NQR SPECTRA OF SOME GROUP IVB ORGANOMETALLIC HALIDES

D F VAN DE VONDEL, H WILLEMEN and G P VAN DER KELEN

Laboratory for General and Inorganic Chemistry-B, University of Ghent, Krijgslaan 271, B-9000 Ghent (Belgium)

(Received April 9th, 1973)

SUMMARY

NQR ^{35}Cl, ^{79}Br and ^{81}Br frequencies have been measured for some organo-metallic halides of tin and germanium. A comparison of the data with earlier results for silicon and carbon indicates that π-bond character exists only in the Si–Cl and, to a lesser degree, the Ge–Cl bond The ionic character in the metal–halogen bond bond decreases in all series with additional halogen substitution. The tin–halogen compounds show a very low lying NQR frequency which can be explained in terms of halogen-bridging in the crystals.

INTRODUCTION

The metal–halogen bond in organometallic halide compounds of Group IVB metals has been extensively studied by many different physicochemical techniques but no general agreement on the bonding characteristics has resulted. Some authors[1] restrict $(d–p)\pi$ bonding only to the Si–F bond, whereas others[2,3] believe that some $(d–p)\pi$ bonding must be taken into account in Sn–halogen bonds also. As the halogen NQR resonance frequency depends directly on the electron configuration of the halogen, NQR spectroscopy seems to offer the prefered method of studying the metal–halogen bond. Some ^{35}Cl NQR measurements on Group IVB compounds have already been published, but ^{79}Br and ^{81}Br NQR data are almost completely lacking. A comparison between both series of data is of special interest because the dipole moments[4] suggest a change in pattern on going from the Sn–Br to the Sn–Cl bond.

EXPERIMENTAL

The preparations and purifications of the compounds were by well known methods[5,6,7]. In order to prevent hydrolysis, the samples were sealed in one cm outer diameter glass tubes. These were immersed in liquid nitrogen inside the fingertip of a Dewar flask, and this tip was inserted into the spectrometer coil.

The NQR signals were detected with a Wilks Inc. NQR 1-A spectrometer This is a self quenching superregenerative spectrometer with Zeeman modulation Frequency measurements were carried out by externally quenching the oscillator by means of a strong R–F signal from a standard laboratory signal generator (McGraw–

Edison division). The signal generator frequency was read from a digital counter (Monsanto counter time model 1500A). It was assumed that this method of measurements did not shift the oscillator frequency by more than a few kHz. This method does not allow to locate the center frequency of the SRO. The frequency pattern observed in each NQR signal shows spacings equal to the quench frequency The strongest signal of these multiplets was assumed to correspond to the resonance induced by the center frequency of SRO. The accuracy is taken as twice the quench frequency This frequency varies from 20 kHz at 10 5 MHz oscillator frequency to 0 5 MHz at 180 MHz. This frequency measurement method is certainly not suited to yield absolute frequencies, but for internal comparisons in closely related series of compounds it can be used with confidence

RESULTS

The observed NQR frequencies and the corresponding accuracy limits for the compounds studied are given in Table 1. Intensities are given as signal to noise ratios. All the samples were scanned at liquid nitrogen temperature with the exception of methyltin trichloride and trimethyltin chloride, which give only a very weak signal at room temperature. Although the signal intensity is known to increase with decreasing temperature we did not study these compounds at liquid nitrogen temperature. The reason is that, using the low temperature Dewar setup, the amount of sample in the R–F coil was much smaller than in the coil for measurements at room temperature The loss of intensity caused by the reduction in the sample volume was to strong in this case Two products, dimethylgermanium dibromide and trimethyl-

