An NQR Study of the Trichloride Ion. Evidence for Three-Center Four-Electron Bonding

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Abstract: The chlorine NQR resonance frequencies are reported for two trichloride salts, Ph_4AsCl_3 and Et_4NCl_3, as well as for Me_4NBrCl_2 and Me_4NICl_2. The charges on the chlorine atoms are calculated with the Townes and Dailey model. In the trichloride ion, the negative charge is split evenly between the two terminal atoms, while the central chlorine atom has a slight positive charge. The negative charge on the chlorine atoms increases as the central atom varies from Cl to Br to I. The charge distributions observed are consistent with a Rundle 3c-4e delocalized bonding scheme and are indicative of little or no d orbital contribution. The resonance frequencies show anomalous, and large, positive temperature coefficients. This is interpreted in terms of the effect of thermal motion of the organic cations on the EFG at the chlorine nuclei.

During the past several decades, numerous investigations of the properties of trihalide ions have been made.[1] They represent a convenient model to study an interesting type of binding: the three-center four-electron bond. A majority of the investigations have concentrated on the more stable species, such as the triiodide ion and ICl_2^-. However, more recently, there has been interest in some of the more unstable ions. Only very limited information about the molecular and electronic structure of the most unstable of all these ions, the trichloride ion, is available. Since this species is the most tractable of the nonfluorine-containing trihalides for semiempirical and *ab initio* molecular orbital calculations, this lack of information is distressing. For this reason, an NQR study of the trichloride ion was initiated. Simultaneously, a similar study of the $BrCl_2^-$ and ICl_2^- ions was undertaken, so that correlations between the behavior of the ions in the series ICl_2^-, $BrCl_2^-$, and Cl_3^- could be drawn. It is the results of the NQR investigations of these three ions which are reported here.

The NQR technique has proven to be a powerful tool for investigating the electronic structure of trihalide ions. The nuclei of all three elements, I, Br, and Cl, possess quadrupole moments whose resonance frequencies occur in regions which are readily detectable, although single crystal studies are necessary in order to determine asymmetry parameters for the Br and Cl nuclei.[2] However, the asymmetry of the valence electric field gradient (EFG) is expected to be small for the trihalide ions, and the lattice EFG often provides only a minor perturbation of the valence EFT. The observed frequencies, then, are transformed readily into charge densities for comparison with theoretical results.

In general, the trihalide ions may be regarded as an addition complex between a halide ion and a halogen molecule

$$X^- + YZ \longrightarrow XYZ^-$$

where X. Y, and Z represent halogen atoms. The stability of the ions in the solid state is dependent upon the cation employed. The ions are all nearly linear but may be asymmetric if the crystalline environment at the two ends of the ion are significantly different. The problem proposed by these systems to the theory of chemical valence is how two filled shell species can interact with each other to form stable chemical bonds. Two dichotic views have been popular: the stability has been attributed to outer d-orbital participation by Gillespie and others,[3] while Rundle has proposed the existence of delocalized three-center four-electron (3c-4e) bonds involving only s and p orbitals.[4] The results presented here will show the 3c-4e bond picture presents a more faithful representation of the experimental data.

The trichloride ion was first successfully prepared in 1923 by Chattaway and Hoyle by reacting gaseous Cl_2 with Et_4NCl.[5] More recently Evans and Lo reported its vibration spectrum, both ir and Raman, and also gave evidence for the existence of the Cl_5^- ion.[6] The data for the trichloride ion were interpreted in terms of a linear, symmetrical ion. The ratio between the stretching force constant K_1 and the bond interaction constant K_{12} was exceptionally high ($K_{12}/K_1 = 0.57$), which implies very weak Cl-Cl bonds. More recently, in a discussion of exchange effects in the nmr spectra of the $Cl^- + Cl_2$ system, Hall, *et al.*, predicted that the symmetric trichloride ion should have an NQR coupling constant in the range 116 ± MHz (central atom) and 51 ± 5 MHz (end atoms).[7]

