Chlorine Substituted Acetic Acids and Salts. Effect of Salification on Chlorine-35 NQR *

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Z. Naturforsch. **51a,** 611–619 (1996); received October 10, 1995

The NQR of a quadrupolar probe nucleus is often used to investigate the effect of substituent in molecules. The inductive effect, based on a partial charge migration along the molecular skeleton is the only one present in saturated aliphatics, the conjugative effect appearing in conjugated molecules, especially aromatics. As the stepwise charge migration mechanism, formerly used to explain the inductive effect, is now believed obsolete, we have wanted to reexamined the case of chlorine substituted acetic acids and salts. The data in literature was extended by observing resonances and determining NQR frequencies in several acids and salts. The present analysis of the salification of mono-, di- and tri-chloroacetic acids, which is equivalent to a deprotonation or the substitution of the acid hydrogen by a negative unit charge, shows that a model based on the polarization of the chlorine atom(s) by the carboxyle group is consistent with experimental results: the polarization energy appears to be proportional to the NQR frequency shifts; experimental data show a correlation between the NQR frequency shifts accompanying salification and the variations of the intrinsic acidity measured in the gas phase; this, in turn shows that there is a proportionality between the polarization energy and the variations in the acid free enthalpy of dissociation. From the comparison between fluorine, chlorine, bromine and iodine, it also appears that an alternative mechanism, the polarization of the carboxyl group by the halogen, would be important only in the case of the fluoroacetic acid.

Key words: ^{35}Cl NQR; Chloroacetic acids; Substituent effect; Inductive effect; Polarization; Intrinsic acidity.

Introduction

In molecules, NQR frequencies depend, via the electric field gradient tensor, on the electric charge distribution around the resonant nuclei, and they have extensively been used for analyzing bonding and substituent effects.

Among the first compounds studied in the early days of NQR spectroscopy are the chloroacetic acids studied by Harry C. Allen in 1952 [1]. The chlorine NQR frequencies in the mono-, di- and tri-chloroacetic acids increase with the number of chlorine atoms in the acid. This increase in frequency is explained as resulting from the electron attraction of the chlorine atom: the substitution of another chlorine atom on the C_2 carbon atom in the molecule reduces the ionic character of the chlorine atoms(s) already present and increases the NQR frequency.

At the same time Allen also reported that the chlorine NQR in sodium mono-chloroacetate at a frequency, 34.794 MHz, is much lower than in the acid, 36.280 MHz. The decrease in frequency observed when passing from the acid to the salt is explained by an increase of the ionic character of the chlorine atom, produced by a stepwise migration of the negative electric charge on the carboxyle group.

The stepwise charge migration model for the inductive effect is now becoming obsolete since theoretical calculations, as well as experimental facts, do not support this model [2]. In particular, ^{13}C NMR shows an electron depletion on the intermediate carbon atom, contrary to the increase expected from the model of a charge migration decreasing with increasing distance from the inductive charge.

Before reexamining the situation, we first tried to get new experimental results in order to have a wider and more reliable set of data as a basis for the discussion. We then tried to develop and propose a new description, based on the polarization of the chlorine atom by the carboxyl group, to interpret the downward chlorine NQR frequency shift observed upon

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* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

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0932-0784 / 96 / 0500-0611 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

deprotonation when passing from the acid to a salt; more precisely, the salification of an acid can be considered as a deprotonation process:

$$\mathrm{RCOOH} \rightarrow \mathrm{RCOO^-} + \mathrm{H^+},$$

and, in turn, the deprotonation can be considered as the substitution of an elementary negative charge for the hydrogen atom in the acid group.

Chlorine-35 NQR

Let us just remember that the NQR frequency for a $I=3/2$ spin is given by the relation (115), Chapt. 3 in [3]

$$\nu_Q = \frac{1}{2}\frac{e^2 Qq}{h}\left(1+\frac{\eta^2}{3}\right)^{1/2} \tag{1}$$

where ν_Q is the NQR frequency, eQ the chlorine quadrupole moment, eq the main component of the electric field gradient tensor (efg), η the efg asymmetry parameter and h the Planck constant.

As the asymmetry parameter, η, cannot be easily obtained from experiment and its value, when it has been measured, appears to be small in the kind of compounds studied, we will make the approximation

$$\nu_Q = \frac{1}{2}\frac{e^2 Qq}{h}. \tag{2}$$

In the frame of the Townes and Dailey model [4] the value of the electric field gradient, $e q_{\mathrm{mol.}}$, is related to the atomic electric field gradient, $e q_{\mathrm{at.}}$, and the populations of the different atomic orbitals of the bonding shell on the chlorine atom as well as the s-p hybridization of the orbitals in the bond direction. Here also, we will use an approximation neglecting the hybridization and the elctric field gradient thus reduces to

$$e q_{\mathrm{mol.}} = e q_{\mathrm{at.}}(2-a), \tag{3}$$

where a is the population of the p_z orbital along the bond direction. The populations of the p_x and p_y, orbitals are taken to be 2.

