863. *Infrared Spectra and Polar Effects. Part VII.* Dipolar Effects in α-Halogenated Carbonyl Compounds.*

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The carbonyl frequencies of α-halogenated ketones, esters, and amides are discussed in relation to their steric arrangements and it is shown that a number of otherwise anomalous frequencies can be explained on the basis of intramolecular dipolar effects.

IN a previous communication[1] it was shown that the carbonyl frequencies of certain ω-chloroacetophenones vary systematically with the steric arrangements of the oxygen and chlorine atoms. The carbonyl frequency is raised about 20 cm.$^{-1}$ above that of aceto-phenone when these atoms are in a *cis*-configuration and near to each other, but it is essentially unaltered when they are in a *gauche* configuration and well separated. This is of course very similar to the well-known cases of α-bromo-keto-steroids[2] and α-chloro-*cyclo*hexanones[3] in which equatorial substitution of the halogen atom raises the carbonyl

* Part VI, *J.*, 1957, 863.

[1] Bellamy, Thomas, and Williams, *J.*, 1956, 3704.

[2] Jones, Ramsey, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 2828; Jones, *ibid.*, 1953, **75**, 4839; Dickson and Page, *J.*, 1955, 447.

[3] Inayama, *Pharm. Bull. (Japan)*, 1956, **4**, 198; Corey, *J. Amer. Chem. Soc.*, 1953, **75**, 2301; Corey, Topie, and Wozniak, *ibid.*, 1955, **77**, 5415; Corey and Burke, *ibid.*, p. 5418.

frequency whereas axial substitution does not. It has been tentatively suggested that this behaviour is due to dipolar or field effects [4,5] and this possibility has now been further studied.

Intermolecular field effects are well known and probably constitute one of the main causes of the frequency shifts which accompany changes of state. In acetone, for example, the fall in the carbonyl frequency from 1738 in the vapour to 1715 cm.$^{-1}$ in the liquid can be attributed to a partial orientation of the $\overset{+}{>}\!C\!=\!\overset{-}{O}$ dipoles so that the positively charged carbon of one molecule is near to the negatively charged oxygen of another.[6] This leads to an increased bond polarity from induced charges, and the frequency falls. This is supported by the higher boiling point of acetone than of related hydrocarbons. However, little consideration appears to have been given to the possibility of intramolecular effects of the same type. In any molecular structure in which a charged atom is brought near in space to a readily polarisable carbonyl-oxygen atom a mutual induction of charges is likely to occur, which will alter the bond polarities and frequencies. In α-halogenated ketones in which a negatively charged halogen approaches near to the carbonyl-oxygen atom the induced charges would diminish the carbonyl bond polarity so that the frequency would rise in the way observed. Also, the size of the resulting shift would be an inverse function of the distance apart of the interacting atoms and so would depend directly on the steric arrangement of the molecule. This is an important distinction from purely inductive effects which may also be present, as these operate along the bonds and are independent of the molecular geometry. It has already been suggested [5,7] that the abnormal carbonyl frequencies of 21-acetoxy-20-keto-steroids may arise in this way, and we have now studied the behaviour of a further range of α-halogenated carbonyl compounds, differing in their degree of halogenation and in the steric resistance they offer to rotational isomerism, to see how far the results are consistent with a similar interpretation.

EXPERIMENTAL AND RESULTS

Samples were examined in either a Grubb-Parsons S.3A double-beam spectrometer with a sodium chloride prism, or a Grubb-Parsons G.S.2 single-beam instrument with a 2400 lines/inch N.P.L. replica grating. The carbonyl frequencies of all the compounds listed were checked by runs against a standard carried out at the same time. For frequencies between 1770 and 1690 cm.$^{-1}$ acetone in carbon tetrachloride (1719 cm.$^{-1}$) was used as standard, and for higher frequencies acetyl chloride vapour (1821 cm.$^{-1}$). The precision of measurement is therefore rather better than ± 2 cm.$^{-1}$. This has resulted in some minor discrepancies between the values now reported for ω-chloroacetophenones in the condensed phase and those given earlier.[1] However, this is due to a small constant calibration error in the earlier work which in no way affects the conclusions.