Experimental Section

Table I lists the various compounds which were prepared, along with their melting points. All the compounds were prepared by the techniques of Chattaway and Hoyle. Listed below are the methods of preparation employed for the three types of trihalides studied.

$$[CH_3]_4NCl + Br_2 + Cl_2\ (g) \xrightarrow[0°]{CH_3OH} [CH_3]_4NBrCl_2\ (s)$$

$$[C_6H_5]_4AsCl\ (s) + Cl_2\ (l) \xrightarrow[\text{acetone}]{\text{Dry Ice}} [C_6H_5]_4AsCl_3\ (s)$$

$$[C_2H_5]_4NI + Cl_2\ (g) \xrightarrow[0°]{\text{glacial acetic acid}} [C_2H_5]_4NICl_2\ (s)$$

The trichloride ion is quite stable in solution; however, it is not possible to recover crystals from solution. The low temperature for the formation of the $(C_2H_5)_4NCl_3$ is necessary since the reacton is so exothermic that a melt is formed otherwise. For this reason the reaction was carried out at Dry Ice-acetone temperatures, using liquid chlorine. At room temperature the solid trichloride salts decompose slowly, losing Cl_2 gas.

The compounds were characterized by their melting points. Good agreement was obtained with literature results, although all of the compounds decompose upon heating, and as a consequence the melting points are not sharp. The arsonium salts were a pale yellow, the rest being bright yellow. All the compounds crystallized as needles with the exception of the Et_4NICl_2 which came down as very thin mica-like plates. The compound had the same form and melting point whether it was crystallized from methanol, ethanol, or acetic acid.

All NQR spectra were recorded on a Wilkes Model 1-A NQR spectrometer using powder samples. Spectra were recorded at both room temperature and liquid N_2 temperature for all compounds. The commercial low-temperature portion was modified in order to use a larger sample size with a better filling factor of the coils. Coils, larger than those supplied with the instrument, were enclosed in a brass container, which was immersed in a Dewar containing liquid nitrogen. The signal-to-noise ratio was enhanced by more than a factor or 2 in this manner. Nevertheless, S/N ratios

Table I. Melting Points

Compd	Mp, deg	Lit.,[a] deg
$(CH_3)_4NICl_2$	224–230	
$(C_2H_5)_4NICl_2$	98–99	98
$(n\text{-}C_3H_7)_4NICl_2$	144–147	145
$(n\text{-}C_4H_9)_4NICl_2$	54–58	
$(C_6H_5)_4AsICl_2$	233–237	
$(CH_3)_4NBrCl_2$	158–159	159
$(C_2H_5)_4NBrCl_2$	67–69	69
$(C_2H_5)_4NCl_3$	43–45	42–45
$(C_6H_5)_4AsCl_3$	195–200	

[a] Reference 5.

were low enough for some resonances that only ^{35}Cl resonances were clearly identifiable. In particular, for the high-frequency resonance in the trichloride salts, only one resonance signal was detected. Because of the frequency limitations of the coils, it could not be ascertained whether this was a ^{35}Cl or ^{37}Cl resonance. It was assigned as a ^{37}Cl resonance on the basis of calculated charge distributions.

All measurements were made using a time constant of 30 sec and a scan rate of 24 hr per coil. Each resonance was scanned at least twice before any attempt was made to measure the resonance frequency. Frequency measurements were made using a BC-221 frequency meter in conjunction with a grid dip meter. The errors in frequency are more a result of not being able to identify the center of the resonance than an error in the frequency measurement itself. Where the center of the resonance was well defined, the scan was stopped at the center and the frequency was measured. On the less well defined resonances, the strip chart was calibrated and the frequencies estimated at the location of the center of the resonance line. The range of frequencies searched at room temperature was 15–65 MHz and at liquid-nitrogen temperature was 17–53 MHz.