As a result of relations, (2) and (3), the variations of $\Delta\nu$, $\Delta q_{\mathrm{mol.}}/q_{\mathrm{at.}}$, and Δa, are proportional.

Experimental Results and General Comments

The experimental data available in the literature when this study was started are shown in Table 1.

Table 1. Average ^{35}Cl NQR frequencies in chlorinated carboxylic acids and their salts, at 77 K, as found in literature.

Compound	$\nu_{\mathrm{av.}}$/MHz	References
Acids		
monochloroacetic acid	36.280	[5]
dichloroacetic acid	38.393	[5]
trichloroacetic acid	40.124	[5]
3-chloropropionic acid	33.953	[6]
Monochloroacetates		
Na^+	34.794	[5]
K^+	34.11	[7]
Rb^+	33.82	[8]
Dichloroacetates		
K^+	36.525	[7]
Rb^+	36.40	[7]
Trichloroacetates		
Li^+	39.65	[8]
Li^+, H_2O	39.006	[7]
Na^+	38.89	[8]
Mg^{++}, 6 H_2O	39.17	[8]
Ca^{++}, 4 H_2O	39.09	[8]
Cs^+, $\times H_2O$	38.11	[9]

In each of the series appearing in Table 1, there is only a small number of compounds; for example, considering sodium salts, the mono-chloroacetate is shown but not the di- and tri-chloroacetates are shown the corresponding anhydrous salts are missing.

This led us to search for more resonances and the results obtained are presented in Table 2.

Unfortunately, some difficulties were encountered.

We could not obtain any complete series: Many compounds are not commerically available and have to be synthetized but some of them are difficult to synthetize because they hydrate or are difficult to extract from the solvent used for the preparation. Several searches were unsuccessful; in particular, no chlorine NQR signal was found in potassium trichloroacetate, prepared in completely anhydrous conditions, starting from potassium tertbutylate in anhydrous benzene. Several samples give quite a broad spectrum limiting the meaning of the frequencies measured. The NQR spectrum in a given compound is generally composed of several lines corresponding to chemically and/or crystallographically nonequivalent sites of the resonant nucleus. In most of the compounds considered in this study, the chlorine NQR spectra contain several resonance lines; in Table 1, which shows results found in literature, only average frequencies are reported when several resonances were observed while, in Table 2, where new results found in this study are reported, all frequencies

Table 2. ^{35}Cl NQR frequencies in chlorinated carboxylic acids and their salts, at 77 K, as obtained in the present work. When the spectrum consist of a single line, its frequency is shown in the average frequency column at right.

Compound	ν/MHz		$\nu_{av.}$/MHz
Acids			
4-chlorobutyric acid			32.857
5-chlorovaleric acid			33.546
2-chlorosuccinic acid			36.034
Monochloroacetates			
Ba^{++}, H_2O	33.423	33.196	33.310
Ca^{++}, $2H_2O$	34.39	34.77	34.58
Dichloroacetates			
Ba^{++}	35.720	36.995	
	37.590	37.850	37.039
K^+	36.392	36.632	36.512
Na^+			37.0*
NMe_4^+			35.8*
Trichloroacetates			
Ba^{++}	38.187	38.541	
	38.625	38.928	
	39.226	39.494	38.833
NMe_4^+	37.504	37.615	
	37.733	37.841	37.673
3-chloropropionate			
Ba^{++}			32.68

* Central frequency of a broad spectrum extending over more than one megahertz.

are shown together with the corresponding average values.

As a result, a greater number of terms are now available; the most complete series is that of the barium salts, although the chloroacetate is a monohydrate. We tried to summarize the data available for discussion by showing, in Table 3, which compounds have or have no reported resonances.

Acids:

As a first comment, it can be observed that the carboxyl group effect on the chlorine resonance in the chloroacetic, 3-chloropropionic, 4-chlorobutyric and 5-chlorovaleric acids decreases quite rapidly with the distance between the chlorine atom and carboxyl group. This is clearly seen when comparing the frequencies in the chlorinated acids with those in the primary chlorides,

chloroacetic acid	36.280 MHz,
3-chloropropionic acid	33.65 MHz,
4-chlorobutyric acid	32.587 MHz,
5-chlorovaleric acid	33.546 MHz,
methyl chloride	34.023 MHz,
ethyl chloride	32.704 MHz,
propyl chloride	32.968 MHz,
butyl chloride	33.255 MHz.

