Inductive Effects in Some Chlorinated Carbonyl Compounds and their Nuclear Quadrupole Resonance Frequencies

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It is well known that the chlorine nuclear quadrupole resonance (NQR) frequency increases with the increasing number of chlorine atoms attached to the same carbon atom, and that the frequency increase depends upon the electronic state of the molecule containing the chlorine atom. In the study of the NQR spectra of molecular crystals, Allen⁽¹⁾ suggested that the electron withdrawal abilities of carbonyl groups from the $-CH_2Cl$ and $-CCl_3$

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1) H. C. Allen, Jr., *J. Am. Chem. Soc.*, **74**, 6074 (1952); *J. Phys. Chem.*, **57**, 501 (1953).

groups are different depending on the type of carbonyl group, and that it is useful to compare the quadrupole coupling constants with the shifts in the carbonyl frequencies in the infrared spectra of these compounds. This discussion has hitherto, however, been only qualitative because C=O stretching frequencies had been measured only for mono-chlorinated carbonyl compounds.

In this paper, the relationships between the nuclear quadrupole coupling constant and the C=O stretching frequency in the infrared spectra are investigated for chlorinated acetylchlorides, chlorinated acetic acids, and chlorinated acetamides.

Experimental

A Perkin-Elmer 112 spectrometer with a calcium fluride prism mounted was used to study the C=O stretching bands. Mono-, di- and tri-chloroacetylchloride and mono-, di- and tri-chloroacetic acids were purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by fractionating prior to measurement. The measurement of the 0.1 mol./l. carbon tetrachloride solutions was done at room temperature.

Results and Discussion

The experimental results are listed in Table I, together with the NQR frequencies observed by Allen(1), Bray(2), and McCall and Gutowsky(3). They show that the C=O stretching frequencies increase with the increase in NQR frequencies, which is accompanied by the progressive introduction of chlorine atoms into the methyl group, though the process is not so obvious for the acetylchlorides. Therefore, let us consider this fact from the viewpoint of the molecular orbital theory.

For a molecule in which the hydrogen atoms of a methyl group adjacent to a π-electron conjugated system are successively replaced by chlorine atoms (Fig. 1), we shall represent a one-electron molecular π orbital Ψ_i as a linear combination of atomic π orbitals in this conjugated system as follows:

$$\Psi_i = \sum_r C_{ri}\phi_r$$

where r is taken over all the atoms with $2p\pi$ or $3p\pi$ electrons in this system. In order to calculate the secular equation, the values for the Coulomb integrals, $\alpha_r = \int \phi_r H \phi_r \mathrm{d}\tau$, the resonance integrals, $\beta_{st} = \int \phi_s H \phi_t \mathrm{d}\tau$, and the overlap integrals, $S_{st} = \int \phi_s \phi_t \mathrm{d}\tau$, are required. From the calculation of the secular equation, we obtain the bond-atom polarizability (denoted by $\pi_{st,r}$). It has been shown by Coulson and Longuet-Higgins(4) that when the Coulomb integral α_r of the r atom in the conjugated system is slightly changed, the π bond-order (P_{st}) in the s−t bond is also changed, and that the change of the π bond-order is represented by the bond-atom polarizability $\pi_{st,r} = (\partial P_{st}/\partial \alpha_r)$ as follows:

$$\delta P_{st} = (\partial P_{st}/\partial \alpha_r)\delta\alpha_r \qquad (1)$$

When the hydrogen atoms in the methyl group are progressively replaced by chlorine atoms, the ionic characters of the C–Cl bonds decrease in the sequence $-CH_2Cl > -CHCl_2 > -CCl_3$. Livingston(5) has shown this to be true in the case of chloromethanes and chloroethanes. The same may be true for a chlorinated methyl group adjacent to a conjugated system. The NQR frequencies of some compounds with such

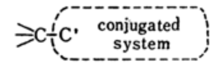
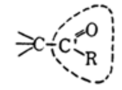


Fig. 1.



R: Cl, OH, and NH$_2$

Fig. 2.

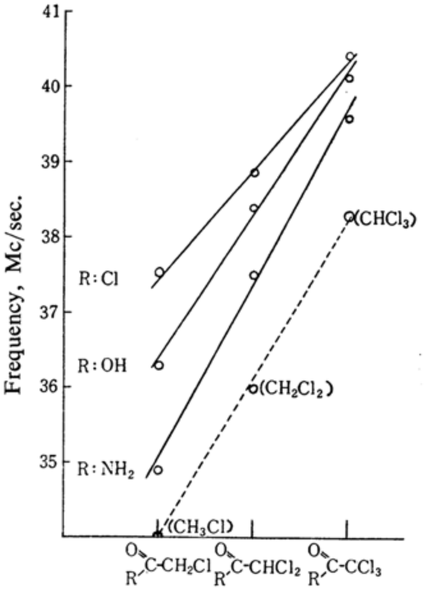


Fig. 3. The ^{35}Cl NQR frequencies were cited from Refs. 1, 2 and 3.