Results

The resonance frequency for a spin $3/2$ system is given by

$$\nu = (e^2Qq/4h)\sqrt{1 + \eta^{2/3}}$$

where Q is the nuclear quadrupole moment, q is the z component of the EFG, and η is the asymmetry parameter. Measured frequencies are given in Table II. Coupling constants were calculated assuming $\eta = 0$. This seems reasonable, since all known trihalide ions are linear and thus valence contributions to the EFG should be axially symmetric. Also, lattice contributions are usually small. NQR measurements on iodine-containing ions have confirmed that η is, indeed, negligibly small.[8]

For $(CH_3)_4NICl_2$, only a single ^{35}Cl resonance was observed, implying that the two terminal chlorine atoms are in identical crystallographic locations. However, for $(CH_3)_4NBrCl_2$, two resonances of nearly the same frequency were observed, indicating that the two chlorine atoms may be in slightly different crystallographic environments. The same is true of the resonance frequencies associated with the terminal chlorine atoms of the trichloride ions. The resonance arising from the central chlorine atom in the trichloride ion is at considerably higher frequency, so there is no ambiguity in its assignment.

The charges on the various atoms were calculated using the theory of Townes and Dailey.[9] The extra electron was assumed to lie in a p_z orbital (the z axis being defined as the molecular axis). It is reasonable to assume that charges so calculated are accurate to at least 5%, the major source of error being the neglect of the lattice contribution to the EFG. If the high-frequency resonance of the trichloride ion is assumed to be due to a ^{35}Cl resonance, a charge of −0.16 e is obtained for the central atom. This value is too large. If, instead, it is assumed to be a ^{37}Cl resonance, a more acceptable value of +0.07 e is obtained. This is in good agreement with what is observed in the triiodide and tribromide ions.

Discussion

Table III compares the experimental and theoretical charge distributions calculated for the trihalide ions. The striking feature is the near constancy of the charges on the central atom of the homonuclear ions and, for the symmetric ions, the constancy of charges on the terminal atoms. This behavior has been predicted by simple Hückel MO calculations on I_3^- and Br_3^-.[10] This fact, plus the actual values of the observed charges, provides strong support for the validity of the Rundle 3c-4e type bonding in these compounds. This approach, which neglects d orbitals to first order, predicts zero charge on the central atom and a charge of −0.50 e on each terminal atom, in very good agreement with the observed charges. Since d orbital participation should be more favorable for I than Cl, the charge distribution should be different in Cl_3^- than in I_3^- if d orbital participation was important. The 3c-4e approach has been corroborated by recent CNDO and *ab initio* calculations on Cl_3^-.[11] Both the CNDO and *ab initio* calculations reproduce the observed charge distribution very satisfactorily when d orbitals are omitted from the basis set. However, if d orbitals are included in the CNDO method, the central chlorine atoms obtain a negative charge, contrary to the NQR results obtained here. It should also be noted that the Hückel calculations mentioned previously[10] gave essentially zero charge on the central atom in Br_3^- and I_3^-.

For the series ICl_2^-, $BrCl_2^-$, and Cl_3^-, it is observed that as the electronegativity difference between the center and terminal atoms decreases, the charge on the end atom gradually becomes less, as one might expect. Thus, the iodine atom in ICl_2^- has a large positive charge, and the central chlorine atom in the trichloride ion is essentially neutral, while the charge on the terminal chlorine atoms decreases from −0.64 e for ICl_2^- to −0.50 e for Cl_3^-. The charges calculated for the trihalide ions, from the NQR frequencies, always add up to a little less than one electron, (due to neglect of the lattice contribution) and thus we expect the charge on the bromine atom to be +0.15 to +0.20 e in the $BrCl_2^-$ ion. This trend makes it clear that d orbitals do not play a dominant role in the bonding in this type of compound. The d orbitals, if they participated in bonding, would tend to equalize the charges. Also, it is generally argued that d orbital participation increases with increasing atomic number. This predicts charge distribution contrary to the experimental behavior. We thus feel that these NQR studies provide very compelling evidence against the necessity of d orbital participation in order to obtain a satisfactory description of the electronic structure of trihalide ions.