Besides the couple methyl chloride – chloroacetic acid, with a frequency difference of 2.25 MHz, another significant difference, although a little less than 1 MHz, 0.68 MHz, is seen in the case of 3-chloropropionic acid. The increase in frequency observed between 5-chlorovaleric and 4-chlorobutyric acids is quite probably due to the corresponding phenomenon observed for other physical properties of nonbranched chlorinated hydrocarbons. An interesting compound for this analysis would have been 3-chloropivalic acid, but, unfortunately, no resonance was found in this compound.

The question may arise of a possible conformational effect on the frequency in chloroacetic acid.

The most favoured conformation for monochloroacetic acid is that in which the carboxyl group is

Table 3. Summary of the available data on chloroacetic acids and salts, and, below, of the searches made during this work.

	mono-	di-	tri-
H^+	Lit.	Lit.	Lit.
Li^+	–	–	Lit. ,$3H_2O$ Lit.
Na^+	Lit.	New	Lit.
K^+	Lit.	Lit.	Uns.
Rb^+	Lit.	Lit.	–
Cs^+	–	–	, $\times H_2O$ Lit.
NMe_4^+		New	New
Be^{++}	–	–	–
Mg^{++}	–	–	,$6H_2O$ Lit.
Ca^{++}	,$2H_2O$ New	–	,$4H_2O$ Lit.
Sr^{++}	–	–	–
Ba^{++}	,H_2O New	New	New

Lit. = literature available data,
New = newly observed resonance(s),
Uns = unsuccessfully searched,
– = not found in literature.

Unsuccessfully searched compounds:
3-chloropivalic acid, potassium trichloroacetate, s-benzyl thioüronium chloropivalate, sodium 3-chloropropionate.

Other acids analyzed:
3-chloropropionic acid, 4-chlorobutyric acid, 5-chlorovaleric acid, 2-chlorosuccinic acid.

Other salts analyzed:
barium 3-chloropropionate, benzylthioüronium 3-chloropropionate.

eclipsed by the C–Cl bond [10]. However, molecular mechanics calculations [11] show that the conformation where the C–Cl bond lies perpendicular to the carboxyl plane is only slightly less stable (240 cal · mole^{-1}). In this respect, it was interesting to consider the chlorine resonance frequency (36.034 MHz) in 2-chlorosuccinic acid which differs from other α-halogenated acids in that its C–Cl bond is both perpendicular to the carboxyl group [12] and longer (1.815 Å) than in, for example, chloroacetic acid (1.759–1770 Å), which is similar to what is observed with the *anomeric* effect. Does this bond orientation have an influence on the NQR frequency? A possible rough approach is to consider known resonance frequencies and use an additivity rule. For an example, replacing a hydrogen atom of the chloromethane molecule by a carboxyl group increases the chlorine resonance frequency by 2.25 MHz and this acid has an eclipsed conformation. The same operation on 3-chloropropionic acid would produce a 2-chlorosuccinic acid molecule with an eclipsed conformation. The corresponding resonance frequency, as calculated from the additivity rule, would then be $33.65+2.25$ MHz $=35.90$ MHz which is very close to the actual value, 36.034 MHz. This simple calculation shows that the conformation does not have a significant effect on the chlorine NQR frequency. The calculation at the STO-3G level [2] shows that the 3p population in the bond direction is slightly higher, by 0.03 electron, than in chloroacetic acid. The situation is in fact different from that in carbohydrates [13], where the carbon bearing a chlorine atom is adjacent to the oxygen, then permitting a significant overlap between oxygen and chlorine nonbonding orbitals.

Salts:

The frequency dispersion for most of the salts studied does not exceed 0.3 MHz, except for barium dichloroacetate (2 MHz) and trichloroacetate (1.3 MHz). The dispersion for the mono-, di- and trichloroacetic acids, as found in [5], is equal to 0.3, 0.8 and 0.5 MHz, respectively.

The high dispersion observed in some salts is not explained. Consideration of the effect of the crystalline field produced by ionic charges in the salt cannot be used because some acids, which are not ionized, also have dispersion of the same order of magnitude. The analysis of the dispersion is not straightforward; in the special case of calcium chloroacetate, with known structure [14] there are two anionic units in the crystallographic unit cell, in one of which the chlorine atom is far from the neighbouring cation while the second is as close as 3.036 Å suggesting, according to the authors of the crystallographic study, some interaction. In spite of this dissymmetry in the chlorine atom environments the NQR frequencies, 34.39 and 34.77 MHz, are not very different from each other compared to the dispersion observed in barium chloroacetates.

