CHEMISTRY LETTERS, pp. 2023-2024, 1990.

^{35}Cl NQR Spectra and the Addition Reactions to 2- Chlorobutadiene of N,N-Dichloromethane- and N,N,p-Trichlorobenzenesulfonamide

Yoshitaka NAGAO* and Shigeyoshi KATAGIRI
Department of Chemistry, Faculty of Science, Hirosaki University,
Bunkyo-cho,Hirosaki 036

^{35}Cl NQR spectra of N,N-dichloromethane- and N,N,p-trichlorobenzenesulfonamide were measured at liquid nitrogen temperature. The former compound showed a single absorption line at 53.570 MHz, while the latter three lines at 52.405, 52.041 and 35.529 MHz. The bond ionicities estimated from ^{35}Cl NQR frequencies for these compounds were related to the yields of the addition reaction to 2-chlorobutadiene.

N,N-Dichloro sulfonamide compounds possess the antimicrobial activity because of producing hypochlorous acid in contact with water. These compounds also react with the molecules containing double bonds.[1] It is worthwhile to measure ^{35}Cl NQR spectra for these compounds because the resonance frequencies give the information about N-Cl bonds. In this paper, the relationship between the ^{35}Cl NQR frequencies and the yields of the addition reaction to 2-chlorobutadiene for these compounds is discussed.

The ^{35}Cl NQR spectra were observed by using a home-made super-regenerative spectrometer. The experimental procedures of the NQR measurements have been reported previously.[2] All measurements were carried out at liquid nitrogen temperature. N,N-Dichloromethane-[3] (DCMS) and N,N,p-trichlorobenzenesulfonamide[4] (TCBS) were prepared according to literature. All samples were purified by recrystallization from benzene.

In Table 1 are shown the results of ^{35}Cl NQR frequencies for N,N-dichloro sulfonamide compounds. DCMS showed a single strong signal. On the other hand, Freidlina et al.[5] have reported two resonance lines at 52.038 and 35.532 MHz for TCBS. In our study, however, three resonance lines were observed as shown in Table 1. p-Chlorobenzenesulfonamide showed a single line at 35.106 MHz. Thus two higher frequency signals arise from the chlorine atoms of N,N-dichloro sulfamoyl group. Freidlina et al. might overlook the line at 52.405 MHz.

Assuming that η =0, coupling constants for these compounds were calculated. The

coupling constant is related to the ionicity of the N-Cl bond by using Townes-Dailey relation.[6] The calculated bond ionicities are shown in Table 1.

Daniher and Butler[1] have reported that the N,N-dichloro sulfonamide compounds added to the olefins with the anti-Markovnikov orientation for the adducts. This means that the addition occurs by a radical mechanism. The ionicity of N-Cl bond is related to the polarity of N-Cl bond. If N,N-dichloro sulfonamide contains a less polar N-Cl bond, this compound would facilitate the addition reaction through the radical mechanism. Therefore, it is expected that the addition yield increases when the ionicity of N-Cl bond decreases. In table 1 are shown the results of addition yield of N,N-dichloro sulfonamide compounds to 2-chlorobutadiene reported by Neale.[7] The bond ionicity of DCMS is close to zero compared with that of TCBS and the former, in accordance with our expectation, adds to the 2-chlorobutadiene with a higher yield.

Table 1. NQR resonance frequencies, coupling constants, ionicities and addition yields to 2-chlorobutadiene of N,N-dichloro sulfonamides

Compound	ν/MHz[a]	e^2Qq/h/MHz	i	Yield/%
$CH_3SO_2NCl_2$	53.570	107.12	-0.02	89
p-$ClC_6H_4SO_2NCl_2$	52.405 52.041 35.529	104.45[b]	-0.05	85

a) The measurements were carried out at liquid nitrogen temperature.
b) averaged value.

References

1) F.A.Daniher and P.E.Butler, *J.Org.Chem.*, **33**,4336(1968).
2) Y.Nagao and S.Katagiri, *Bull.Chem.Soc.Jpn.*, **59**,641(1986).
3) A.G.Newcombe, *Can.J.Chem.*, **33**,1250(1955).
4) R.R.Baxter and F.D.Chattaway, *J.Chem.Soc.*, **107**,1814(1915).
5) R.Kh.Freidlina, N.A.Rybakova, G.K.Semin, and E.A.Kravchenko, *Dokl.Akad.Nauk SSSR*, **176**,352(1967).
6) B.P. Dailey and C.H.Townes, *J.Chem.Phys.*, **23**,118(1955).
7) N.S.Neale, *Synthesis*, **1971**,1.

(Received August 8,1990)