Conventional hot and cold cells were used as necessary for the examination of vapours, molten films, or crystalline forms. Liquids were studied at a stepwise series of temperatures, and changes in the carbonyl intensities recorded. Measurements on the relative intensities of individual bands were also made on solutions of similar concentration in solvents of different polarity. The results are summarised in Tables 1 and 3.

The trifluoroacetyl halides were fractionated until no further changes could be detected in their vapour spectra. All the ketones studied of sufficient volatility were checked for purity by vapour-phase chromatography. In a few instances it proved virtually impossible to obtain an absolute purification of the main component, but the impurities were in each case reduced to a level at which they would not influence the observed carbonyl frequencies. These cases were chloroacetone (less than 1% of dichloroacetone), 1 : 1-dichloroacetone (0·5% of chloroacetone; 2% of trichloroacetone), and *tert.*-butyl chloromethyl ketone (4% of *tert.*-butyl dichloromethyl ketone).

[4] Bellamy and Williams, *J.*, 1957, 861.
[5] Jones and Sandorfy, " Chemical Applications of Spectroscopy," Interscience, New York, 1956, p. 479.
[6] Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, p. 52.
[7] Bellamy and Williams, *J.*, 1957, 863.

Halogenated ketones prepared in this laboratory were made as follows: Chloroacetone was prepared by the action of sulphuryl chloride on acetone, and *tert.*-butyl chloromethyl ketone by that of chlorine on *tert.*-butyl methyl ketone. The 1 : 1-dichloro-derivatives of these were made by the action of chlorine on the monochloro-derivatives. Trifluoroacetyl chloride and bromide were obtained by reaction of the acid with benzoyl chloride and with phosphorus pentabromide respectively. Trifluoroacetyl fluoride was produced by reaction of the acid with KHF_2 and benzoyl chloride, and the iodide by treatment of the chloride with hydriodic acid. Carbonyl bromide was obtained directly by interaction of carbon monoxide and bromine in sunlight.

DISCUSSION

(1) *α-Halogenated Ketones.*—The ω-chloroacetophenones have been shown to exhibit rotational isomerism which gives rise to two carbonyl frequencies, and the higher of these has been assigned [1] to the form in which the chlorine atom is *cis* with respect to the carbonyl oxygen and therefore near to it in space. This assignment rests in part on the analogy with the α-halogeno-keto-steroids and also on the fact that the higher frequency is associated in all cases with the form which is more stable in the liquid and the solid state. Dipole-moment studies have established that the more polar *cis*-configuration is the stable form under these conditions in chloroacetone.[8, 9] However, as some discrepancies appeared to arise with the assignments for chloroacetone itself (see below), we have sought further confirmation of the configurations of the ω-chloroacetophenone isomers by studying the changes which occur in the relative intensities of the individual carbonyl bands in solvents of different polarity. It is well known that solvents of high dielectric constant favour the more polar forms of rotational isomers so that the carbonyl absorption which corresponds to this form should increase sharply at the expense of the other on changing from a non-polar to a polar solvent. Table 1 shows that marked changes of this type do occur and that the higher-frequency carbonyl absorption is intensified in acetonitrile as compared with carbon tetrachloride in all cases. This again associates the higher of these two frequencies with the more polar *cis*-form in which the oxygen and halogen atoms are close together. We have also extended our study of this series to include the spectra of the vapours. In general, simple α-halogenated ketones exist only in the *gauche* configuration in the vapour state [8, 9] (see below), and this has been ascribed to the predominance of the electrostatic repulsion between the oxygen and chlorine atoms over the steric repulsion exerted by the alkyl group.[8]

This appears to be true of ω-chloroacetophenone itself which shows only a single carbonyl absorption at 1709 cm.$^{-1}$, at the same point as acetophenone itself. However, in ωω-dichloroacetophenone two bands are shown at 1729 and 1707 cm.$^{-1}$. The introduction of the second chlorine atom has therefore increased the proportion of the more polar form. Doubling of the carbonyl absorption is also found in the vapour spectra of many substituted ω-chloroacetophenones. This is particularly marked in the *ortho*-substituted compounds in which the influence of steric repulsions would be at a maximum.