Temperature Dependence

One of the striking features of this study is the large positive temperature coefficient for the resonance frequencies of the terminal chlorine nuclei of the trichloride ion. Positive temperature coefficients are unusual, and the values observed here are a factor of 3 larger than other observed values. Table IV gives some representative values. The explanations given to account for the positive coefficients have involved the vibronic coupling of electronic states with larger EFG into the ground state wave function.[12,13] We are not satisfied with this explanation for the trichloride ion and propose instead that the anomalous dependence is due to thermal motion of the counterions in the lattice.

Supporting evidence for this explanation comes from NQR studies on a series of copper chloride salts.[14] In $KCuCl_3$, all the NQR frequencies have the normal negative temperature coefficients. However, in the isomorphous NH_4CuCl_3, the coefficients are all positive. The only rea-

Table II. Resonance Frequencies for ^{35}Cl Nuclei in Trihalide Ions

Compd	Temp, °K	Frequency,[a] MHz (^{35}Cl)	Atom	Charge	S/N
Atomic chlorine[b]		54.873		0	
$CsICl_2$[c]	298	19.86	M(I)	+0.36	
			E	−0.66	
$KICl_2$[c]	298	18.95	M(I)	+0.36	
			E	−0.65	
$(CH_3)_4NICl_2$	298	19.36 ± 0.03	E	−0.65	8
	77	19.72 ± 0.05	E	−0.64	4
$(CH_3)_4NBrCl_2$	77	24.00 ± 0.10	E	−0.56	1.5
	77	24.11 ± 0.04	E	−0.56	2
$(C_2H_5)_4NCl_3$	298	46.42 ± 0.01	M(^{37}Cl)	+0.07	3.5
	298	28.94 ± 0.007	E	−0.47	12
	298	28.83 ± 0.04	E	−0.47	5
	77	27.58 ± 0.02	E	−0.50	8
	77	27.47 ± 0.05	E	−0.50	3
$(C_6H_5)_4AsCl_3$	300	46.38 ± 0.01	M(^{37}Cl)	+0.07	3.5
	300	29.001 ± 0.007	E	−0.47	12
	300	28.86 ± 0.04	E	−0.47	5
	77	27.46 ± 0.02	E	−0.50	3

[a] The values listed are 1/2 of the coupling constants. [b] V. Jaccarino and J. G. King, *Phys. Rev.*, **63**, 471 (1951). [c] Reference 1c.

Table III. Comparison of Charge Distributions

		Middle atom		End atom	
Compd	Symmetry	Exptl	Calcd	Exptl	Calcd
NH_4I_3[a]	Asymmetric	0.06		−0.31, −0.75	
$(C_2H_5)_4NI_3$[a]	Symmetric	0.04	−0.01[b]	−0.49, −0.51	−0.49[b]
$CsBr_3$[c]	Asymmetric	0.06		−0.34	
$[(CH_3)_3NH]_2Br\cdot Br_3$[d]	Symmetric		−0.01[b]		−0.49[b]
$(C_2H_5)_4NCl_3$	Symmetric	0.07	0.07[e]	−0.50	−0.54[e]
$CsICl_2$[f]	Symmetric	0.36	0.12[b]	−0.66	−0.56[b]
$(CH_3)_4NBrCl_2$	Symmetric		0.05[b]	−0.56	−0.52[b]

[a] Reference 1a. [b] Reference 10. [c] G. L. Breneman and R. D. Willett, *J. Phys. Chem.*, **71**, 3084 (1967). [d] C. Romers and E. W. M. Keulemans, *Proc. Kon. Ned. Akad. Wetensch., Ser. B*, **61**, 345 (1958). [e] Reference 11. [f] Reference 1c.

