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# $^{14}$N Nuclear Quadrupole Resonances of the Molecular Complexes of Urea

Hisao Negita, Tsuneo Kubo, and Michio Maekawa
*Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730*

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The $^{14}$N nuclear quadrupole resonance (NQR) was studied on three kinds of molecular complexes of urea, such as the urea-hydrogen peroxide complex ($H_2O_2$ complex), the urea-sodium chloride-water complex (NaCl complex), and the urea-sodium bromide-water complex (NaBr complex). The $^{14}$N quadrupole coupling constants and asymmetry parameters are as follows: $|e^2Qq/h|=3493.8$ kHz and $\eta=0.3456$ for the $H_2O_2$ complex; $|e^2 \cdot Qq/h|=3597$ kHz and $\eta=0.293$ for the NaCl complex, and $|e^2Qq/h|=3636.7$ kHz and $\eta=0.2778$ for the NaBr complex. From the temperature dependence of the resonance frequencies, it is considered that the hydrogen bonds in the $H_2O_2$ complex are stronger than those in the NaCl complex. The electron densities at nitrogen atoms in these complexes were derived from the corresponding NQR parameters, and were compared with those in urea.

The molecular complexes of urea have been investigated by various spectroscopic methods.[1,2] The NQR method is particularly useful for investigating the charge distributions in these complexes. However, only a few $^{14}$N NQR data on molecular complexes have been reported thus far. Therefore, we planned to examine $^{14}$N NQR in molecular complexes of urea, such as the urea-hydrogen peroxide complex ($H_2O_2$ complex), the urea-sodium chloride-water complex (NaCl complex), and the urea-sodium bromide-water complex (NaBr complex). On the basis of the $^{14}$N NQR in these complexes, the strength of the hydrogen bonds and the charge distributions at the nitrogen atoms were compared with those in urea itself.

## Experimental

The $^{14}$N NQR spectra of the $H_2O_2$ complex, the NaCl complex, and the NaBr complex were obtained by the use of a frequency-modulated spectrometer described previously.[3] The resonance frequencies were measured by means of a heterodyne-type frequency meter, the frequency of which was checked by means of a frequency counter, TR-5104, from the Takeda Riken Co. Measurements were carried out at several temperatures between the temperature of liquid nitrogen and room temperature. The temperatures were measured by the use of a copper-constantan thermocouple.

*Preparation of Samples.* The sample of the $H_2O_2$ complex was obtained by cooling a solution of urea in 30% hydrogen peroxide, in a molar ratio of 2 : 3, the solution had been heated for a few minutes at a temperature of about 60 °C.[4] Found: C, 12.96; H, 6.39; N, 30.02; $H_2O_2$, 34.6%. Calcd for the $H_2O_2$ complex: C, 12.77; H, 6.43; N, 29.78; $H_2O_2$, 36.2%.

The sample of the NaCl complex was prepared by slowly evaporating an equimolar solution of urea and sodium chloride.[5] Found: C, 9.48; H, 4.39; N, 21.81; Cl, 25.4%. Calcd for the NaCl complex: C, 8.80; H, 4.43; N, 20.52; Cl, 26.0%.

The sample of the NaBr complex was obtained from an equimolar solution of urea and sodium bromide. Found: C, 6.62; H, 3.24; N, 15.66; Br, 43.4%. Calcd for the NaBr complex: C, 6.64; H, 3.34; N, 15.48; Br, 44.2%. All the samples were ground into powder after drying, and about a 20-g portion of the samples was used for the measurement.

## Results and Discussion

Generally a pair of $^{14}$N NQR frequencies, $\nu_-$ and $\nu_+$, are observed for a species of nitrogen atoms:

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

where $|e^2Qq/h|$ and $\eta$ are the quadrupole coupling constant and the asymmetry parameter respectively. In the $H_2O_2$ complex and the NaBr complex, a pair of resonance lines was found, as is shown in Fig. 1. The quadrupole coupling constants and asymmetry parameters derived from these frequencies are listed in Table 1. In the case of the NaCl complex, four resonance lines were found, as is shown in Fig. 1. However, these lines could not be paired because both higher and lower lines of the two pairs were closely spaced. Accordingly, the quadrupole coupling constant and the asymmetry parameter were derived from the average values of $\nu_-$ and $\nu_+$; they are listed in Table 1.

