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^{35}Cl NQR and Ionicities of a Few *N*-Chloroimides

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Synopsis. ^{35}Cl NQR frequencies were measured for *N*-chlorosuccinimide (NCS), *N*-chlorophthalimide (NCP), *N,N'*-dichlorobarbital (NDCB), sodium *N,N'*-dichloroisocyanurate dihydrate (Na-NDCI·2H$_2$O) and *N,N',N''*-trichloroisocyanuric acid (NTCI). The ionicities estimated by a ^{35}Cl NQR study increased in the following order; NCS<NCP<NDCB<Na-NDCI·2H$_2$O<NTCI. A linear relationship between the ionicities of chlorine atoms and the polarographic reduction potentials of N–Cl bonds was found. The ionicity was related to the reactivity.

Since the first report on a ^{35}Cl NQR study of the N–Cl bond by Segel et al.,[1] several papers about ^{35}Cl NQR studies of molecules with this bond have been published.[2–6] The ^{35}Cl NQR frequency is higher for a N–Cl bond than for a C–Cl bond because the electronegativity of chlorine is practically the same as that of nitrogen.

N-halogenoimides are effective reagents for the halogenation and the oxidation of olefins, alcohols and carbonyl compounds. In this paper, we report on the ^{35}Cl NQR frequencies for a few *N*-chloroimides and the reactivities of these compounds.

Experimental

The materials, except for *N,N'*-dichlorobarbital, were purified several times by the recrystallization of commercial products. *N,N'*-dichlorobarbital was prepared by a method described in the literrature[7] and purified by recrystallization. It was identified by its IR spectrum.

An NQR spectrometer of the type described by Dean[8] was used. The signals were either observed on a CRO or recorded on a chart. The resonance frequencies were measured on a CRO screen with the help of an RF-signal generator (Trio, Model SG-2) and a frequency counter (Anritsu, MF-55D).

Sample tubes of about 22-mm diameter were used. All measurements were made at liquid-nitrogen temperature.

Results and Discussion

The ^{35}Cl NQR frequencies of the *N*-chloroimides at liquid-nitrogen temperature are given in Table 1. For *N*-chlorosuccinimide (NCS) and *N*-chlorophthalimide (NCP), the observed frequencies agree with those found in the literature.[3] *N,N',N''*-trichloroisocyanuric acid[†] (NTCI) showed two resonance lines ν_1=58.902 MHz and ν_2=46.423 MHz. The latter agrees with the result of Fitzky et al.[4] The frequency ratio, ν_1/ν_2=1.2688, agrees with the isotope frequency ratio, $\nu(^{35}\mathrm{Cl})/\nu(^{37}\mathrm{Cl})$. Therefore, it was found that the result of Fitzky et al. corresponds to the ^{37}Cl NQR frequency of NTCI. According to Hart et al.,[3] all the nitrogen atoms of the compounds cited in Table 1 have tr^{1}tr^{1}tr$^1\pi^2$ hybridization states and their structures are either planar or near planar.[9] This conclusion is consistent with the IR and Raman spectra.[10,11]

Table 1. ^{35}Cl NQR Parameters of *N*-Chloroimides at Liquid Nitrogen Temperature

Compound	ν/MNz	e^2Qq/h / MHz	i
N-Chlorosuccinimide	54.095	108.2	−0.01
N-Chlorophthalimide	55.402	110.8	0.01
N,N'-Dichlorobarbital	57.036	114.1	0.03
Sodium *N,N'*-dichloroisocyanurate dihydrate	58.208	116.4	0.05
N,N',N''-Trichloroisocyanuric acid	ν_1=58.902 ν_2=46.423	117.8	0.06

The asymmetry of the field gradient in this case originates from the π-bond character of the N–Cl bond. From the possible resonance structures, the π character can be excluded. Therefore, the asymmetry parameter, η, must be negligibly small and the quadrupole coupling constant, e^2Qq/h, is twice the resonance frequency. We have calculated the quadrupole coupling constant (Table 1). The coupling constant of NCS is smaller and the values for other compounds are larger than that of the chlorine atom (109.74 MHz for ^{35}Cl[2]). This indicates that the chlorine atom of NCS has a negative charge and others are posively charged. According to Townes and Dailey,[12] the coupling constant is given by

$$e^2Qq = (1+\alpha i)(e^2Qq)_{\mathrm{atom}}$$

where i stands for the bond ionicity and $(e^2Qq)_{\mathrm{atom}}$ denotes e^2Qq of the atomic chlorine. For a negative ionicty, $\alpha=-1$ is used and for a positive ionicity $\alpha=1.28$. Here, the s and d characters of chlorine are neglected because the electronegativity of chlorine is practically the same as that of nitrogen and the d character is always less than 5% for the chlorine atom.[12] By the use of this relation, the ionic character of the N–Cl bonds were evaluated (Table 1). Sodium *N,N'*-dichloroisocyanurate[††] dihydrate (Na-NDCI·2H$_2$O) has a lower ionicity than that of NTCI since the sodium ion decreases the inductive effect of the carbonyl group to the N–Cl bond. The ionicity increases in the following orde; NCS<NCP<NDCB<Na-NDCI·2H$_2$O<NTCI.

Figure 1 shows the relationship between the ionicity, i, and the polarographic reduction potential,[13] $E_{1/2}$, of *N*-chloroimides. The reduction of the N–Cl bond becomes easier when the polarity of the N–Cl bond increases. The result of a polarographic study shows

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[†] Systematic name: 1,3,5-trichloro-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione.

[††] Systematic name: 1,3-trichloro-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione sodium salt.

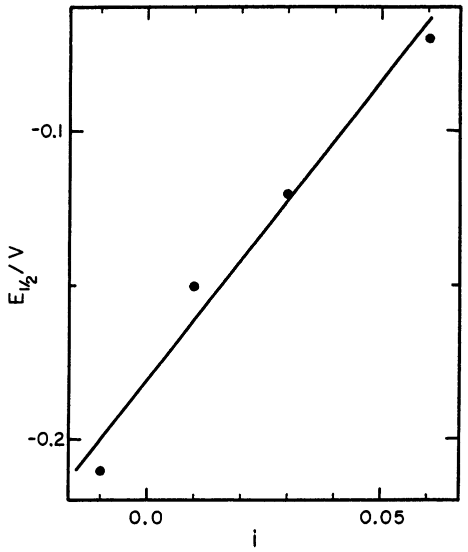

Fig. 1. The relationship between the ionic character, i, and reduction potential, $E_{1/2}$ of *N*-chloroimide.

that the polarity of *N*-chloroimide increases in the following order; NCS<NPC<NDCB<NTCI. This is in agreement with the results of our ^{35}Cl NQR study.

Reactions of NTCI and NCS with some metal alkyls and metal chlorides were studied by Leimeister et al.[14] Substitution reactions occur with NTCI, whereas NCS reacts only with $SnCl_5$, forming hexachloroantimonate. This fact shows that the chlorine atom of NTCI is more positive than that of NCS. Otsuji et al.[13] sudied the reactions of cyclohexanone with NTCI and NDCB. The results show that the N–Cl bond is more polar in NTCI than in NDCB. They also studied the chlorination of cyclohexene with NDCB and NCS and concluded that the polarity of the N–Cl bond increases from NCS to NDCB. These three facts explain why the polarity of the N–Cl bond increases in the following order; NCS<NDCB<NTCI. This agrees with the order of the ionicity evaluated in the present study. Thus, we conclude that the ionicity of *N*-chloroimides (as estimated by the ^{35}Cl NQR study) provides a good measure of the reactivities of the *N*-chloroimides.

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