TABLE 1

NQR SPECTRA OF ^{35}Cl, ^{79}Br AND ^{81}Br IN SOME ORGANOTIN AND ORGANOGERMANIUM COMPOUNDS AT 77 K

Compound	Nucleus	Obs freq (MHz)	Accuracy (MHz)	Signal/Noise	$e^2Qq(mol)$
MeSnCl$_3$	^{35}Cl	20 82	0 05	2[a]	41 64
Me$_3$SnCl	^{35}Cl	11 40	0 05	2[a]	22 80
MeSnBr$_3$	^{81}Br	137 37	0 24	10	
		147 05	0 32	5	284 42
	^{79}Br	162 60	0 39	6	
		174 37	0 80	3	336 97
Me$_2$SnBr$_2$	^{81}Br	108 97	0 24	19	
		110 17	0 24	15	219 14
	^{79}Br	128 14	0 24	13	
		129 23	0 24	12	257 38
Me$_3$SnBr	^{81}Br	69 88	0 14	2	139 76
MeGeBr$_3$	^{81}Br	155 20	0 37	11	
		157 19	0 38	5	312 39
	^{79}Br	183 40	0 88	5	
		185 63	0 88	3	369 03
Me$_3$GeBr	^{81}Br	119 08	0 24	14	238 16
	^{79}Br	141 58	0 29	10	283 16

[a] Only gives a signal at room temperature

germanium dichloride failed to give a signal at 77 K Both are liquids at room tempe-rature, and consequently they cannot be scanned at room temperature.

Depending on the number of halogen atoms per molecule more than one NQR signal was observed in many cases. The separation between the components of the multiplets was very small and therefore this multiplet structure was ascribed to lattice inequivalence.

For both halogens investigated the two isotopes respectively ^{35}Cl, ^{37}Cl and ^{79}Br, ^{81}Br have spin $\frac{3}{2}$. The coupling constants $e^2 Qq$ listed in Table 1 were calculated from the average of the multiplets due to non equivalent crystalline sites by using the formula[8] $V = \{1 + \eta^2/3\}^{1/2} e^2 Qq/2$. We can assume that there exists axial symmetry around the M–X bond so that η equals zero and $e^2 Qq = 2V$. Even a relatively high value of η would not affect appreciably the magnitude of the coupling constant.

DISCUSSION

Because only terminal halogen atoms in M–Hal bonds have been studied, the Townes and Daily approximation is best fitted for the interpretation of the data In that theory the field gradient at the halogen atom is ascribed to the unbalance of the n_p electrons. This quantity is given the symbol U_p, and is expressed as in eqn. (1) as the ratio of the quadrupole coupling constant of the halogen in the molecule to the

$$U_p = e^2 Qq(\text{mol})/e^2 Qq(\text{at}) \tag{1}$$

quadrupole coupling constant of the free atom. For $e^2 Qq(\text{at})$ of ^{35}Cl and ^{81}Br, respectively, the values of 109.75 MHz and 643 03 MHz[9] were taken. Values for U_p are tabulated in Table 2. Included are also the U_p values of the corresponding carbon and silicon compounds reported in the literature

According to the Townes and Dailey approximation, neglecting the participation of the halogen d orbitals to the hybridization of the halogen atom in the σ bond[10], U_p can be described by eqn. (2). This assumes that the halogen bonding orbital is a

$$U_p = (1 - s)(1 - I) - \pi \tag{2}$$

sp_z hybrid with s-percent s character I and π are respectively the ionic character of the σ bond and the double bond character of the metal–halogen bond, the p_x and p_y halogen orbitals contributing equally to the π-bonding The only experimental parameter available is U_p, and therefore some further simplifying features are necessary. We use eqn. (2) but with omission of the last term (π), to solve for I and s; i.e. eq. (3) is used.

$$U_p = (1 - s)(1 - I) \tag{3}$$

We thus neglect the contribution of any $(p_{\text{Hal}} \rightarrow d_m)\pi$ bond character This assumption will be almost certainly true for the carbon series, since the energy of the carbon d orbitals is much higher than the energy of the p halogen orbitals*. The ionic character I

