α^u, $(\alpha\eta)^u$, α^c, and $(\alpha\eta)^c$. Defining the differences in the α and $\alpha\eta$ values between urea and its complexes by $\Delta\alpha=\alpha^u-\alpha^c$ and $\Delta(\alpha\eta)=(\alpha\eta)^u-(\alpha\eta)^c$,

$$\Delta\alpha = (n^u-n^c) - (2/3)(\sigma^u_{NH}-\sigma^c_{NH}) - (1/3)(\sigma^u_{NC}-\sigma^c_{NC}), \qquad \Delta(\alpha\eta) = (\sigma^u_{NH}-\sigma^c_{NH}) - (\sigma^u_{NC}-\sigma^c_{NC}) \tag{4}$$

are obtained. Letting

$$\Delta n=n^u-n^c,\ \Delta\sigma_{NH}=\sigma^u_{NH}-\sigma^c_{NH},\ \text{and}\ \Delta\sigma_{NC}=\sigma^u_{NC}-\sigma^c_{NC} \tag{5}$$

then

$$\Delta\alpha = \Delta n-(2/3)\Delta\sigma_{NH}-(1/3)\Delta\sigma_{NC}, \qquad \Delta(\alpha\eta) = \Delta\sigma_{NH}-\Delta\sigma_{NC}. \tag{6}$$

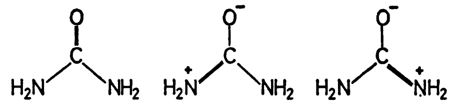
Assuming that in these complexes $\Delta\sigma_{NC}=0$ and $|e^2Qq_p/h|=9$ MHz, the $\Delta\sigma_{NH}$ and Δn values can be calculated from Eq. 6; the values are listed in Table 2.

Table 2. The $\Delta\sigma_{NH}$ and Δn values in the molecular complexes of urea

Complex	$\Delta\sigma_{NH}$	Δn
$OC(NH_2)_2 \cdot HNO_3$	−0.04	−0.01
$OC(NH_2)_2 \cdot H_3PO_4$	−0.03	−0.01
$OC(NH_2)_2 \cdot (COOH)_2$	−0.01	0
$OC(NH_2)_2 \cdot NH_4Cl$	+0.01	0

The $\Delta\sigma_{NH}$ values in the HNO_3 complex, the H_3PO_4 complex, and the $(COOH)_2$ complex are negative. This indicates that the hydrogen bonds in these complex are stronger than that in urea. On the contrary, in the case of the NH_4Cl complex, the $\Delta\sigma_{NH}$ value is positive so that the hydrogen bond in this complex is weaker than the bond in urea.

On the other hand, the Δn values in the HNO_3 complex and the H_3PO_4 complex are positive, that is, the electron populations in the lone-pair orbitals of the nitrogen atoms in the urea molecules are smaller in these complexes than in urea. This may be explained by the decrease of the lone-pair electron population due to the formation of the hydrogen bond such as N···H–N, in which the lone-pair orbital of a nitrogen atom is used, or to the increase of the contribution of the following resonance structures II and III. However, the hydrogen bond such as N···H–N is absent in these complexes⁵,⁶⁾ and urea.¹⁰⁾ Therefore, the decrease of the lone-pair electron is attributed to the latter reason. The resonance structures bring about the increase of the double-bond character in the N–C bond in the urea molecule, resulting in the shortening of this bond. The average N–C bond lengths are 1.314 Å in the HNO_3 complex and 1.322 Å in the H_3PO_4 complex, whereas the value in urea is 1.352 Å.¹¹⁾ Furthermore, it is considered that the negative charge on the oxygen atom of the urea molecule increases and the C–O bond becomes longer because of the contribution of the structures II and III in these complexes. From these combined effects, the strong hydrogen bond, O···H–O, is formed. In fact, the C–O distances in urea, the HNO_3 complex, and the H_3PO_4 complex, are 1.260, 1.298, and 1.281 Å, respectively. The O···H–O dis-



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tances in the HNO_3 complex and the H_3PO_4 complex are 2.596 and 2.424 Å respectively, and the acidic protons are attached to the carbonyl oxygen atom of urea.

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