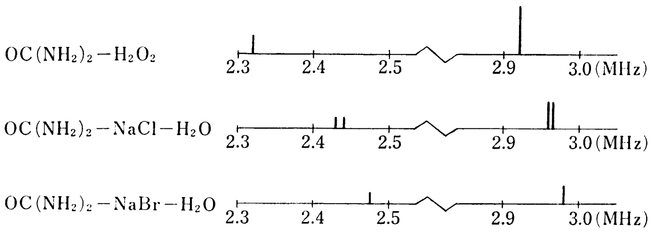

Fig. 1. NQR absorption lines in urea complexes at liquid nitrogen temperature.

Table 1. NQR parameters in urea complexes

| Complex | $\nu_-$/kHz | $\nu_+$/kHz | $\lvert e^2Qq/h\rvert$/ kHz | $\eta$ |
|---|---|---|---|---|
| $OC(NH_2)_2$-$H_2O_2$ | 2318.4 | 2922.3 | 3493.8 | 0.3456 |
| $OC(NH_2)_2$-NaCl-$H_2O$ | 2428.7<br>2439.1 | 2958.8<br>2964.5 | 3597 | 0.293 |
| $OC(NH_2)_2$-NaBr-$H_2O$ | 2474.8 | 2980.1 | 3636.7 | 0.2778 |

Figure 2 shows the temperature dependence of the resonance frequencies of the $\nu_+$ lines in the $H_2O_2$ complex, the NaCl complex, and urea.[6] In the case of the NaCl complex, the intensities of the $\nu_+$ lines decrease gradually as the temperature rises, and become too weak to be observed at 181 K. The temperature dependence in the $H_2O_2$ complex is slightly smaller than that in urea, as is shown in Fig. 2. In the case of the $H_2O_2$ complex, each nitrogen atom of the urea molecule makes two hydrogen bonds, N–H···O, with lengths of 2.94 Å and 3.04 Å,[4] as is shown in Fig. 3,

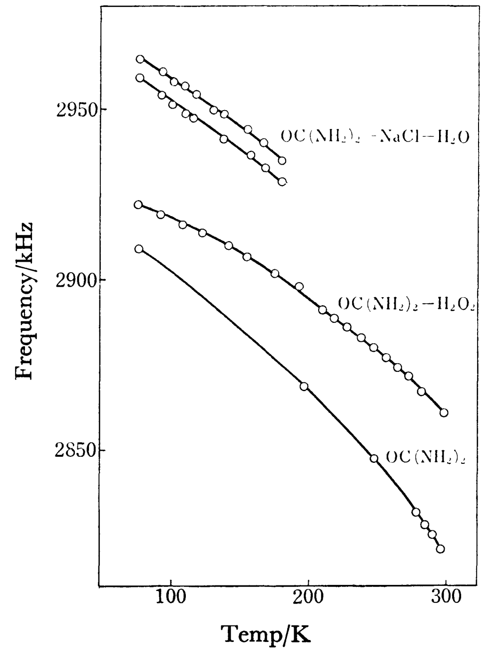

Fig. 2. The temperature dependence of the resonance line, $\nu_+$, in urea-sodium chloride-water, urea-hydrogen peroxide, and urea.

whereas those in urea are 2.99 and 3.04 Å.[7] The smaller temperature dependence in the $H_2O_2$ complex can be explained by the difference in the hydrogen-bond distance between the $H_2O_2$ complex and urea. That is, the hydrogen bonds in the $H_2O_2$ complex are slightly stronger than in urea. On the other hand, Fig. 2 shows that the temperature dependence in the NaCl complex is nearly equal to that in urea. This suggests that the hydrogen bonds in the NaCl complex are nearly equal to those in urea and are weaker than in the $H_2O_2$ complex.