Table IV. Temperature Dependence of ^{35}Cl NQR Resonances

Compd	dv/dt, kHz/deg	Compd	dv/dt, kHz/deg
K_2ReCl_6	+0.13	Et_4NICl_2	−1.6
K_2WCl_6	+0.44	Et_4NCl_3	+6.95
Pyridine ICl	+2.2	$(C_6H_5)_4AsCl_3$	+6.95
4-Methylpyridine ICl	+2.5		

sonable explanation is the one proposed above. In compounds of the type $(RNH_3)_2CuCl_4$, two resonances are observed, one with a positive, and one with a negative coefficient. Diffraction and nmr studies in this laboratory have shown that the RNH_3^+ ions are undergoing very extensive thermal motion. In these compounds, one type of chlorine atom is exposed to the RNH_3^+ group, the other type is part of a two-dimensional Cu–Cl layer. It seems reasonable to assume that the chlorine with the positive temperature coeffiient is the one exposed to the environment of the RNH_3^+ groups.

In order to examine possible sources of the temperature dependence, we write down various contributions to the EFG. As before, the asymmetry parameter is assumed to be small and will be neglected. Thus, in terms of the z component of the EFG tensor

$$q = q_v^0 + q_v^T + q_l^0 + q_l^T$$

where the subscripts v and l refer to the valence and lattice contributions to q, respectively, and the superscripts 0 and T refer to the values of q at absolute zero and the temperature-dependent contributions to q, respectively.

It is the term q_v^T which is assumed to give rise to the usual negative temperature coefficient of the resonance frequency. This term averages q over various excited vibrational states, *i.e.*

$$q_v^T = \sum^{\infty} q_v^i \exp(-E_{v,i}/kT)$$

where q_v^i is the contribution to q_v from the ith vibrational excited state of the trichloride ion and $E_{v,i}$ is the energy of that state. It is supposed that q_v^T opposes q_v^0 since the thermal motion will tend to average out the EFG. Hence, this gives rise to a negative temperature coefficient. Similarly

$$q_l^T = q_l^i \exp(-E_{l,i}/kT)$$

where q_l^i is the contribution to q from the ith vibrational excited state of the lattice and $E_{l,i}$ is its energy. Again, q_l^T should oppose q_l^0 and hence be of the same sign as q_v^0 since q_l^0 opposes q_v^0. Thus, q_l^T will give rise to a positive contribution to the temperature coefficient. Normally, the terms in q_v dominate those in q_l. However, when the lattice contains organic cations capable of undergoing extensive thermal motion at low temperatures, q_l^T may become dominate over q_v^T. It is felt that this is the case for the trichloride salts.

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Electrostatics and the Chemical Bond.[1]
I. Saturated Hydrocarbons

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Abstract: A model of the C-H bond is proposed in which each H atom in an alkane bears a formal charge of $+0.278 \times 10^{-10}$ esu (0.0581 electronic charge) and each C atom a neutralizing negative formal charge. Summing up all of the electrostatic interactions in an alkane due to these formal charges gives rise to a net stabilizing electrostatic energy for each alkane $E_{el}(C_nH_{2n+2})$ which depends only on the geometrical structure. This is then shown to lead to a surprisingly simple formula for the standard enthalpies of formation for alkanes given by: $\Delta H_f{}^\circ{}_{298}(C_nH_{2n+2}\text{ gas}) = -2.0(n+1) - 0.5 + E_{el}(C_nH_{2n+2})$. This fits the observed values of $\Delta H_f{}^\circ{}_{298}$ for all the n-alkanes to n-C_7H_{16} and for the branched alkanes up to C_5H_{12} to ±0.2 kcal/mol. It is also shown that the observed dipole moments of propane and i-C_4H_{10} agree well with the formal charge distribution if proper account is taken of mutual group polarization. It is further shown that the barrier to rotation about single bonds and the unfavorable gauche conformations in hydrocarbons cannot be quantitatively accounted for by electrostatic interactions. The rotation barrier, the gauche interaction, and the anomalously large C-C-C and C=C—C angles in alkanes and olefins are discussed instead in terms of a purely van der Waals H···H interaction, predominantly repulsive.