---

* Thus d orbital participation in these compounds could eventually be of two kinds The halogen d orbital could hybridize in the σ bond of the halogen, and the metal d orbitals could act as unhybridized acceptors for the halogen p_π electrons There is at the moment no evidence of halogen d_π or metal d_σ involvement (see ref 12)

can be expressed in function of the electronegativity difference between the two bonding orbitals[12]:

$$I = \tfrac{1}{2}|\chi_m - \chi_x| \tag{4}$$

Both χ_m and χ_x are orbital electronegativities. According to Hinze et al.[13], the relation between the orbital electronegativity of a hybrid χ^{hybr} and the individual orbital electronegativities of the pure s and p orbitals, χ^s and χ^p for a given atom can be expressed by a simple linear relation (5):

$$\chi^{hybr} = s\chi^s + (1-s)\chi^p \tag{5}$$

For totally symmetric tetrahedral compounds, the hybridization of the central atom is exactly sp^3. For these compounds we used the χ^{hybr} values for $M(\chi_m)$ as listed by Whitehead and Jaffé[12]. The χ^s and χ^p values of the halogen were also taken from the same source. The values used are $\chi^s_{Cl} = 5.69$, $\chi^p_{Cl} = 2.95$, $\chi^s_{Br} = 5.93$, $\chi^p_{Br} = 2.61$, $\chi_C = 2.51$, $\chi_{Si} = 2.32$, $\chi_{Ge} = 2.59$ and $\chi_{Sn} = 2.52$. The electronegativity for the last four atoms obviously relates to the sp^3 state. Since the values of χ_M are fixed, combination of eqns. (3), (4) and (5) gives a quadratic equation in s for the U_p value of the halogen atom,

TABLE 2

HYBRIDIZATION ELECTRONEGATIVITIES AND IONIC CHARACTER

Compound	U_p	s	χ_{Cl}	χ_M	I
CCl_4	0.740[a]	0 097	3 216	2 86	0 174
CH_3CCl_3	0.690[b]	0.097	3 216	2 745	0 235
$(CH_3)_2CCl_2$	0 636[b]	0 097	3 216	2.627	0 294
$(CH_3)_3CCl$	0 564[b]	0 108	3 246	2 51	0 368
$SiCl_4$	0 370[a]	0 371	3 92	3 14	0 408
$MeSiCl_3$	0 348[a]	0 321	3 829	2 854	0 487
Me_2SiCl_2	0 324[a]	0 280	3 710	2 614	0 548
Me_3SiCl	0 300[a]	0 244	3 618	2 415	0 601
$GeCl_4$	0 468[a]	0 323	3 82	3 21	0 31
$MeGeCl_3$	0 416	0 302	3 777	2 972	0 402
Me_2GeCl_2	0 370[a]	0 284	3 728	2 752	0 488
$SnCl_4$	0 438[a]	0 338	3 87	3 19	0 338
$MeSnCl_3$	0 380	0 318	3 821	2 951	0 435
Me_2SnCl_2	0 282[a]	0 337	3 874	2 741	0 566
Me_3SnCl	0 208	0 340	3 882	2 515	0 683
$GeBr_4$	0 546[a]	0.283	3 549	3 069	0 24
$MeGeBr_3$	0 486	0 280	3 539	2 892	0 323
Me_3GeBr	0 370	0 277	3 530	2 540	0 495
$SnBr_4$	0 512	0 299	3 603	3 061	0 271
$MeSnBr_3$	0 442	0 302	3 613	2 882	0 365
Me_2SnBr_2	0 340	0 328	3 699	2 712	0 493
Me_3SnBr	0 218	0 366	3 825	2 515	0 655

[a] Ref 9, [b] Ref 15

which can be solved. Of the two roots only one has a physical meaning. Substitution of s in eqn. (3) allows us to calculate the corresponding I value for these compounds.

For non totally symmetric compounds we do not know the hybridisation of the central atom. In these cases the orbital electronegativity value of the central atom M for pure sp^3 hybridisation is corrected by a formula[12] which takes account of the orbital electronegativities of the atoms bounded to the central atom. Using these data, and applying the calculating procedure outlined above, we obtained the s and I values given in Table 2.

