Hydrogen Transfer in a Hydrogen-Bonded 1:2 Complex of Chloranilic Acid with 1,2-Diazine Studied by ^{35}Cl NQR

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(Received September 18, 2000; CL-000858)

^{35}Cl NQR frequencies and spin–lattice relaxation time, and ^{1}H NMR spin–lattice relaxation time were measured on (chloranilic acid)-(1,2-diazine) 1:2 molecular complex to detect H-transfer motions in the H-bonded three molecular system. Only a single H-jump mode was observed by ^{1}H NMR, whereas three kinds of H-transfer modes were obtained in ^{35}Cl NQR in good agreement with the prediction.

We reported double H-transfer in solid *p*-chlorobenzoic acid[1] containing a dimer structure[2] by the ^{35}Cl NQR technique, and showed for the first time that the NQR relaxation can be a quite sensitive probe for detecting H-transfer in H-bonded systems compared with conventional ^{1}H NMR relaxation studies. As an application of this technique, we tried to find H-motions in a new three-molecular H-bonded system, (chloranilic acid)–(1,4-diazine) 1:2 complex[3] [$(C_6Cl_2O_2(OH)_2)–(C_4N_2H_4)_2$] (abbreviated to 1,4-complex) in the previous study,[4] and succeeded in observing two kinds of modes of H-transfer motion, one of which was a new kind of mode undetected by the ^{1}H NMR method. In the analysis of the H-bonded structure in 1,4-complex, we predicted three kinds of H-transfer modes, namely, H-jumps between two equivalent monovalent chloranilate(1–) ions, between (1–) and (2–) ions, and between (1–) ions and neutral chloranilic acid(0) molecules. We could detect the first mode by both NQR and NMR relaxation measurements in the low-temperature range, but nothing in NMR and only a single relaxation increase in NQR at high-temperatures. This disagreement could provide some doubt on the sensitivity of NQR and also the validity of our H-transfer models.

In the present study, we intend to solve this problem and measure NQR and NMR in a three-molecular H-bonded system, (chloranilic acid)–(1,2-diazine)1:2 complex [$(C_6Cl_2O_2(OH)_2)–(C_4N_2H_4)_2$][5] (abbreviated to 1,2-complex). Analogously to 1,4-complex, 1,2-complex crystals contain almost isolated three molecular units bonded by OH---N type H-bonding with a short O---N distance of 2.582 Å,[5] where a chloranilic acid molecule is located on an inversion center and only one of two N sites in a 1,2-diazine molecule takes part in the H-bonding. If we consider that pK_{a1} in 1,4-diazine is 0.57,[6] while 2.24 in 1,2-diazine,[6] and pK_{a1} and pK_{a2} in chloranilic acid are 0.76 and 2.72,[6] respectively, we can expect that the stability of chloranilate ions with high ionic charges increases in 1,2-complex compared with in 1,4-complex. This implies the easier formation of chloranilate(1–) and (2–) ions, suggesting that the above three kinds of H-transfer motions can be observed below room temperature.

^{35}Cl NQR frequencies observed in a range 77–265 K in 1,2-complex are shown in Figure 1. Its temperature dependence showed an anomalous positive temperature coefficient in the low-temperature range77–160 K, which is unexplainable by the conventional Bayer theory[7] taking into account of the influence from lattice and molecular vibrations. The origin of this unusual behavior will be discussed at the end of the paper. It should be noted that ^{35}Cl resonance frequency 34.940 ± 0.001 MHz observed at 77 K is much lower than 36.40 MHz obtained in the foregoing 1,4-complex.[4] It has been reported that ^{35}Cl NQR frequency in crystalline chloranilic acid($C_6O_2Cl_2(OH)_2$) is 37.15 MHz at 77 K,[8] while its divalent sodium salt containing $[C_6O_2Cl_2O_2]^{2-}$ ions gives an averaged frequency of ca. 35.20 MHz (two lines : 35.538 and 34.853 MHz) at 77 K.[8] From these frequencies, we can expect that the present 1,2-complex contains chloranilic acid with a formal charge close to 2– in crystal at 77 K. This contrasts with the result in the previous 1,4-complex[4] in which the monovalent chloranilate(1–) was shown to be the most populated species at low temperatues from the observed ^{35}Cl frequency. The present result in 1,2-complex can be supported by pK_a value in 1,2-diazine much larger than in 1,4-diazine favoring the formation of the H-transferred $–N–H^+$ structure in 1,2-complex.