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2) P. J. Bray, *J. Chem., Phys.*, **23**, 703 (1955).

3) D. W. McCall and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1300 (1953).

4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).

5) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).

TABLE I. C=O STRETCHING AND ^{35}Cl NQR FREQUENCIES IN SOME CHLORINATED CARBONYL COMPOUNDS

Compound	C=O Stretching frequency, cm^{-1}	^{35}Cl NQR Frequency*** (Mc/sec.) at 77°K
Monochloroacetylchloride	1783 (sh w) 1818.8(vs)	37.517
Dichloroacetylchloride	1779.1(vs) 1808.7(vs)	38.862(av)
Trichloroacetylchloride	1800.9(vs)	40.406(av)
Monochloroacetic acid	1736.3(vs) (1736)*	36.280(av)
Dichloroacetic acid	1743.4(vs) (1751)*	38.393(av)
Trichloroacetic acid	1749.4(vs) 1785 (sh w) (1764)*	40.124(av)
Monochloroacetamide	1695**	34.882
Dichloroacetamide	1716**	37.494(av)
Trichloroacetamide	1732**	39.569(av)

sh, shoulder; w, weak; vs, very strog; av, average.

* R. H. Gillette, *J. Am. Chem. Soc.*, **58**, 1143 (1936). His measurements were made for 0.025 mol./l. CCl_4 solutions at 25°C.

** See Ref. 15.

*** See Refs. 1, 2 and 3.

chlorinated methyl groups are plotted in Fig. 3, together with those (the dotted line in Fig. 3) of chloromethanes for comparison. In this figure, it can be seen that the frequency changes of these conjugated compounds are similar to those of chloromethanes[5]. In the conjugated compounds shown in Table I and Fig. 3, the ionic character of the C–Cl bond in dichloroderivatives is smaller than that of a C–Cl bond in monochloroderivatives. According to Townes and Dailey's rule[6], however, the amount of the ionic character of the C–Cl bond in dichloroderivatives is larger than one-half of that in monochloroderivatives. Similarly, the amount of the ionic character of the C–Cl bond in trichloroderivatives is larger than two-thirds of that in dichloroderivatives. From these considerations, it is supposed that the positive formal charge of the carbon atom in the chlorinated methyl group becomes larger in the order, $-CH_2Cl < -CHCl_2 < -CCl_3$. The increase in the positive formal charge of this carbon atom may be responsible for the inductive effect in the C–C′ bond connecting the methyl group and the conjugated system (see Fig. 2). This effect may increase also in the order of mono-, di- and tri-chloroderivatives. This effect will result in a slight increase in the electronegativity of the C′ atom adjacent to the methyl group, and in the electron withdrawal by the C′ atom from the other atom in the conjugated system. Therefore, the absolute value of the Coulomb integral of the C′ atom may be expected to increase slightly in the order of $-CH_2Cl$, $-CHCl_2$ and $-CCl_3$. On the other hand, it is well known that the C=O stretching vibration is one of the characteristic vibrations which are scarcely perturbed by the coupling with other parts of the molecule. Therefore, the frequency change originates mainly from the change in the force constant, which may be associated with the change in the bond order δP_{st} in the present case. In the C=O bond, however, both π and σ bonds contribute to the force constant. If the influence of the inductive effect due to the introduction of chlorine atoms into the methyl group is much smaller in the σ bond than in the π bond, the $\delta P_{c=o}$ given by Eq. 1 would be connected to the displacements of the C=O stretching frequencies*. Consequently, the NQR frequencies and the C=O stretching frequencies can be correlated through the Coulomb integral of the C′ atom.

For the practical investigation of this correlation by using Eq. 1, it is necessary to evaluate

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[6] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); ibid., **23**, 118 (1955).