Discussion

Substitution in a chlorinated molecule causes a shift in the chlorine NQR frequency as compared to the unsubstituted molecule. The measurement of the shift allows an estimation of the corresponding charge displacement. A puzzling fact is that in some cases the shifts appear to be consistent with an obsolete mechanism for the inductive effect, that is the stepwise migration of the charge from atom to atom in a saturated molecule. For instance, the regular decrease of the chlorine NQR frequency in the series chloromethane, chloroethane, 2-chloropropane, 2-chloro-2-methylpropane, could be interpreted as a result of the accumulation of "electron donating" groups on the carbon bearing the chlorine atom. However, this interpretation is incorrect [15].

Acid Strength, Inductive Effect and Intrinsic Acidity

The first attempt to build a *quantitative theory of reactivity* was developed for *aromatic compounds.* Later on, the theory was extended to *aliphatic acids* in *aqueous solution* and based on the comparison of pK_a's which are proportional to the free enthalpy of dissociation in these conditions. Each substituent was characterized by an "inductive constant" which, together with pK_a was used as a basis to discuss the relation between the NQR frequency of a chlorine atom and the nature of the attached radical [16]. However, from its definition, the inductive effect is a property of an isolated molecule, while acidity in water is strongly influenced by the difference in solvation of the neutral molecule and the anion. Accordingly, the ordering of carboxylic acids by their values is quite different from that resulting from the dissociation free enthalpies in the gas phase. Thus, pK_a's and like quantities cannot be used as a basis for the discussion of an intrinsic effect, independent of the environment, such as electric field gradient at the sitet of an atomic nucleus.

Taft and Topsom [17] modified their theory by introducing new parameters which led to acceptable values for the dissociation free enthalpy of fluoro- and chloroacetic acids. We prefer to use experimental values rather than calculated parameters. Let us call $\Delta G^0(\mathrm{CH_3})$ and $\Delta G^0(\mathrm{R})$, respectively, the free enthalpy variations in reactions (4) and (5):

$$\mathrm{CH_3COOH} \rightarrow \mathrm{CH_3COO^-} + \mathrm{H^+} \quad \Delta G^0(\mathrm{CH_3}), \tag{4}$$

$$\mathrm{RCOOH} \rightarrow \mathrm{RCOO^-} + \mathrm{H^+} \quad \Delta G^0(\mathrm{R}). \tag{5}$$

We will use the differences $\Delta\Delta G^0 = \Delta G^0(\mathrm{CH_3}) - \Delta G^0(\mathrm{R})$ to characterize intrinsic acidities.

The NQR Frequencies of the Salts of Chlorinated Acids

It is well known that the increase of intrinsic acidity, accompanying the substitution of halogen atoms in the radical R of an acid R-COOH, is explained by a relative stabilization of the anions by the halogen atoms. In other words, there is an interaction between the carboxylic group and the halogen atom(s) which is an intrinsic property of the molecule and a primary cause of the NQR frequency variation.

As NQR measurements are made on crystals, in the presence of the cations and other anions, the contribution of the crystalline field resulting from all other ions in the crystal and depending on the crystal structure, adds to the electric field produced by the carboxylic group on the chlorine atom(s). This "crystal effect" thus appears as a perturbation of the primary, intraionic effect of the carboxyl group on the halogen frequency. Biedenkapp and Weiss [8] tried to determine its magnitude from frequency measurements in a series of salts and complexes of trichloroacetic acid.

To measure resonance frequencies in the same conditions as intrinsic acidities, the anion should be separated from other ions by an infinite distance. Practically, the separation can be increased by using large cations such as cesium or tetramethylammonium cations. In Table 4, the salts are arranged in order of decreasing NQR frequencies and it is seen that this order is also that of increasing cationic radii; this behaviour is clearly seen in Fig. 1 which summarize the contents of the table.

In the trichloroacetic group, and for divalent cations, the order is $\mathrm{Mg^{++}}$, $\mathrm{Ca^{++}}$, $\mathrm{Ba^{++}}$, although these cations show different hydration. For monovalent cations, the known resonance frequencies of the mono- and dichloroacetates decrease in the order $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Rb^+}$, and those of the trichloroacetates in the order $\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{Cs^+}$. The resonance of the lithium salt trichloroacetate monohydrate is very close to that of the sodium salt, but this may be a consequence of the water molecule. These observations led us to examine the salts of the bulky tetramethylammonium cation, with a Van der Waals radius of the order of 300 pm. It was not possible to make determinations on the chloroacetate which is a low melting and very hygroscopic compound. The physical properties of the dichloroacetate are more favorable and the trichloroacetate is a high melting solid, poorly soluble in organic solvents. As expected, the resonances of these salts are, by far, the lowest we have observed in the two categories.

