# $^{35}$Cl NQR Spectra of Organyl(chloroalkyl) Sulfides *

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The $^{35}$Cl NQR spectra of organyl(chloroalkyl) sulfides $ClCH_2S(CH_2)_nCH_3$, $n = 0–11$, $Cl(CH_2)_mSR$, $m = 1–3$ and alkyl(chloromethyl selenides $ClCH_2SeR$ ($R = C_2H_5$, $C_3H_7$) have been obtained. In going from $m = 1$ to $m = 2$, the electron density on the Cl atom in the series $Cl(CH_2)_mYR$ increases when $Y = S$ and decreases when $Y = O$.

## Introduction

The electron densities on the Cl atoms and, consequently, the reactivities of the latter in α- and β-chloroalkyl(alkyl) ethers differ much [1]. As is known, due to the geminal effect (through-atom interaction) the chlorine atom in α-chloro ethers is highly reactive, whereas the chlorine atom in β-chloro ethers is rather inert owing to the vicinal effect (through-bond interaction) [1]. This is well supported by the $^{35}$Cl NQR spectra of chloroalkyl(alkyl) ethers [2–6].

Analogous data for isostructural alkyl(chloromethyl) sulfides [2, 7, 8] are rather scarce and do not give any clear idea of the relationship between the position and electron density of the chlorine atom in the alkyl group.

## Results

To compare the electron density distribution in molecules of the series $ClCH_2YR$ ($Y = O$, $CH_2$, S) we have measured the $^{35}$Cl NQR frequencies $\nu^{77}$ of organyl(chloroalkyl) sulfides at 77 K (Tables 1 and 2). In the series $ClCH_2O(CH_2)_nCH_3$, $\nu^{77}$ oscillates about an average value of ~29.95 MHz as $n$ increases from 0 to 4 and is nearly constant for $n$ from 4 to 9 [3]. In 1-chloroalkanes ($Y = CH_2$) the NQR frequency oscillates about $33.06 \pm 0.20$ MHz as $n$ increases. The dependence of $\nu^{77}$ in the isostructural series of alkyl(chloromethyl) sulfides $ClCH_2S(CH_2)_nCH_3$ on the length of the alkyl group turns out to be quite different (Table 1). With increasing $n$, $\nu^{77}$ increases and oscillates irregularly. In so doing, the lower points ($n = 0$, 2, 3, 5, 7, 11) on the $\nu^{77}$ vs. $n$ curve correlate within certain limits with $n$ (Figure 1). The correlation is as follows:

$$\nu^{77} = 33.085 + 0.102\,n, \quad r = 0.997 \text{ for } n = 6\,.$$

The frequency range and oscillations of the $\nu^{77}$ vs. $m$ curve of the alkyl(chloromethyl) sulfides (from 33.1 to 34.3 MHz) are considerably greater (Table 1) than those for the isostructural alkylchloromethyl ethers (see above). The first member of the series $ClCH_2S(CH_2)_nCH_3$ shows the lowest $\nu^{77}$. This indicates that the electron density of the Cl atom in the molecules of higher homologues of this series is lower than that in those with $n = 0$. On the induction constant $\sigma$* scale the methyl group is taken as the refer-

Table 1. $^{35}$Cl NQR frequencies at 77 K ($\nu^{77}$) of the compounds $ClCH_2S(CH_2)_nCH_3$, $Cl(CH_2)_mSR$ and the signal/noise ratio (S/N).

| $n$ | $\nu^{77}$ [MHz] | S/N | $m$ | R | $\nu^{77}$ [MHz] | S/N |
|---|---|---|---|---|---|---|
| 0* | 33.104 | | 1 | $CH(CH_3)_2$ | 33.619 | 70 |
| 1 | 33.781 | 70 | 1 | $CH(CH_3)C_2H_5$ | 33.193 | 10 |
| 2 | 33.270 | 35 | 1 | $C(CH_3)_3$ | 33.856 | 15 |
| 3 | 33.363 | 10 | 1 | $C_6H_5$ | 34.558 | 30 |
| 4 | 33.745 | 8 | | | 34.732 | 32 |
| | 33.649 | 7 | 2 | $C_6H_5$ | 33.582 | 17 |
| 5 | 33.625 | 25 | 3 | $C_6H_5$** | 33.2 | 2 |
| 6 | 34.106 | 60 | 4 | $C_6H_5$ | 32.866 | 23 |
| 7 | 33.776 | 6 | 5 | $C_6H_5$ | 33.262 | 3 |
| 9 | 34.269 | 35 | 1 | $CH_2C_6H_5$ | 34.005 | 10 |
| 11 | 34.213 | 10 | 1 | 2-$C_4H_3S$ | 34.040 | 27 |
| | | | | | 34.160 | 7 |
| | | | 2 | 2-$C_4H_3S$ | 33.220 | 5 |
| | | | 3 | 2-$C_4H_3S$** | 33.1 | 2 |

* Ref. [2]. – ** NQR spectra measured in the glass.