We have also studied a series of acetone derivatives with various degrees of chlorination. Of these, perhaps the most important is chloroacetone itself, which has been previously studied by Mizushima *et al.*[8] The values for the carbonyl frequencies of this compound in various states are listed in Table 1, and, with the exception of the solid state these agree very well with the previous results. Dipole-moment and spectroscopic studies have shown that the more polar *cis*-form (I) is the more stable in the liquid and solid states whereas form (II) *(gauche)* appears to be favoured in the vapour. However, Mizushima *et al.*[8] have assigned the 1745 and 1725 cm.$^{-1}$ absorptions of the liquid to forms (II) and (I), respectively. This is the inverse of what would be expected from the dipolar considerations above, but is in accord with the 1718 cm.$^{-1}$ frequency which they report for the solid state.

[8] Nakagawa, Ichishima, Kurakani, Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1952, **20**, 170.

[9] Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shida, *ibid.*, 1953, **21**, 815.

TABLE 1. *Frequencies in the carbonyl region* (cm.$^{-1}$).

Substance	Vapour	Liquid	Solid	Solution in CCl$_4$	Solution in CH$_3$·CN
COMe$_2$	1738	1715	—	1719	1715
COMeEt	1739	1719	—	1723	1715
COMePr^l	1734	1715	—	1719	1711
COMeBu^t	1726	1711	1705	1711	1704
COMeBu^l	1736	1717		1721	1712
CMe$_3$·CO·CHMe$_2$	1722	1708		1709	1702
CH$_3$·COPh	1709	1687	1682	1692	1688
Ph·CO·CH$_2$Cl	1709	1709, 1693 0·75	1703	1715, 1696 1·58	1710, 1694 0·52
Ph·CO·CHCl$_2$	1729, 1707 1·35	1707, 1690 0·66	1709	1716, 1692 1·29	1713, 1695 0·19
p-Cl·C$_6$H$_4$·CO·CH$_2$Cl	1709	1707, 1695 1·00	1696	1715, 1696 2·22	1711, 1695 0·54
3:4-Cl$_2$C$_6$H$_3$·CO·CH$_2$Cl	1709	1710, 1694 0·73	1708	1718, 1698 2·25	1714, 1698 0·59
2:4- ,,	1720	1723, 1707 >1·31	1713	1733, 1710 ≥3·28	1727, 1711 ≤0·82
2:5- ,,	1721	1728, 1710 >1·35	1716	1736, 1713 ≥2·42	1731, 1714 ≤0·77
2:4:6-Cl$_3$C$_6$H$_2$·CO·CH$_2$Cl	1731	1741, 1721 0·80	1735	1747, 1722 1·23	1739, 1721 0·45
CH$_3$·CO·CH$_2$Cl	1743	1743, 1725 0·98	1742, 1728	1752, 1726 2·75	1744, 1726 0·81
CH$_3$·CO·CHCl$_2$	1756, 1722 0·10	1740	1732 cryst. 1742 glassy	1743, 1724 <0·15	1745, 1716 <0·15
CH$_2$Cl·CO·CH$_2$Cl	1746	1755, 1742, 1728	1745	1746, 1730 0·80	1752, 1744 ≥1·39
CHCl$_2$·CO·CHCl$_2$	1770	1773, 1762 1·21	1770, 1739 cryst. 1768, 1733 glassy	1774, 1764 2·00	1772, 1758 1·07
CCl$_3$·CO·CCl$_3$	1784	1778, 1750 0·37	1779, 1757, 1745	1780, 1751 0·35	1780, 1751 ≤0·49
CH$_2$Cl·CO·CBu^t	1732	1732, 1720 <0·66	1722	1740, 1720 1·90	1734, 1719 ≥0·48
CH$_2$Cl·CO·CBu^t	1733	1726, 1712 <0·10	1717	1732, 1713 <0·30	1725, 1709 ≥0·08
CHCl$_2$·COBu^t	1750	1743, 1731 >1·59	1730	1745, 1734 1·13	1742, 1729 ≥3·03

