^{35}Cl NQR Study and Addition Reactions to Cyclohexene of Cyclic *N*-Chloro Amides (Imides)

Yoshitaka NAGAO* and Shigeyoshi KATAGIRI
Department of Chemistry, Faculty of Science, Hirosaki University, Bunkyo-cho, Hirosaki 036
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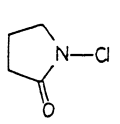
Synopsis. ^{35}Cl NQR frequencies were measured for *N*-chloro-2-pyrrolidinone, *N*-chloro-4,4-dimethyl-2-oxazolidinone, *N*-chloro-2-oxazolidinone, *N*-chloroglutarimide, and *N*-chlorosuccinimide. The ionicities of the N-Cl bonds were estimated on the basis of those measurements. These ionicities were related to the total yields of the 1,2-addition in the photochemical reaction with cyclohexene. When the value of the ionicity neared zero, the total yield increased.

N-Chloro imides are effective reagents for the chlorination and the oxidation of olefins, alcohols, and carbonyl compounds. Thus, it seems that it would be interesting to investigate the character of the N-Cl bonds in *N*-chloro amides (imides). It is worth while to measure the ^{35}Cl NQR frequencies of *N*-chloro amides (imides), because these frequencies give information on the bond character of N-Cl bonds. If the quadrupole coupling constant is obtained from the observed ^{35}Cl NQR frequency, the bond ionicity may be evaluated. In a previous paper,[2] the ^{35}Cl NQR frequencies for some *N*-chloro imides were observed, and the N-Cl bond ionicities of these compounds were evaluated. The ionicities were related to the reactivities of these compounds. If the value of the ionicity is near zero, the chlorine radical is produced easily and a high yield can be expected in a radical reaction.

In this study, we observed the ^{35}Cl NQR frequencies for the cyclic *N*-chloro amides(imides) shown below and estimated the ionicities of these compounds. The ionicities were then compared with the yields of 1,2-addition in the photochemical reaction of these compounds with cyclohexene.



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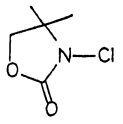

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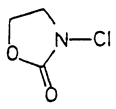

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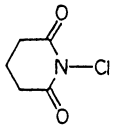

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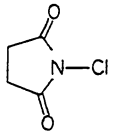

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Experimental

The *N*-chloro amides(imides) were prepared as follows: *N*-Chloro-2-oxazolidinone (**3**) and *N*-chloro-4,4-dimethyl-2-oxazalidinone (**2**) were obtained by the method of Kosugi et at.[4] after the corresponding amides had been prepared by Homeyer's method.[5] The *N*-chloro-3-pyrrolidinone (**1**) was prepared by passing chlorine gas into 2-pyrrolidinone dissolved in water containing sodium hydrogencarbonate.[6] The *N*-chloroglutarimide (**4**) was obtained by the reaction of glutarimide with a bleaching-powder solution[7] after the glutarimide had been prepared by the reaction of glutaric anhydride with aqueous ammonia.[8] These compounds were purified several times by recrystallization.

The NQR spectrometer described by Dean was employed.[9] The signals were modulated by the reference signal from a lock-in amplifier (FM Circuit Design Block Co., Ltd., Model LI-572B) and were displayed on a CRO screen (National, VP-5250). The frequency measurement was made by a method described previously.[2,3] All the measurements were made at the temperature of liquid nitrogen. Glass vessels containing 8—10 g of the samples were used.

Results and Discussion

The ^{35}Cl NQR frequencies of the *N*-chloro compounds at the temperature of liquid nitrogen are given in Table 1. The resonance lines appear in the region from 52.7 to 54.1 MHz. This region lies in the ^{35}Cl NQR frequency range of the N-Cl bond with a tr^1 tr^1 tr^1 π^2 hybridized nitrogen atom proposed by Hart and Whitehead.[1] The resonance frequency of **3** is higher than that of **1**. This difference results from the fact that **3** has an oxygen which is electron-attractive instead of the methylene group in **1**. In the cases of **2** and **3**, the latter has a higher frequency than the former. The presence of methyl groups is responsible for the decrease in the resonance frequency of **2**, for the methyl group is electron-donative. The resonance frequency of **5** is higher than that of **1** because of having another electron-attractive carbonyl group on the ring. Cyclic compounds show an increase in the nuclear quadrupole resonance frequency which rises with an increase in the ring strain.[10] This tendency is observed in the cases of both **4** and **5**.