Table 4. Comparison between average ^{35}Cl NQR frequencies ($\nu_{\mathrm{av.}}$) in chlorinated carboxylic acids and their salts, at 77 K, and cationic radii (*r*).

Compounds	$\nu_{\mathrm{av.}}$/MHz[a]	r/pm[b]
Chloroacetates		
$\mathrm{Na^+}$	34.79	97
$\mathrm{Ca^{++}, 2H_2O}$	34.58	99
$\mathrm{K^+}$	34.11	133
$\mathrm{Rb^+}$	33.82	147
$\mathrm{Ba^{++}, H_2O}$	33.31	134
Dichloroacetates		
$\mathrm{Ba^{++}}$	37.04	134
$\mathrm{Na^+}$	37.0*	97
$\mathrm{K^+}$	36.53	133
$\mathrm{Rb^+}$	36.40	147
$\mathrm{NMe_4^+}$	35.8	300
Trichloroacetates		
$\mathrm{Li^+}$	39.65	68
$\mathrm{Mg^{++}, 6H_2O}$	39.17	72
$\mathrm{Li^+, H_2O}$	39.01	68
$\mathrm{Ca^{++}, 4H_2O}$	39.09	99
$\mathrm{Na^+}$	38.89	97
$\mathrm{Ba^{++}}$	38.83	133
$\mathrm{Cs^+, \times H_2O}$	38.11	168
$\mathrm{NMe_4^+}$	37.67	300

* Central frequency of a broad spectrum extending over more than one megahertz.

[a] compounds are in order of decreasing NQR frequency;

[b] radii for uncomplexed cations.

The Polarization Contribution to the Anion Stabilization

The words "polarizability" and "inductive effect" are often quoted in qualitative interpretations of the intrinsic acidity scale [18].

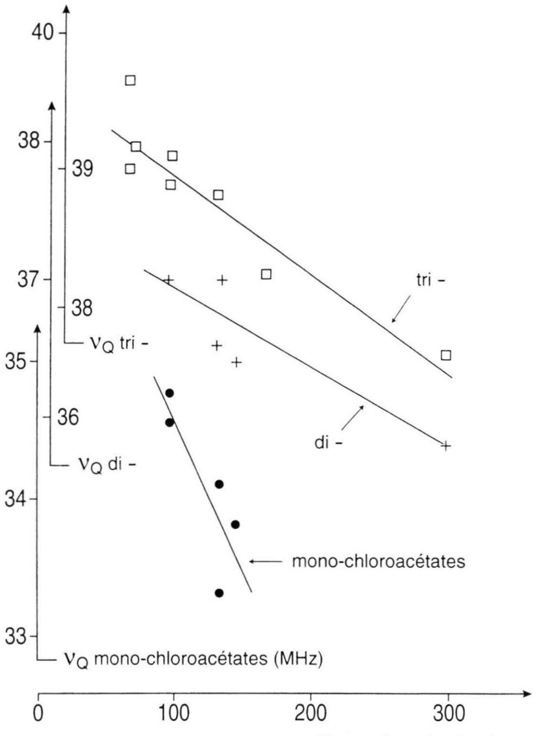

Fig. 1. Relationship between NQR frequencies in salts of mono- di- and trichloro-acetic acids and the radii of the cations.

Here, to analyse the experimental data in a semi-quantitative manner, we will use the atomic polarizabilities, α's, of the halogen atoms; these polarizabilities are physically well-defined and their values can be found in the Tables of constants [19]. Then, we consider the electrostatic energy related to this polarization as a term in the stabilization of the anion. This energy, ΔW, is given by

$$\Delta W = \frac{1}{2} \alpha E^2, \tag{6}$$

where E is the electrostatic field at the site of the halogen atom and α its atomic polarizability.