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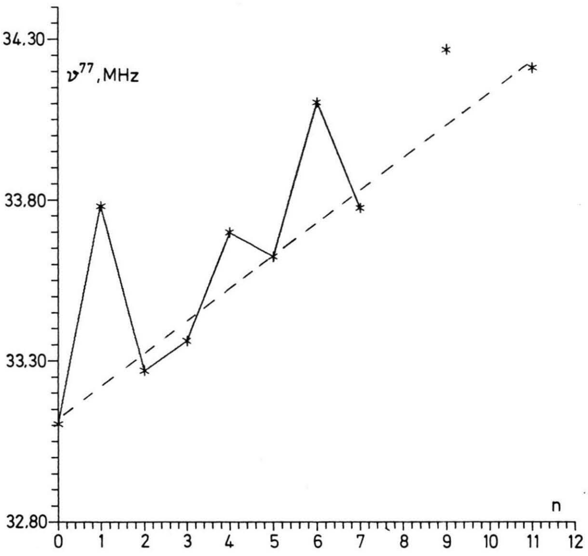

Fig. 1. Average $^{35}$Cl NQR frequencies of compounds $ClCH_2S(CH_2)_nCH_3$ as a function of the number of methylene groups $n$.

ence point of the induction effect of substituents ($\sigma^*_{CH_3} = 0$). Other alkyl groups show a considerably higher electron-donating effect, which becomes constant for $n \geq 3$ [9]. However, judging by $\nu^{77}$ in the series $ClCH_2SR$, all the $n$-alkyl groups, $R = (CH_2)_nCH_3$ ($n > 0$), show, against expectations, an electron-acceptor effect which decreases the electron density on the Cl atom. In compounds of the series $ClCH_2SR$ an even larger electron-acceptor character is displayed by branched alkyl groups, $R = CH(CH_3)_2$, $CH(CH_3)C_2H_5$ and $C(CH_3)_3$, since the corresponding sulfides possess an even higher $\nu^{77}$. In sulfides of the series considered with $R = (CH_2)_6CH_3$, $(CH_2)_9CH_3$ and $(CH_2)_{11}CH_3$, $\nu^{77}$ turns out to be even higher than with $R = CH_2C_6H_5$ ($\sigma^*_{CH_2C_6H_5} = 0.16 \div 0.34$ [10]) (Table 1). These data are in agreement with the hydrolysis rate of organyl(chloromethyl) sulfides, which decelerates in the series $ClCH_2SR$ in the following order of changing R (the relative hydrolysis rate with $R = C_6H_5$ is taken to 1): $CH_3$ (220) = $C_2H_5$ (220) > $(CH_3)_2CH$ (200) > $C_3H_7$ (170) > $C_6H_5CH_2$ (17) [8]. At the same time, $\nu^{77}$ of compounds of the series $ClCH_2SR$ with $R = C_6H_5$ and $CH_2C_6H_5$ qualitatively corresponds to the inductive effect of a more electronegative phenyl group. In the series $ClCH_2SR$ the electron-donor effect of the substituent R with $R = CH_2C_6H_5$ and $2\text{-}C_4H_3S$ is practically the same, although the $\sigma^*$ value of the 2-thienyl group is much higher ($\sigma^*_{2\text{-}C_4H_3S}$ and $\sigma^*_{CH_2C_6H_5}$ range from 0.9 to 1.1 and from 0.16 to 0.34, respectively [9, 10].

Table 2. $^{35}$Cl NQR frequencies at 77 K ($\nu^{77}$) of the compounds $Cl(CH_2)_mYR$ ($m = 1$ and 2) and their difference ($\Delta\nu^{77} = \nu^{77}_{m=1} - \nu^{77}_{m=2}$).

| Y | R | $m = 1$ | $m = 2$ | $\Delta\nu^{77}$ |
|---|---|---|---|---|
| S | $CH_3$ | 33.104 [2] | 32.634 | 0.470 |
| | $C_6H_5$ | 34.645 | 33.582 | 1.063 |
| | $2\text{-}C_4H_3S$ | 34.100 | 33.220 | 0.880 |
| O | $CH_3$ | 30.01 [3] | 33.453 [5] | −3.44 |
| | $C_2H_5$ | 29.917 [3] | 33.708 [5] | −3.791 |
| | $C_6H_5$ | 32.250 [4] | 34.316 [5] | −2.066 |
| $CH_2$ | $CH_3$ | 32.968 [5] | 33.255 [5] | −0.287 |
| | $C_2H_5$ | 33.255 [5] | 33.103 [5] | 0.152 |