In the $H_2O_2$ complex, the hydrogen bonds are not very strong, as is shown in Fig. 3. Therefore, the electronic state of nitrogen in the $NH_2$ group may be considered to be nearly equal to that in urea, and we assumed the nitrogen $\sigma$-bond orbitals to be $sp^2$-hybrids. In the case of the NaCl complex, there are two crystallographically nonequivalent nitrogen atoms, and each nitrogen atom forms only one hydrogen bond with a chloride ion of sodium chloride, the length of which is 3.05 or 3.22 Å.[5] However, the electronic state of nitrogen in the $NH_2$ groups may be considered not to be largely different from that in urea, and we assumed that the nitrogen $\sigma$-bond orbitals are $sp^2$-hybrids. As is shown in Table 1, the quadrupole coupling constant and the asymmetry parameter in the NaBr complex are nearly equal to those in the NaCl complex. Therefore, we assumed $sp^2$-hybridization for nitrogen, as above.

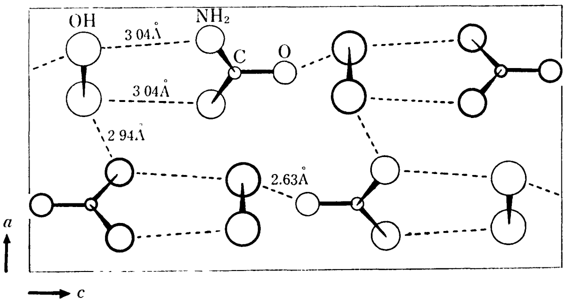

Fig. 3. The crystal structure of urea-hydrogen peroxide (b-axis projection).

The electron densities of the nitrogen atoms in these complexes can be calculated by means of the following equations derived by Lucken:[8)]

$$2\eta\cdot|e^2Qq/e^2Qq_p| = 3(c-b)(1-\cot^2\gamma), \qquad (2)$$

$$(1-\eta/3)\cdot|e^2Qq/e^2Qq_p| = a-c, \qquad (3)$$

where $a$ is the electron density in the lone-pair orbital; $b$ and $c$ are the $\sigma$-electron densities in the N–C and N–H bonds respectively; $2\gamma$ is the ∠HNH bond angle, approximately 120°, and $|e^2Qq_p/h|$ is the quadrupole coupling constant due to one 2p-electron of a nitrogen atom. In the case of the $H_2O_2$ complex, the NaCl complex, and the NaBr complex, it is assumed that $|e^2Qq_p/h|$ is 9 MHz and that the $\sigma$-electron density for the N–C bond is the same as that for the N–C bond in urea (1.206);[8] therefore, the values of the $a$ and $c$ parameters can be evaluated. Table 2 lists the values thus obtained. The $\sigma_{NH}$ values in these complexes decrease in the order of the $H_2O_2$ complex, the NaCl complex, and the NaBr complex, showing that the strength of the hydrogen bond decreases in this order.

TABLE 2. ELECTRON DENSITIES IN UREA AND ITS MOLECULAR COMPLEXES

| Compound | $\sigma_{NH}$ | Lone-pair |
|---|---|---|
| $OC(NH_2)_2$ | 1.331 | 1.679 |
| $OC(NH_2)_2-H_2O_2$ | 1.340 | 1.684 |
| $OC(NH_2)_2-NaCl-H_2O$ | 1.323 | 1.684 |
| $OC(NH_2)_2-NaBr-H_2O$ | 1.318 | 1.685 |

On the other hand, the $\sigma_{NH}$ value in the $H_2O_2$ complex is larger than that in urea. This suggests that the hydrogen bonds in this complex are stronger than those in urea, which is parallel to the conclusion from the temperature dependence of the resonance frequencies.

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