The s values obtained (Fig. 1 and Table 2) are nearly constant in all the series except those involving for the Si–Cl and Sn–Br compounds. These constant s values can be regarded as an experimental confirmation of the Townes and Dailey rule[11] that there is constant s character in series of related halogen compounds. Nevertheless the constant values of 15% or 0% s character used respectively by Townes et al. and Gordy seem to be inappropriate, as our calculations indicated, s values varying from 0.097 to 0.371 in different series.

The i values (Table 2) show clearly that the ionic character of the M–X bond is decreased by further halogen introduction. There is no deviation from this trend for the Sn–Cl bond, since such deviation would be indicated by the dipole moment variations. In fact the ratio $\mu(Me_3SnCl)/\mu(MeSnCl_3)$ is smaller than 1, suggesting a lower Sn–Cl bond moment and thus a lower ionic character for the Sn–Cl bond in Me_3SnCl than in $MeSnCl_3$, whereas for the other Group IVB elements this ratio is
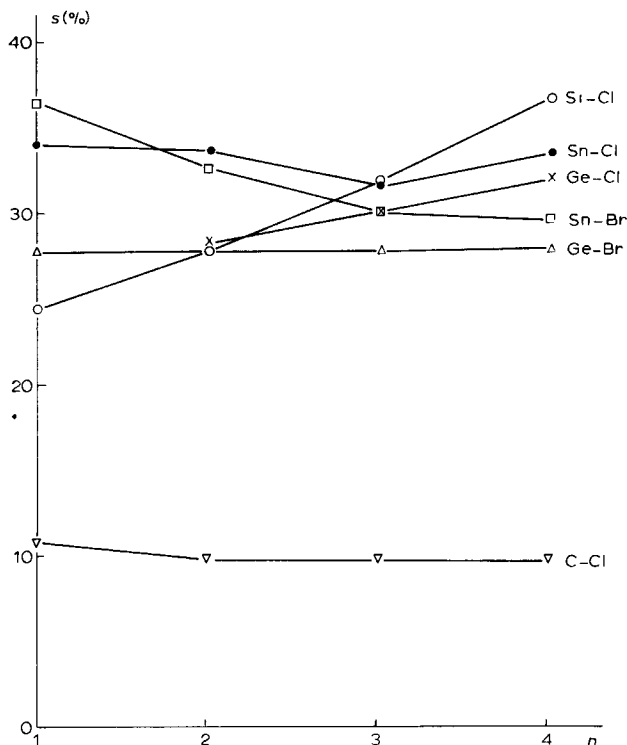

Fig 1   % s character in the halogen p_z orbital versus the number of halogen atoms (n)

higher than 1. The NQR results therefore strenghten the interpretation of the dipole moments[4] in terms of the angle variations and polarisability of the bonds.

In comparison with other series, the Si—Cl series shows a smaller decrease in the ionic character on further halogen introduction. This can be interpreted as evidence for increasing π-bond character in the Si—Cl bond as the number of chlorine atoms increases. Neglecting the cross-term Is in eq. 3, we have eqn. (6). The abnormally high I

$$U_p = 1 - s - I \tag{6}$$

character for large Cl numbers can be thought as a sum of two effects, *viz* the normal decrease of I character and the increase in π character on further halogen introduction.

This increasing π bond character can be expected because of the contraction of the Si-d orbitals. In our calculations a decreasing s character as a function of the halogen substitution seems to indicate π bonding. Extension of this reasoning to the other series points to a small π character in the Ge—Cl bond and no π character in the other series.