The pure quadrupole resonance frequency can be expressed as functions of the quadrupole coupling constant, e^2Qq/h, and the asymmetry parameter, η, of the field gradient. These two parameters cannot be determined uniquely from the observed frequencies. However, if it is assumed that $\eta=0$, the coupling constant is equal to twice the resonance frequency for the chlorine atom with a 3/2 nuclear spin. On this assumption, we have calculated the coupling constants given in Table 1. The adequacy of this assumption for the compounds cited in Table 1 is supported by a consideration of the resonance structures, for the most probable main factor leading to the asymmetry of the field gradient in molecules of this type is the π-bond character of the nitrogen-chlorine bond and the axially symmetric charge distribution of σ-electrons does not contribute to the parameter. The calculated quadrupole coupling constants for *N*-chloro compounds are lower than that of the chlorine atom (109.74 MHz for ^{35}Cl). This indicates that the chlorine

Table 1. ^{35}Cl NQR Parameters of *N*-Chloro Compounds at the Temperature of Liquid Nitrogen and the Total Yield of the 1,2-Addition Reaction to Cyclohexene

Compound	ν/MHz	e^2Qq/h	i[a]	Yield/%[d]
N-Chloro-2-pyrrolidinone	51.732	103.46	−0.06	9
N-Chloro-4,4-dimethyl-2-oxazolidinone	52.244	104.49	−0.05	
N-Chloro-2-oxazolidinone	52.805	105.61	−0.04	34
	52.914			
N-Chloroglutarimide	53.096			
	(53.005)[c]	106.01	−0.03	
N-Chloroglutarimide	54.095[b]	108.19	−0.01	54

a) The minus sign indicates that the chlorine atom has a negative fractional charge. b) From Ref. 1. c. 2. c) Averaged values. d) From Ref. 1. c. 12.

atom of the *N*-chloro compound cited in Table 1 has a negative fractional charge. According to Dailey and Townes,[11] $(e^2Qq)_{mol}$ is expressed by:

$$(e^2Qq)_{mol} = (1-i)(e^2Qq)_{atom}$$

where i stands for the bond ionicity and where $(e^2Qq)_{atom}$ denotes the e^2Qq value of the atomic chlorine. In this equation, the contribution from the s character of the bonding orbital of chlorine is assumed to be zero, for the electronegativity of chlorine is practically the same as that of nitrogen. The contribution from the d character is ignored because it is always less than 5% for the chlorine atom. The ionic characteristics of the N-Cl bonds shown in Table 1 were calculated from this relation.

Lessard et al.[12] investigated the total yield of 1,2-addition in the photochemical reaction of cyclic *N*-chloro amides (imides) with cyclohexene. They proposed that 1,2-addition occurs through a radical-chain mechanism as follows:

$$\text{-CO-N-Cl} \xrightarrow{h\nu} \text{-CO-N}\cdot + \text{Cl}\cdot \quad (1)$$

$$\text{-CO-N}\cdot + \text{C=C} \longrightarrow \text{-CO-N-C-C}\cdot \quad (2)$$

$$\text{-CO-N-C-C}\cdot + \text{Cl-N-CO-} \longrightarrow \text{-CO-N-C-C-Cl} + \cdot\text{N-CO-} \quad (3)$$

They also suggested that the total yield of the 1,2-addition reaction increases when the *N*-chloro compound in Reaction 3 is a good chlotine-atom donor. When the *N*-chloro compound is a good chlorine-atom donor, the value of the ionicity of the N-Cl bond should be near zero. Thus, we compared the total yield of the 1,2-addition with the ionicity of the *N*-chloro compound. The total yield for the photochemical addition to cyclohexene is shown in Table 1. *N*-Chlorosuccinimide (**5**) gives rise to the highest yield and has the nearest value to zero for the ionicity. When the value of the ionicity is far from zero, the yield decreases.

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