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^{35}Cl NQR due to the N-Cl Bonds and 1,2-Addition Reaction to Cyclohexene of *N*-Chloro Amide Compounds

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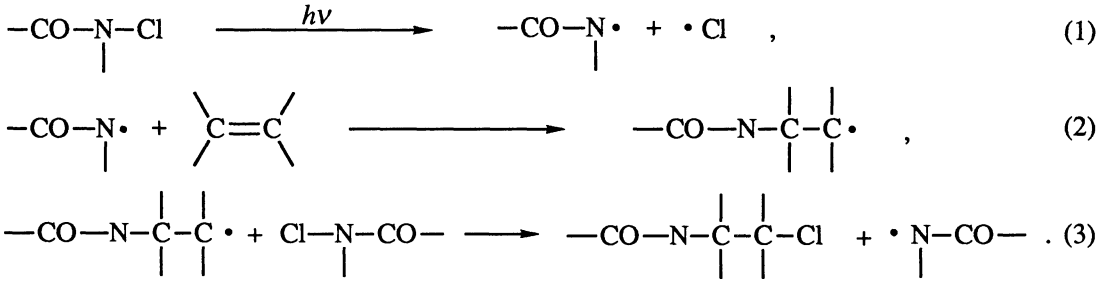
^{35}Cl NQR spectra of N-Cl bonds were measured for $CCl_3CONHCl$, $CHCl_2CONHCl$, $CH_2BrCONHCl$ and $Cl(CH_2)_2CONHCl$. The ionic character of N-Cl bonds was estimated for these compounds according to Townes and Dailey. The ionic character was compared with the yield of the 1,2-addition to cyclohexene under the photochemical reaction. The yield increased as the value of the ionic character neared zero.

N-Chloro amide compounds, ZCONHCl, practice the 1,2-addition to olefins under the photochemical reaction through a radical-chain mechanism as follows:[1)]



(1)

(2)

(3)

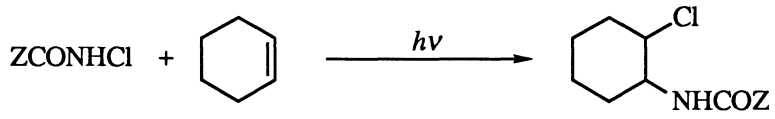
The yield of the 1,2-addition reaction increases when the *N*-chloro amide in reaction (3) is a good chlorine-atom donor. The *N*-chloro amide is expected to be a good chlorine-atom donor, when the polarity of N-Cl bond is low and the value of the ionicity of the N-Cl bond is close to zero. Thus it is worthwhile to measure ^{35}Cl NQR spectra for these compounds because the resonance frequencies give the information about the polarity of N-Cl bonds.

Seven *N*-chloro acetamides were prepared by the chlorination of parent amides according to Beckwith and Goodrich.[2)] The ^{35}Cl NQR spectra due to N-Cl bonds of these compounds were observed by means of a homemade Dean type spectrometer already described [3)]. All measurements were carried out at liquid nitrogen temperature. Only four compounds gave ^{35}Cl NQR signals and the results were shown in Table 1. Unexpectedly, *N,a,a*-trichloroacetamide gave the highest frequency among four compounds given in Table 1. Its resonance frequency higher than that of $CCl_3CONHCl$ was assured by several repetitions of measurement on the

newly prepared *N*-chloro amides.

The ^{35}Cl NQR frequency can be expressed as a function of the quadrupole coupling constant, e^2Qq/h, and the asymmetry parameter, η, of the field gradient and these two constants cannot be determined uniquely from a single observed frequency. The asymmetry of the field gradient originates from the π-bond character of N-Cl bond. From the possible resonane structures of these compounds, the π character can be excluded. Therefore, the asymmetry parameter is negligibly small and the coupling constant is equal to twice the resonance frequency. With this assumption, the couplng constants were calculated and listed on the third column in Table 1. All these values are smaller than that of chlorine atom (^{35}Cl; 109.74 MHz[4]). This means that all the chlorine atoms on N-Cl bonds of *N*-chloro acetamides in Table 1 have a negative charge. By using Townes-Dailey relation,[5] the ionicity of N-Cl bond was estimated and the results are listed in Table 1. The ionicity increases by changing Z in the order CCl_3~CCl_2H<$CBrH_2$<$Cl(CH_2)_2$.

N-Chloro acetamides practice the 1,2-addition to cyclohexene under the photochemical reaction. The 1,2-addition reaction occurs through a radical mechanism.



The increase of yield is expected as *N*-chloro amide is a good chlorine-atom donor. The yields of 1,2-addition reaction to cyclohexene are shown on the fifth column in Table 1. As the ionicity of bond increases, the yield deceases.

Table 1. ^{35}Cl NQR Parameters and the Yields of Photochemical Additions of *N*-Chloro Amides to Cyclohexene

Compound	ν/MHz	e^2Qq/h/MHz	i	Yield/%[a]
$CCl_3CONHCl$	53.520	107.04	-0.02	99
$CHCl_2CONHCl$	53.602	107.20	-0.02	94
$CH_2BrCONHCl$	52.862	105.74	-0.04	79
$Cl(CH_2)_2CONHCl$	51.359	102.74	-0.06	66

a) Ref. 1.

References

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