Notes. (1) Only major peaks are recorded. Inflexions and minor bands are often observed especially in the aliphatic compounds in the solid state.
(2) The figure after the frequency, when quoted, refers to ε (lower frequency)/ε (higher frequency), where ε is the apparent max. extinction coefficient.

In view of this discrepancy we have studied this compound in some detail. As indicated earlier, we have been unable to reproduce their findings for the solid state, but find instead a main peak at 1728 cm.$^{-1}$ with a shoulder at 1742 cm.$^{-1}$. This observation has been checked a number of times both at $-80°$ and at liquid-nitrogen temperatures, and care has been taken to ensure that the sample was truly crystalline and not a glass, by examination through polarisers. Under these conditions only one rotational isomer can be
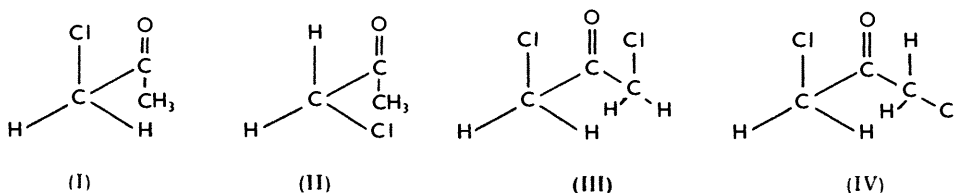
present and the splitting must arise either from crystal splitting effects or from the presence of a unit cell of two or more molecules in which the carbonyl groups are in different environments. As both frequencies are higher than the 1725 cm.$^{-1}$ liquid-state frequency they are almost certainly derived from the form absorbing at 1745 cm.$^{-1}$, so it appears reasonable to reverse the original assignments and identify the 1745 cm.$^{-1}$ absorption of the liquid with the *cis*-form (I). This is fully supported by the results of temperature-dependence studies. As the temperature of the liquid is raised, the intensity of the 1725 cm.$^{-1}$ band increases at the expense of the 1745 cm.$^{-1}$ band, indicating that the latter is to be associated with the more stable form in this state (*i.e.*, *cis* as in I). Finally, a very marked change in the relative intensities of these bands occurs on passing from solutions in carbon tetrachloride to those in acetonitrile. The intensification of the 1745 cm.$^{-1}$ band in the latter, more polar, solvent again identifies this band with the more polar form (Table 1). Whatever the origins of the splitting of the carbonyl absorption in the crystal, these findings are clear evidence for the presence of genuine rotational isomers, and the revised assignments are fully consistent with the concept of dipolar interaction outlined above.

The behaviour of 1 : 1-dichloroacetone is in many ways very similar. The more polar form could exist either with one chlorine atom eclipsed by the oxygen or in a staggered arrangement similar to (X*a*). From the electrostatic point of view these alternatives are approximately equivalent, so that it is to be expected that the observed frequencies will be closely parallel to those of chloroacetone itself. It will be seen that this is generally so, although there is a marked intensification of the higher-frequency absorption in the liquid. In the vapour phase the main carbonyl absorption at 1756 cm.$^{-1}$ corresponds to a more polar configuration. This band is accompanied by a weak shoulder at 1722 cm.$^{-1}$. This is at a lower frequency than would be expected from a configuration in which both chlorine atoms were *gauche* with respect to the carbonyl oxygen atom which should be similar to that of methyl *iso*propyl ketone in the vapour state (1734 cm.$^{-1}$). There is little or no change in the relative intensities of these bands with temperature, so it is likely that the weak 1722 cm.$^{-1}$ absorption represents a combination band from lower-frequency fundamentals. In the crystalline state the main carbonyl absorption is at 1732 cm.$^{-1}$, and this is clearly the more polar form and corresponds to the liquid frequency of 1740 cm.$^{-1}$. Although the band is not doubled it is accompanied by a series of minor weak absorptions on both sides which probably also arise from overtone or combination bands.