The next step will be to show that α may appear in the difference of the electric field gradients at the site of the halogen atom, in the neutral acid molecule and the carboxylate anion. The systematic analysis of halogen NQR frequencies in halogenated hydrocarbons lead to the conclusion that the efg seen by a halogen nucleus in the molecule R X may be described using a product of two factors, f_X and f_R, f_X being the polarizability of the halogen X and f_R the polarizing power of the radical R (see [3], p. 198):

$$e^2 Q q_{RX} = e^2 Q q_0 (1 + f_X f_R). \tag{7}$$

Comparing the frequencies for two radicals R1 and R2 one gets

$$\frac{\Delta e^2 Q q}{e^2 Q q_0} = \frac{\Delta q}{q_0} = f_X (f_{R1} - f_{R2}) \tag{8}$$

Application to the CH_2XCOOH/CH_3X series, where X = F, Cl, Br, and I, shows clearly that the differences $\Delta q/q_0$ should be proportional to f_X, and using α's for f_X, it is seen, from Table 5 and in Fig. 2 that the experimental points are well on a straight line, show-

Table 5. Dependence of $(\Delta q)/q_0$ upon the atomic polarizability, α, of the halogen[a]

Halogen	α/Å^3	10^3; $\Delta q/q_0$	
		Found	Calculated[b]
Chloroacetates			
F	0.557		11.4
Cl	2.15	41.3	40.3
Br	3.05	54.9	55.8
I[c]	5.35	94.9	96.7

[a] $\Delta q/q_0$ is the difference between the electric field gradients at the nucleus of the halogen atom in CH_2X-COOH and CH_3X.

[b] With help of the formula $\Delta Sq/q_0 = 1.55 + 17.78$ (a/Å^3).

[c] From Kojima et al, [20]; for iodine,

$$\frac{\Delta q}{q_0} = \frac{20}{3} \frac{\Delta \nu}{2292.712}.$$

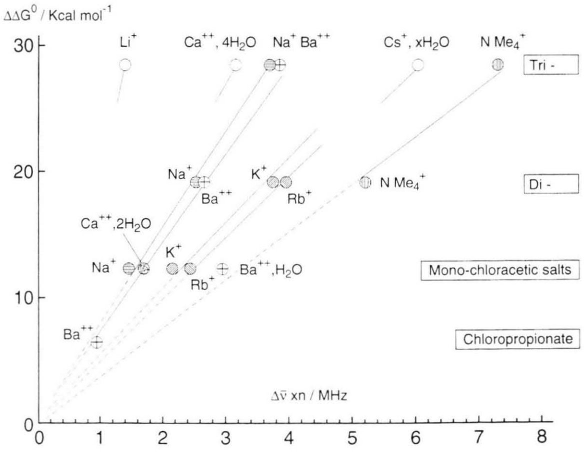

Fig. 2. The linear relationship observed between the efg shifts, $\Delta q/q_0$, and the atomic polarisabilities α.

ing that taking α's for f_X is quite acceptable; the energies corresponding to the action of the $-COOH$ group on the chlorine are then proportional to the α's and the $\Delta q/q_0$'s. If more than one halogen atom is present in the molecule, the total interaction energy would be the sum of the individual contributions, i.e. $n\,\Delta q/q_0$, n being the number of halogen atoms.

As we do not precisely know what is the actual contribution of the halogen polarization to the stabilization energy of the anion in the series of chlorinated compouonds studied, we will, as a first approach, compare the $n\,\Delta q/q_0$ or, for the sake of convenience, $n\,\Delta \nu_{av.}$ to the differences $\Delta\Delta G^0$, at 300 K, between the gas phase dissociation energies, ΔG^0, in the chloroacetic acids and the corresponding salts (Fig. 3); subscript av., for "average", refers to cases where the spectrum contains several lines due to the presence of inequivalent crystalline sites. The $\Delta\Delta G^0$ values, as they result from the ΔG^0 quoted in literature, are respectively 12.5, 19.6, and 28.3 kcal mol^{-1} for the mono- [18], di- [18] and trichloroacetic [21] acids. The $\Delta\Delta G^0$ value for 3-chloropropionic acid is 6.1 kcal mol^{-1} [18].

In the diagram, Fig. 3, a regular behaviour is observed. Points corresponding to one cation are approximately located on a straight line passing through the origin, thus indicating a proportionality between $\Delta\Delta G^0$ and $n\,\Delta \nu_{av.}$. One of the largest inorganic cations in this diagram is rubidium with a 147 pm ionic radius. We have no value for rubidium trichloroacetate. Extrapolation by extending the straight line yields $n\,\Delta \nu_{av.} = 5.8$ MHz, slightly less than the 6.0 MHz value observed for the hydrated cesium trichloroacetate and much less than the 7.4 MHz value observed for the trichloroacetate of tetramethylammonium, the cationic radius of which is of the order of 300 pm. Considering that, in this last salt, we have the best available equivalent to an isolated anion, the best slope would then be 0.226 MHz/kcal mol^{-1}.