* For Eq. 1, a more discreet expression would require the total differential form:

$$\delta P_{c=o}=\frac{\partial P_{c=o}}{\partial \alpha_c}\delta\alpha_c+\frac{\partial P_{c=o}}{\partial \alpha_o}\delta\alpha_o+\frac{\partial P_{c=o}}{\partial \alpha_R}\delta\alpha_R \quad (1')$$

where R is Cl, (OH) and (NH_2). What we are estimating, however, are the relative differences among the $\delta P_{c=o}$'s of the three groups of chloroderivatives. Therefore, we consider that the first term in the right-hand side of Eq. 1′, which is directly affected by the introduction of chlorine atoms into the methyl group, is most important and that the last two terms are less important.

the bond-atom polarizabilities. Such evaluations are, however, beset by the difficulty of estimating suitable parameters for the hetero atoms. Nevertheless, in order to make a rough guess as to what might be observed, a computation was made for the three derivatives which are shown in Fig. 2. For the Coulomb integrals of the hetero atoms, Coulson's prescription[7]

$$\alpha_r - \alpha_c = (X_r - X_c)\beta_{cc}$$

was used, where X_r, X_c are the electronegativities of the r atom and the C atom respectively. For the resonance integrals between the s atom and the t atom, Wheland's expression[8]

$$\beta_{st} = (S_{st}/S_{cc})\beta_{cc}$$

was adopted. In the above expression, α_c, β_{cc} and S_{cc} were taken to be equal to the corresponding values for benzene. Electronegativity values were used for various atoms where $X_c = 2.5$, $X_o = 3.5$ and $X_{Cl} = 3.0$. The conception of group electronegativity[9] was introduced for the (OH) and (NH_2) groups, and the values 3.72 and 3.36 were used for the two groups. In order to evalute the magnitude of β_{st}, the overlap integrals were calculated by interpolation from the published table[10], using the electron diffraction values of 1.77 Å for the C–Cl bond[11], 1.22 Å for the C=O bond of acetylchlorides[11] or acetamides[12], 1.24 Å for the C=O bond of acetic acids, 1.43 Å for the C–O bond[13], and 1.36 Å for the C–N bond[12]. The order of the obtained bond-atom polarizabilities for the three derivatives is:

$$\left(\frac{\partial P_{c=o}}{\partial \alpha_c}\right)_{O=C-Cl} < \left(\frac{\partial P_{c=o}}{\partial \alpha_c}\right)_{O=C-NH_2} < \left(\frac{\partial P_{c=o}}{\partial \alpha_c}\right)_{O=C-OH} \tag{2}$$

Now for hypothetical equal changes of α_c in the three chloroderivatives, the incured displacements of the C=O frequencies for chlorinated acetic acids or chlorinated acetamides should be larger than that for chlorinated acetylchlorids. Moreover, it is seen in Table I that the rise in the NQR frequencies due to the progressive introduction of chlorine atoms into the methyl group is larger in chlorinated acetic acids or chlorinated acetamides than in chlorinated acetylchlorides. As has been explained above, these changes in the NQR frequencies indicate that the changes of the inductive effect for the former are larger than that for the latter. Therefore, the $\delta\alpha_c$ for chlorinated acetylchlorides, which rise in the sequence mono- to tri-chloroderivatives, is smaller than that for chlorinated acetic acids or chlorinated acetamides. Consequently, the shifts of the C=O frequencies can be expected to be larger for chlorinated acetic acids or chlorinated acetamides than for chlorinated acetylchlorides, as witnessed by the observed C=O frequencies listed in Table I. Although the comparison of these C=O frequencies is beset by splittings of these absorption bands resulting from rotational isomerism or other interplay of several factors[14], close investigation of the relation between wave numbers and the intensities of these bands undoubtedly shows that the increase in wave numbers from mono- to tri-chloroacetic acid (or from mono- to tri-chloroacetamide) is larger than that from mono- to tri-chloroacetylchloride.

For the series of chloroacetamides and chloroacetic acids, the bond-atom polarizability of the former is smaller than that of the latter, as is shown in Eq. 2. On the other hand, on can see in Table I and Fig. 3 that the changes in the NQR frequencies for the former are larger than that for the latter; namely, $\delta\alpha_{c(O=C-NH_2)} > \delta\alpha_{c(O=C-OH)}$ is supposed. The obstruction comes in the estimation of the relative difference of the $\delta P_{c=o}$'s by the product of $\delta\alpha_c$ and $(\partial P_{c=o}/\partial\alpha_c)$, viz. Eq. 1. In the experimental data shown in Table I, the changes in C=O frequencies for the former are slightly larger than that for the latter. It seems that the second term in Eq. 1′ (see footnote p. 604) can fairly easily be altered to $\delta P_{c=o}$, because of the large resonance integral for C–N bond. (β_{C-N} is 0.82 β_{cc}, while β_{C-Cl} and β_{C-OH} are equal to 0.56∼0.57 β_{cc}).

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