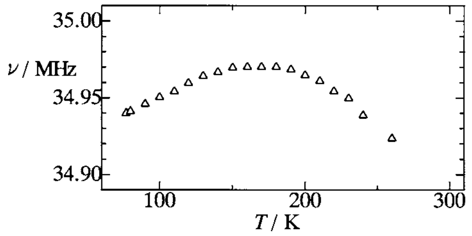

Figure 1. A temperature dependence of ^{35}Cl NQR frequencies(ν) observed in solid chloranilic acid-1,2-diazine (1:2) complex.

A temperature dependence of ^{1}H NMR spin–lattice relaxation time (T_{1H}) is shown in Figure 2. The very long T_{1H} observed in the whole temperature range studied and a single shallow minimum of 45 s around 110 K are quite analogous to reported results in 1,4-

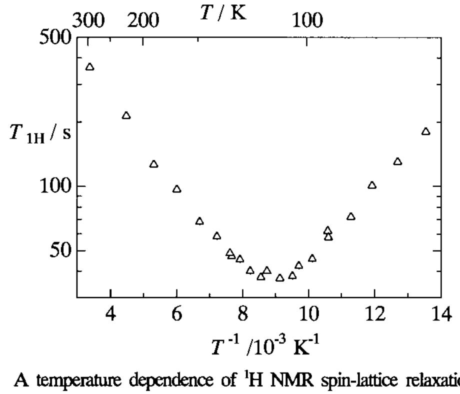

Figure 2. A temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_{1H}) observed at a Larmore frequency of 54.3 MHz in solid chloranilic acid-1,2-diazine (1:2) complex.

complex.[4] Applying the same discussion as in 1,4-complex, we can reasonably assign this T_{1H} minimum observed in 1,2-complex to the fluctuations of the magnetic dipolar interactions caused by the H-transfer between chloranilic acid and two 1,2-diazine molecules H-bonded with each other. As an H-transfer model averaging H–H dipolar interactions, H-jumps between the divalent and monovalent chloranilate ions can be accepted, because H-motions should be excited from the most populated chloranilate(2–), and in this case, the next stable form is monovalent chloranilate(1–). Accordingly, starting from the chloranilate(2–) ion, H-jumps, I↔II and I↔III shown in Figure 3 are expected to take place with the same rate and contribute to the ^{1}H relaxation at low temperatures, where two stuctures, II and III; were assumed to be equivalent from the crystal symmety of 1,2-complex.[5]

A temperature dependence of ^{35}Cl NQR spin–lattice relaxation time(T_{1Q}) is shown in Figure 4. The observed T_{1Q} gave a complicated temperature dependence compared with that of T_{1H} and is explainable by the superposition of at least three T_{1Q} minima. Here, for simplicity, we assume the Debye type relaxation process as observed in ^{1}H NMR and the Arrhenius-type activation equation as used in the previous study on 1 ,4-complex.[4] We fitted superimposed three relaxation curves on T_{1Q} and the best fitted calculated values are shown in Figure 4. In the fitting for the lowest-temperature minimum, we used the T_{1H} slopes obtained in the T_{1H} curve and the minimum temperature after adjusting the frequency difference in the NQR and NMR measurements. In the present study, we could clearly observed separated three relaxation processes assignable to three kinds of H-transfer modes we predicted.[4] The lowest-temperature relaxation was explained by the two equivalent modes I↔II and I↔III shown in Figure 3 taking place with the same probability as derived from the above discussion of T_{1H}. As for the two other mechanisms expected in the high temperature range, one is the symmetric H-exchange keeping the chloranilate(1–) structure named the correlated motion in the previous study[4] given by II↔III in Figure 3. The other should be the H-transfer between chloranilate(1–) and (0) expressed by II↔IVand III↔IV in Figure 3. We can assign the former to the relaxation giving the minimum around 160 K, and the latter to that observed around room temperature. This indicates that the latter process has a higher barrier than the former, because, in the present 1,2-complex, the time averaged structure of chloranilic acid was shown to be close to 2– implying a high barrier for getting a neutral molecule. This can also be shown from the consideration of a marked difference in pK_{a1}(= 0.76) and pK_{a2}(= 2.72)[6] of chloranilic acid and also pK_{a1}(= 2.24)[6] of 1,2-diazine in solution.