The structure and some properties of chloromethyl ether, $ClCH_2OCH_3$, and of the isostructural sulfide, $ClCH_2SCH_3$, are similar [1, 8]. The gauche conformation is energetically most advantageous for these molecules [11–12]. The electron density on the Cl atoms in molecules of $ClCH_2YCH_3$ (Y = O, S) is higher than one should expect from the inductive effect of $OCH_3$ and $SCH_3$ groups. As stated previously, the Cl atom reactivity in organyl(chloromethyl) sulfides is intermediate between those observed in isostructural organyl(chloromethyl)ethers and chloroalkanes. In Table 2 the $^{35}$Cl NQR frequencies of compounds of the series $Cl(CH_2)_mYR$ ($Y = S, O, CH_2$) with $m = 1$ and $m = 2$ are compared. It turns out that on going from organyl(chloromethyl) sulfides to organyl(2-chloroethyl) sulfides (Y = S), $\nu^{77}$ is lowered by 0.5–1.1 MHz. In the series of compounds with Y = O on the contrary, $\nu^{77}$ is higher by 2.1–3.8 MHz. In 1-chloroalkanes ($Y = CH_2$), when $m$ increases from 1 to 2, $\nu^{77}$ oscillates within a range of ±0.2 MHz.

Thus, in the series $Cl(CH_2)_mYR$ with Y = S the transition from $m = 1$ to $m = 2$ increases the electron density on the Cl atom, whereas with Y = O a decrease in the electron density is observed. Consequently, the reactivity ratio of the α- and β-chlorines in alkyl(chloroalkyl) ethers and thioethers is exactly opposite. Accordingly, organyl(2-chloroethyl) sulfides are much more quickly hydrolized than isostructural organyl(2-chloroethyl) ethers. Thus, for example, in the series $RY(CH_2)_2Cl$ the hydrolysis rate constants (min$^{-1}$) at 100 °C are as follows [13]:

| R \ Y | S | O | $CH_2$ |
|---|---|---|---|
| $C_2H_5$ | $1.7 \cdot 10^{-1}$ | $1.1 \cdot 10^{-5}$ | $6.2 \cdot 10^{-5}$ |
| $C_6H_5$ | $5.5 \cdot 10^{-3}$ | $5.6 \cdot 10^{-6}$ | – |

It is also known that ethyl(chloromethyl) sulfide is hydrolized 1000 times more slowly than the isostructural ethyl(chloromethyl) ether [8]. Previously the higher reactivity of the chlorine atom organyl(2-chloroethyl) sulfides was explained by the formation of the intermediate episulfonium ion, able to abstract the halogen anion [8]. However, the NQR data show that the Cl atom in organyl(2-chloroethyl) sulfides is very reactive even in the ground state.

In the series $Cl(CH_2)_mSC_6H_5$ $\nu^{77}$ quickly decreases with increasing $m$ to $m = 4$ and with subsequently increases to $m = 5$ (Table 1). $\nu^{77}$ changes similarly in the series of 2-thienyl(chloroalkyl) sulfides ($m = 1 \div 3$, Table 1). The decrease in the α-Cl atom electron density in organyl(chloromethyl) sulfides is due to the effect of geminal interaction of the chlorine and sulfur atoms.

We have measured the $^{35}$Cl NQR frequencies of $ClCH_2SeCH_2CH_3$ (34.169 and 34.426 MHz), S/N 20), $ClCH_2Se(CH_2)_2CH_3$ (34.138 MHz, S/N 10) and $ClCH_2CH_2SeC_6H_5$ (33.228 MHz, S/N 25). The $\nu^{77}$ values of the chloromethyl selenides indicate a smaller electron density transfer from the chlorine atom to the C–Se σ-bond than in the isostructural sulfides.

## Experimental

Organyl(chloromethyl) sulfides were prepared by reaction of the corresponding organylthiols with paraform and trimethylchlorosilane according to a procedure described in [14]. The reaction of α,β-dichloroalkanes with organylthiols yielded compounds of the series $Cl(CH_2)_mSR$ ($m > 1$).

The spectra were run on an IS-3 spectrometer.

## Conclusions

1. The $^{35}$Cl NQR spectra of organyl(chloroalkyl) sulfides $ClCH_2S(CH_2)_nCH_3$, $n = 0$–11 and $Cl(CH_2)_mSR$, $m = 1$, $R = CH(CH_3)_2$, $CH(CH_3)C_2H_5$, $C(CH_3)_3$, $CH_2C_6H_5$, $m = 1$–3, R = 2-$C_4H_3S$, $m = 1$–5, $R = C_6H_5$ have been obtained.

2. In molecules of the series $ClCH_2SR$ the substituents which are believed to be electron-donors (R = alkyl group) produce at the Cl atom an electron-withdrawing effect contrary to $R = CH_3$.

3. In going from $m = 1$ to $m = 2$, the electron density on the Cl atom in the series $Cl(CH_2)_mYR$ increases when Y = S and decreases when Y = O.

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