Fig. 2 represents the mean halogen NQR frequencies as a function of n, the number of halogens in the molecule. While for every series a linear relationship results, the Sn—halogen series yields a curve with an anomalous decrease of NQR
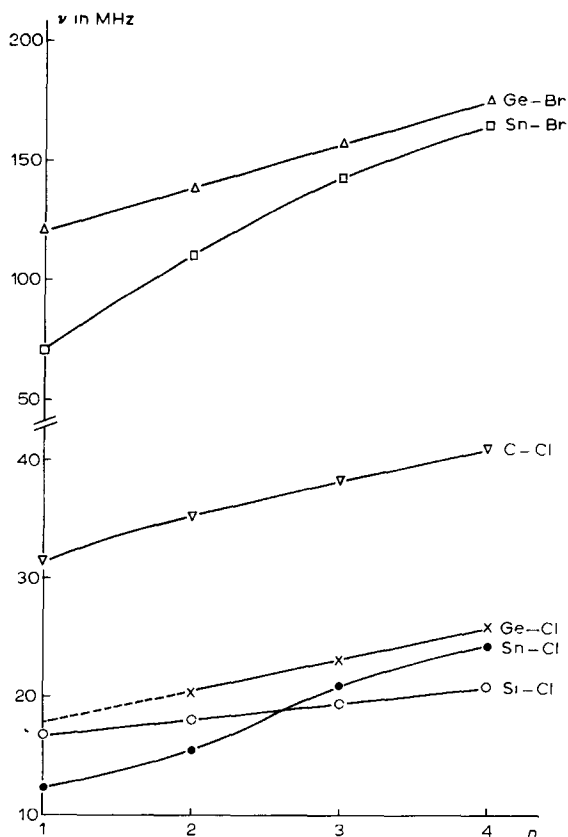

Fig 2 The NQR frequencies v (in MHz) *versus* the number of halogen atoms (n)

frequency for decreasing n. This anomalous behaviour can be ascribed in part to intramolecular metal–halogen bridge formation in the crystal phase. Several examples in the literature[14] show that the halogen frequency is lowered by polymerisation. In our Sn–halogen series, the experimental data indicate that the polymerisation is strongest in the monohalide, and decreases on further introduction of halogen atoms, a conclusion which is supported by the ionic character of the bond, which is largest in the monohalide. For the compounds CH_3SnBr_3, two signals are observed, one at 137.37 MHz and one with a double intensity at 147.05 MHz. The difference between those two signals is too large to be ascribed to inequivalent sites in the unit cell. As the smallest frequency has double the intensity of the larger, we can with some certainty predict, that the structure of CH_3SnBr_3 in the solid phase is a polymer in which the Sn atoms are bonded together by two bromine bridges

The other Sn–Br compounds show no double signal. This indicates that all the bromine atoms take part in bridge formation This bridge formation could be responsible for the increasing s character of Sn–Br bond on halogen substitution (Fig. 1).

Although bridge formation in the Sn–Cl series is also indicated by the curved line in Fig. 2, it seems that it is smaller than in the bromine series. This could explain the constant s character (*versus* increasing s character in the Br series) and the absence by overlap, of two signals for $MeSnCl_3$. The additional metal–halogen interactions in the solid state could be regarded as originating in valence expansion for Sn to 5-coordination in $(CH_3)_3SnCl$ and 6-coordination in CH_3SnBr_3. We believe that such forces are weaker, and that therefore the arguments developed above based on sp^3 hybridization around the central atom are valid.

REFERENCES

1 E A Ebsworth, *Organometallic Compounds of the group IV elements*, Part 1, Marcel Dekker Inc, New York, 1968, p 88
2 P J Green and J D Graybeal, *J Amer Chem Soc*, 89 (1967) 4305
3 D E Williams and C W Kocker, *J Chem Phys*, 52 (1970) 1480
4 D F van de Vondel and G P van der Kelen, *J Organometal Chem*, 55 (1973) 85
5 D F van de Vondel, *Doktoraatsthesis Gent*, 1964
6 E V van den Berghe, *Doktoraatsthesis Gent*, 1965
7 G van Hooydonk, *Licentiaatsthesis Gent*, 1966
8 T P Das and E L Hahn, *NQR Spectroscopy*, Academic Press Inc, New York, 1958, p 14
9 E A Lucken, *NQR Coupling Constants*, Academic Press, London and New York, 1969, p 139
10 See ref 9, p 129
11 See ref 8, p 142
12 M A Whitehead and H H. Jaffe, *Theor Chim Acta*, 1 (1963) 209
13 J Hinze and H H Jaffe, *J Amer Chem Soc*, 84 (1962) 540 .
14 See ref 9, p 264
15 E D Swiger and J D Graybeal, *J Chem Soc*, 5 (1965) 1464