Comparison of Monohaloacetic acids

The values of $\Delta\Delta G^0$ for the monohalogenoacetic acids, CH_2XCO_2H, which are, for X = fluorine to iodine 9.9, 12.5, 13.3, and 13.8 kcal mol^{-1} respectively, increase much less rapidly than the corresponding atomic polarizabilities, 0.557, 2.15, 3.05, and 5.35 Å^3 [19]. This difference can be understood by considering the contribution of two effects of opposite trends: the polarization of the halogen by the carboxylate and the "field inductive effect" or FIE, decreasing from fluorine to iodine [18]. No mechanism seems to have been proposed for the latter effect; it may be considered as a stabilization effect due to the polarization of the highly polarizable carboxylate ion by the negative charge on the halogen atom. The polarization of the carboxylate ion by the halogen is quite normal after having considered the polarization of the halogen by the carboxylate.

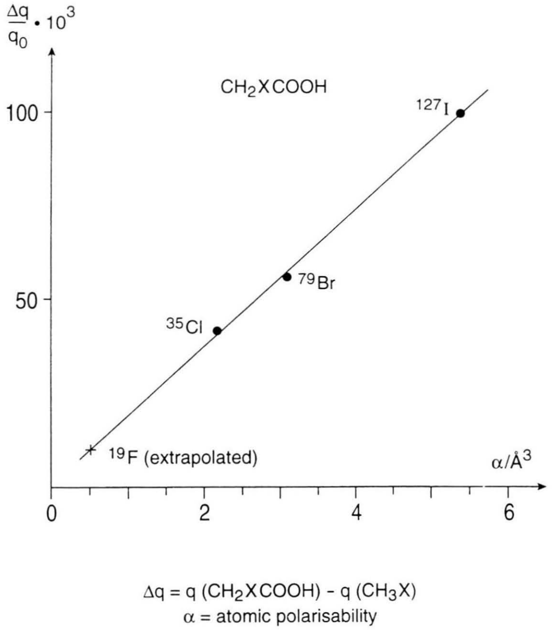

Fig. 3. The variations of the dissociation enthalpy, between chloroacetic acids and acetic acid, versus the NQR frequency shifts, between the salts and the parent acid, times the number of chlorine atoms.

To develop this idea we will examine the fluoroacetate anion, where the effect is surely important. As a basis for the discussion, we shall use molecular orbital calculations reported in [2]. Table 6 contains some of the most significant results. These calculations predict, for fluoroacetate anion, an ionization potential of 4.8 eV, much less than the 11.4 eV found for the undissociated fluoroacetic acid. In addition, the net atomic charge (NAC) on the fluorine does not vary much between the acid and the anion: the stabilization term corresponding to the action of the fluorine on the carboxylate group results from the increase in the polarizability of this group rather than from an increase of the fluorine charge.

Table 6. Some net atomic charges and their variations, as calculated at the STO 6-31 G level, for acetic, chloroacetic and fluoroacetic acids.

	Acetic acid		Fluoroacetic acid		Chloroacetic acid	
	N.A.C.[a]	Δ(N.A.C.)[b]	N.A.C.	Δ(N.A.C.)[b]	N.A.C.	Δ(N.A.C.)[b]
C(1)	0.715	−0.020	0.660	−0.001	0.760	−0.012
Carbonyl oxygen	−0.545	−0.235	−0.503	−0.237	−0.519	−0.196
Hydroxyl oxygen	−0.715	−0.064	−0.702	−0.071	−0.704	−0.006
C(2)	−0.521	0.018	−0.100	−0.027	−0.578	0.070
H or halogen	0.208	0.084	−0.426	−0.056	−0.056	−0.208
(C)-H	0.211	−0.087	0.212	−0.080	0.266	−0.073
(O)-H	0.436		0.447		0.451	
Proton affinity of the anion (kcal mol^{-1}):	379.5 (Exp.: 348.5)		350 (Exp.: 338.6)		344 (Exp.: 336.0)	

[a] Net atomic charge.

[b] Variation on deprotonation.

The charge on the halogen can be written as λe where e represents the elementary charge. The field produced by this charge is proportional to λ and the corresponding polarization energy to $\alpha' \lambda^2$, where α' is the polarizability of the $-COO^-$ group. The sum of the two (halogen and carboxylate) polarization energies is

$$\Delta W = \frac{1}{2}(\alpha' \lambda^2 + \alpha) K \qquad (9)$$

where K is a geometrical factor depending, in particular, on the distance between the halogen and the carboxylate. Comparing NAC's for fluoro- and chloroacetic acids, the ratio $(\lambda_{Cl}/\lambda_F)^2$ is 0.3 which means that in the chloroacetate the FIE is about three times smaller than in the fluoroacetate. It should be negligible in the dissociation of iodoacetic acid, in which the acidity, or the anion stabilization, would mainly come from the polarization of the iodine atom. The changes in the NAC's with deprotonation of acetic, fluoro- and chloro-acetic acids are illustrated in Figure 4.