It is interesting to compare these findings with those for 1 : 3-dichloroacetone. This compound has been previously studied by Daasch and Kagarise,[10] who demonstrated the existence of rotational isomers but did not attempt to associate any particular bands with individual isomers. Our own findings are listed in Table 1 and show only minor differences

[10] Daasch and Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 6156.

from theirs. Unfortunately, the spectra in the carbonyl region of the liquid and solid forms are very complex and show a number of weak bands in addition to the main absorptions. This renders interpretation difficult, but the results would nevertheless appear to be reasonably consistent with the theory of dipolar interactions outlined earlier. On this basis 1 : 3-dichloroacetone would be expected to show three main peaks corresponding to forms (III), (IV), and (V), as form (VI) is almost certainly excluded on steric grounds.

In the liquid state the main carbonyl absorptions occur at 1755, 1742, and 1728 cm.$^{-1}$ with weak bands at 1785 and 1722 cm.$^{-1}$. Both the 1755 and the 1785 cm.$^{-1}$ band diminish in intensity with increase in temperature so that either could be associated with form (III). However, the size of the frequency shifts of the 1755 cm.$^{-1}$ band as compared with that of

(V) (VI) (VII)
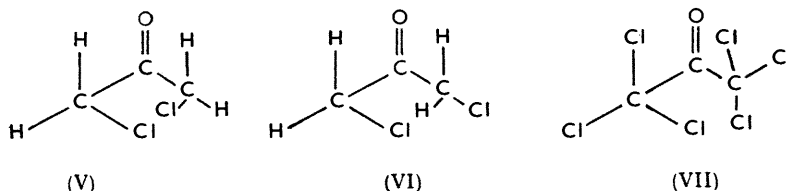
liquid acetone is of the order to be expected from two *cis*-chlorine atoms, and this appears the most likely choice. This is supported by the fact that the most intense absorption in the crystal, which is likely to be form (III), is at 1745 cm.$^{-1}$, which would correspond to a similar fall of the 1755 cm.$^{-1}$ band with change of state to that which occurs in the chloroacetophenones. The 1785 cm.$^{-1}$ band could well arise as a combination of the strong absorptions [15] at 1051 and 732 cm.$^{-1}$. The persistence of the 1755 cm.$^{-1}$ band in acetonitrile and its disappearance in the less polar carbon tetrachloride also support the assignment to the most polar configuration. The 1742 cm.$^{-1}$ band would then arise from form (IV), and it represents the most intense absorption in the liquid and solution states. As the temperature rises the intensity of this band increases with respect to the 1755 cm.$^{-1}$ and falls with respect to the 1728 cm.$^{-1}$ absorption which indicates a form of intermediate stability between (III) and (V). The 1728 cm.$^{-1}$ band as indicated above is the least stable form in the liquid and is therefore probably associated with form (V), and the absence of any notable frequency shift over that of acetone is in line with this assignment. It is possible that the 1722 cm.$^{-1}$ band which shows similar temperature dependence could be due to this form, but this band is much weaker and is more likely to be a combination band of the absorptions at 951 and 765 cm.$^{-1}$. These assignments are supported by the intensity changes which occur on passing from acetonitrile to carbon tetrachloride. The 1730 cm.$^{-1}$ band, for example, is very weak in acetonitrile and strong in carbon tetrachloride, as would be expected from the least polar configuration. In the solid a multiplicity of peaks again occurs many of which must be combination bands as only one configuration is possible. However, the main peak in both the cubic and the needle crystalline modification is at 1745 cm.$^{-1}$ which, allowing for the frequency fall accompanying a change of state, is consistent with its assignment to the expected *cis/cis*-form (III). In the vapour phase the stability relations of compounds of this type appear to be the reverse of those for the liquid state and, as with chloroacetone and ω-chloroacetophenone, the main frequency of 1 : 3-dichloroacetone (1743 cm.$^{-1}$) is very close to that of acetone itself and is clearly due to the least polar form (V). However, it is accompanied in this case by a weak shoulder at 1767 cm.$^{-1}$. After allowance for the rise of 23 cm.$^{-1}$ which follows a change of state in acetone from liquid to vapour, this probably corresponds to the liquid frequency of 1742 cm.$^{-1}$ and indicates the presence of a small proportion of form (IV).