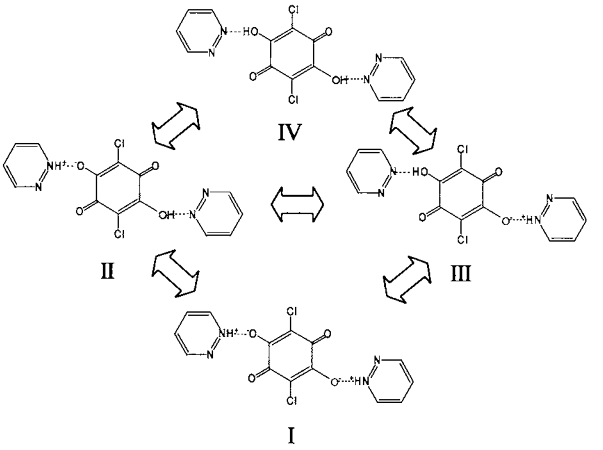

Figure 3. H-transfer models in crystalline chloranilic acid-1,2-diazine (1:2) complex. The most stable structure at low temperatures is given by I containing chloranilate(2–) ions. Structure II and III consisting of equivalent chloranilate(1–) ions are formed with thermal excitation of I. At high temperatures, the less stable chloranilic acid(0) molecules IV are made from II and III by H-transfer.

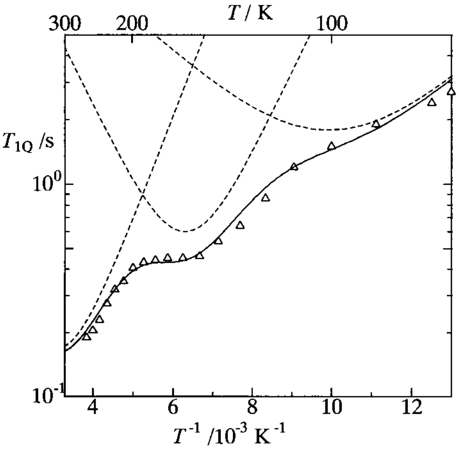

Figure 4. A temperature dependence of ^{35}Cl NQR spin-lattice relaxation time (T_{1Q}) observed in sold chloranilic acid-1,2-diazine (1:2) complex. Broken lines show three relaxation processes and the solid line is the best-fitted calculated values.

The reason why the marked ^{35}Cl NQR relaxation, but no ^{1}H NMR T_{1H} change was observed in the high-temperature range is explained by the facts that H-transfer once excited affords a little further fluctuation of the magnetic field at ^{1}H nuclei, whereas remarkable changes in EFG at Cl nuclei are formed by the change of formal charges on chloranilic acid molecules.

The positive temperature coefficient of the NQR frequencies observed in a range 77–170 K unexplainable by the conventional Bayer-type lattice motions[7] can be attributable to the effect of H-transfer described above. Upon heating from 77 K,we can expect that the population of chloranilate(2–) ions decreases, while that of (1–) ions increases. Since the NQR frequency is determined by the time-averaged EFG at the resonance nuclei, the increase in the number of chloranilate(1–) ions which affords a higher frequency than (2–) ions can explain the increase of efg with increasing temperature. The frequency decrease observed on further heating can be explained by considering that contributions to the EFG decrease from lattice vibrations increase more than from the H-transfer.

This works was partly supported by Grant-in-Aid for scientific research No.(B) 12440192 and (C)10640554 from the Ministry of Education, Science, Sports and Culture.

References and Notes

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