Application of (6) with values $\Delta W = \Delta\Delta G^0 = 13.8$ kcal mol^{-1} and $\alpha = 5.35$ Å^3, for iodoacetic acid, indicates that the polarizing field, E, should be of the order of $1.79 \cdot 10^{10}$ V m^{-1}. A rough calculation shows that this figure is of the correct order of magnitude. In the iodoacetate, in an eclipsed conformation, with standard geometry, the field of two charges $e/2$ on each oxygen atom is $1.14 \cdot 10^{10}$ V m^{-1} at the nucleus of the iodine atom; this figure changes to $1.04 \cdot 10^{10}$ V m^{-1} for the perpendicular conformation where the iodine is equidistant from the two carboxylic oxygen atoms. These values are of the same order of magnitude as the preceding one though smaller by a factor of about 0.6, which can be explained by the crudeness of the calculation which neglects the polarization of the other atoms in the molecule; they support the polarization model proposed for the inductive effect of the carboxyl group on the halogen.

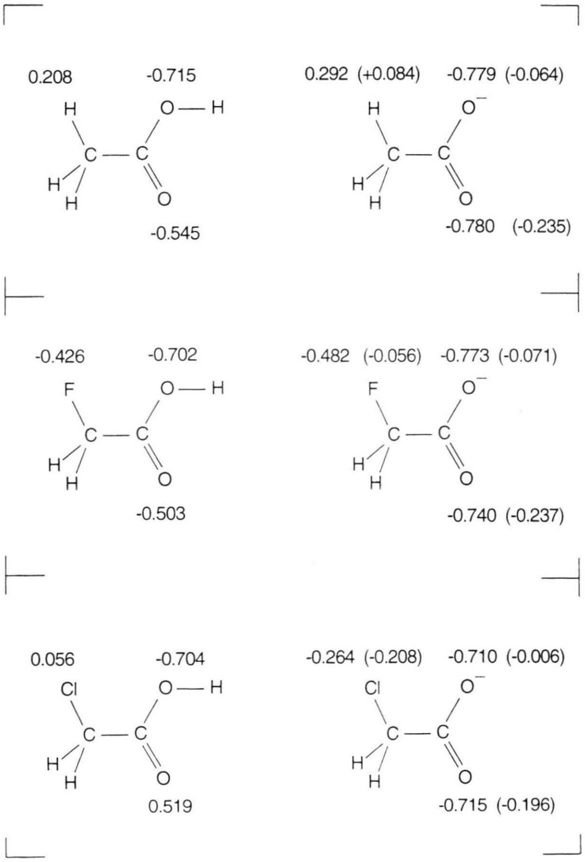

Fig. 4. The net atomic charge (NAC) and variations (shown between parentheses) for acetic, fluoro- and chloro-acetic acids under deprotonation as obtained from MO calculations.

Conclusion

This work brings new chlorine NQR frequencies measured in a few chlorinated acids and several salts of chloroacetic acids.

The discussion of these new data together with those available in the literature leads to several conclusions concerning the effect of the substituent on the chlorine NQR. The substituent may be the $-$COOH group when chlorinated acids are studied, or the negative charge born by the carboxylate when resonances in salts are compared to the resonances in the parent chlorinated acids. As the study of acid deprotonation was the main goal of this work, the latter situation has been extensively studied.

Though the old stepwise charge migration mechanism for the inductive effect still explains the NQR frequency shifts observed upon salification, it is now obsolete and a different mechanism is proposed, based on the polarization of the halogen by the electric field of the substituent. To discuss the frequency shifts in term of the acid strength we had to rely upon intrinsic acidities defined as the variations of the dissociation enthalpies measured in the gas phase. A remarkable linear relationship is found between enthalpy variations and the frequency shift times the number of chlorine atoms in the acid (Figure 3). In the discussion not only NQR data are analyzed, but also, arguments from MO calculations are used. A very simple calculation of the electric field produced at the halogen site by the negative charge on the carboxylate is consistent with the value that can be derived from the stabilization energy.

The effect of the cation size on the chlorine NQR in the salts has also been analyzed. Though a regular behaviour is observed (Fig. 1), the problem of the dispersion in the frequencies measured remains difficult to manage and no special conclusion could be obtained.

Besides the polarization of the halogen by the field produced by the carboxylate, the action of the halogen on the carboxylate is also analyzed as it is important in the case of the fluoroacetates contributing to the anion stabilization; it is much less important for the other halogens.

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