s-Tetrachloroacetone has also been studied. Steric effects are likely to be considerable in this molecule and one must also expect an intensification of any combination bands associated with the C–Cl stretching modes at lower frequencies. It is, however, unlikely on steric grounds that any modification can exist in which all the halogen atoms are *gauche*

with respect to the carbonyl oxygen, and in accordance with this idea no carbonyl frequency is found which corresponds to that of acetone. Two bands are observed in the liquid at 1773 and 1762 cm.$^{-1}$. These are markedly temperature-dependent, indicating rotational isomerism, and solvent studies identify the higher frequency with a more polar form. It is possible, therefore, that the first is derived from a form analogous to (III) in which two halogen atoms are *cis* to the carbonyl oxygen atom, and the second from a form similar to (IV). However, it is also possible in view of the considerable steric hindrances that skewed configurations may be involved. However, the observation that in the solid and in the vapour form the carbonyl frequencies remain high is consistent with the view that a form in which both hydrogen atoms are *cis* with respect to the carbonyl oxygen atom does not exist.

Hexachloroacetone has also been examined. As a symmetrical molecule this can exist in only one form, and an elevated carbonyl frequency is to be expected. The main carbonyl band in all states occurs in the range 1778—1784 cm.$^{-1}$ but is accompanied by a weaker absorption near 1750 cm.$^{-1}$. The behaviour of the latter band with changes of temperature or of solvent is in marked contrast to that shown by genuine carbonyl absorptions arising from rotational isomerism. Practically no change of the relative intensities of the two bands is shown under these conditions, and the 1750 cm.$^{-1}$ absorption is therefore almost certainly a combination band. Strong bands are found at 1095 and 656 cm.$^{-1}$ which would account for this absorption. As *s*-tetrachloroacetone is apparently precluded from existing in a form in which all the chlorine atoms are *gauche* to the carbonyl oxygen, it is likely that hexachloroacetone will assume some type of configuration such as in (VII) in which one halogen atom is *cis* to the carbonyl whilst the other CCl_3 group takes up a skew arrangement with two halogen atoms each at 60° to the C=O axis.

From the point of view of simple electrostatic interactions this latter pair would behave in the same way as one chlorine in the *cis*-position. The observed carbonyl frequencies should therefore correspond to compounds with two *cis*-chlorine atoms. In the vapour phase the 1784 cm.$^{-1}$ band is 29 cm.$^{-1}$ higher than the 1755 cm.$^{-1}$ liquid frequency of 1 : 3-dichloroacetone which has been assigned to a *cis/cis*-form. Allowance being made for the usual shifts which accompany change of state, this agreement is reasonable. However, the liquid (1778 cm.$^{-1}$) and solid (1779 cm.$^{-1}$) frequencies are both appreciably higher than would be expected on this basis. This may be due to residual inductive effects of the CCl_3 groups but could also arise from an intermolecular dipolar interaction between the carbonyl oxygen and the halogen atoms of other molecules in the condensed phases.