The standard heats of formation of compounds from their elements ($\Delta H_f{}^\circ$) have been shown to follow more or less accurately simple additivity laws.[3] The law of group additivity is capable of reproducing known values of $\Delta H_f{}^\circ$ for most species to within the experimental uncertainty when small (*i.e.*, ≤1.0 kcal) corrections are made for recognizable steric effects. A few compounds of very high polarity, such as CH_3CF_3, CH_2CCl_2, and the cyanocarbons, deviate from group additivity by amounts which may be as large as 8-9 kcal/mol, but such examples are so far relatively rare. In all such cases, it has been proposed that the deviations arise from polar interactions[4-6] and relatively simple electrostatic models have been used to rationalize these deviations.[7]

The law of group additivity is based on the decomposition of molecular properties into contributions from groups, a group being defined as a polyvalent atom together with all of its atomically bound neighbors (*e.g.*, C_2H_6 is composed of two identical groups, C-(C)(H)$_3$, carbon bound to three H atoms, and one C atom). The fact that group additivity works so well, particularly for the not-too-polar compounds and radicals,[3c] can be rationalized by the deduction that interactions between next-next-nearest neighbors is very small. The group, by definition, includes all interactions between nearest neighbors (bonded atoms) and next-nearest neighbors (1,3-nonbonded interactions).

The law of bond additivity, which is the next simpler stage in the hierarchy of additivity laws, uses a decomposition of molecular properties into sums of contributions from bonds. Average deviations of observed and calculated $\Delta H_f{}^\circ$ with this law are about ±3 kcal for nonpolar compounds, ±6 kcal for polar compounds, and up to ±12 kcal in extreme cases. It is the purpose of the present paper to examine the theoretical basis for these differences in accuracy between the laws of bond and group additivity and to present a very simple electrostatic model which can account quantitatively for the interactions responsible for the deviations observed.

I. The Methane Problem

The alkanes are considered the least polar of all organic compounds and, consequently, they should be expected to show the smallest deviations from simple bond additivity laws. In actual fact, they do follow reasonably well simple bond additivity schemes, but the observed deviations are not small. This is illustrated by the data in Table I showing values of $\Delta H_f{}^\circ$ for compounds in the series $CH_n(CH_3)_{4-n}$.

If these methyl-substituted methanes followed the law of bond additivity, then the change in $\Delta H_f{}^\circ$ on successive CH_2 insertion (*i.e.*, CH_3 for H substitution), given by the column labeled Δ_1, should be a constant. This constant would be equal to the contribution of one C-C bond plus two C-H bonds gained by the CH_2 insertion. In fact, we observe that Δ_1 becomes progressively more negative indicating progressively greater stability with increasing branching. This has been a somewhat unexpected finding, since one might have intuitively expected that the steric crowding of the methyls would lead to decreased stability. A comparison of the $\Delta H_f{}^\circ$ values for i-C_4H_{10} with n-C_4H_{10} and of neopentane with n-C_5H_{12} shows similarly that the branched compounds are 2.0 and 5.0 kcal/mol more stable respectively than their straight-chain isomers. This paradoxical result can be called "the methane problem."

The stability of the branched compounds might be ascribed to a general van der Waals' attraction of the CH_3 groups. However, the fact that the more stable form of n-butane occurs with the terminal-CH_3 groups trans to each other, rather than gauche, would conflict with such a hypothesis.

The methane problem is by no means unique to hydrocarbons, since we find similar behavior in the fluorinated methanes (Table II). We note in this case a much more pronounced increase in stability on F/H substitution than for CH_3/H substitution as seen by comparing the columns labeled Δ_1.