The factors which determine the relative stabilities of rotational isomers of α-halogenated ketones must be the electrostatic repulsion between the chlorine and oxygen atoms on the one hand and the steric repulsion between the chlorine atom and the other carbonyl substituent on the other.[8] In general, the former effect predominates in the vapour phase but the effect of dielectric constant makes the latter more important in the liquids and solids. It therefore seemed of interest to examine the rotational isomerism of ketones containing bulkier substituents to see how far this influenced the relative stabilities of the different isomers. We have accordingly studied chloromethyl *iso*propyl ketone and *tert.*-butyl chloromethyl ketone. It will be seen from Table 1 that in both cases the electrostatic repulsion effect predominates as before in the vapour phase and that, as with ω-chloroacetophenone, the carbonyl frequencies found in this state are the same as those of the parent ketones. In the liquid and solution two forms occur and the higher carbonyl frequency in each case is readily identified with the more polar *cis*-chlorine–oxygen configuration by the temperature-dependence behaviour, by the changes with solvents of different polarity, and by the solid-state frequencies. The latter again show the anomalous doubling observed in other cases, but the main absorption in each case can be identified with the higher liquid frequency. It would seem therefore that in monochlorinated compounds the steric repulsions of the *iso*propyl, *tert.*-butyl, and phenyl groups are insufficient to overcome the electrostatic repulsions and stabilise the *cis*-configurations in

the vapour phase. In *ortho*-substituted phenyl compounds, however, the situation is reversed and the more polar form predominates in the vapour. It is interesting to compare these findings with the results obtained in the *gem*-dichloromethyl compounds, in which the more polar isomer is the stable form in the vapour phase. It has been suggested above that in this series it is perhaps more probable that the polar forms will assume configurations analogous to (X*a*) rather than to (X) and from the point of view of electrostatic effects upon the carbonyl frequency the two forms are equivalent. The introduction of the second halogen atom has, however, increased the steric resistances to internal rotation, whilst the electrostatic repulsion forces remain approximately the same, so that the proportion of the more stable form is increased. Nevertheless, it remains difficult to understand why the more polar form of 1 : 1-dichloroacetone should appear exclusively in the vapour whereas in ωω-dichloroacetophenone in the same state both forms are found.

(2) *α-Halogenated Esters.*—The available data on α-halogenated esters indicate that they behave in a very similar way to the ketones. Studies on pure liquids[11] or in highly polar solvents[12] have given rather conflicting results as some mono- or di-halogenated esters show only one carbonyl absorption whilst others show two. This is probably due to the fact that the liquids themselves are highly polar, so that the concentrations of the less polar isomers would be much reduced. Josien and Callas,[13] using a high-dispersion instrument, have demonstrated the existence of rotational isomers in carbon tetrachloride solutions, and the observed frequencies are readily understandable on the basis of dipolar interaction. For example, methyl acetate absorbs at 1750 cm.$^{-1}$ and both methyl chloroacetate and methyl dichloroacetate show two bands at 1775 and 1750 cm.$^{-1}$. The higher frequency can be assigned to forms (VIII) and (X) (or X*a*) respectively whilst the lower corresponds to forms (IX) and (XI) and is the same as for methyl acetate. The trichloro-

(VIII)   (IX)   (X)   (X*a*)   (XI)
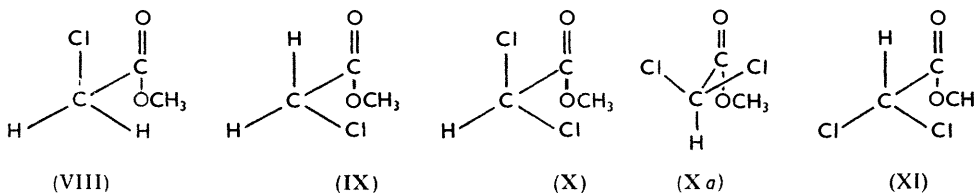
derivative, in which either one halogen is *cis* to the carbonyl oxygen or two are in an electrostatically equivalent arrangement similar to (X*a*), confirms this, as it shows a single absorption at 1770 cm.$^{-1}$.

(3) *α-Halogenated Amides.*—The influence of α-halogen substitution on amide-carbonyl frequencies is difficult to study owing to limited solubilities and to hydrogen-bonding effects in the solids. Nevertheless it is clear that such effects follow a different pattern from those of the corresponding ketones or esters. In *N-n*-butylchloroacetamide, for example, the carbonyl frequency in carbon tetrachloride is the same as in the original amide and it is not until a second halogen atom is introduced that any frequency shift occurs.[14] Similarly, the di-*n*-butylamide absorbs only 9 cm.$^{-1}$ higher than the unchlorinated compound. This can be explained on the basis of dipolar interactions, as mesomerism leaves the nitrogen atom with an effective positive charge. The electrostatic repulsion between the chlorine and oxygen atoms is reinforced by the electrostatic attraction between the chlorine and nitrogen atoms; and the isomer in which the chlorine is *gauche* with respect to the carbonyl-oxygen atom is stabilised. This probability has been independently confirmed in the case of methyl chloroacetamide in which dipole-moment studies have shown that, in contrast to chloroacetone, the *gauche* configuration is the more stable in the liquid and the solid state and that the more polar isomer is almost non-existent in non-polar

[11] McBee and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 755.
[12] Bender, *ibid.*, 1953, **75**, 5986.
[13] Josien and Callas, *Compt. rend.*, 1955, **240**, 1641.
[14] Letaw and Groop, *J. Chem. Phys.*, 1953, **21**, 1621.

solvents.[15] Data on dihalogenated amides are limited, but the NN-di-n-butyl derivatives of dichloro-, difluoro-, and chlorofluoro-acetamide show the expected two carbonyl frequencies [14] which would arise from rotational isomerism. On the other hand, the corresponding secondary amides show only a single absorption throughout. This may be due to differences in steric effects in the two series but more work is required before any final conclusions are possible.

General.—The demonstration that in all the cases described above it is the more polar forms of α-halogenated ketones which show raised carbonyl frequencies is clear evidence for the existence of a stereospecific effect. This cannot be normal induction and is most easily explained as a simple electrostatic interaction across intramolecular space. This idea then allows a simple explanation of a number of otherwise anomalous carbonyl frequencies; *e.g.*, it explains the differences between the behaviour of α-monohalogenated ketones and amides, the presence of two carbonyl frequencies in partially chlorinated compounds and of only one in the fully chlorinated product, the absence of any further frequency rise when a second halogen atom is introduced at an α-position, and the occurrence of such a rise when it is introduced at the α'-position.

The data indicate clearly that the dipolar field effects are the major factors involved in frequency shifts in these cases. However, this does not imply that inductive effects are wholly absent. Some changes in the inductive effect must occur on passing through the series $CH_3 \longrightarrow CCl_3$ and the fact that mono-halogenated materials in the *gauche* configuration with respect to the chlorine and oxygen atoms show substantially the same frequencies as the unhalogenated compounds probably arises from the existence of weak field effects in this configuration also. These would be expected to be of opposite sign to those arising in *cis*-configuration so that they would roughly offset the increased inductive effect. The small frequency changes which sometimes follow the introduction of a third α-halogen atom may well arise in this way. Thus in methyl trichloroacetate the carbonyl frequency is 5 cm.$^{-1}$ lower than in the *cis*-disubstituted or monosubstituted materials [13] and ethyl trifluoroacetate absorbs at about 9 cm.$^{-1}$ higher than the difluoro-compound.[12]

Quantitative aspects. The concept of dipolar interactions appears to provide an adequate qualitative explanation for much of the above data, but it is desirable to show that interactions of this kind can lead to frequency shifts of approximately the same order of magnitude as those observed.

A very convenient means of estimating the magnitudes of inductive effects in molecules is provided by the theory of Smith, Ree, Magee, and Eyring.[16] In this method, a semi-classical approach is used to calculate the approximate net charges on the atoms in a molecule, it being assumed that the only electrical effects are inductive ones, operating along the bonds. To evaluate these charges, each atom in a particular bond is associated with two parameters, β and γ. The former can be calculated from the longitudinal bond polarisability, bond length, and Slater screening constant, and in, *e.g.*, a bond AB β_{AB} represents the inductive effect on the charge on atom A by the charge on atom B. The parameter γ_{AB}, which represents the charge on atom A before the effect of induction from B is considered, cannot easily be calculated from atomic and bond properties in a similar manner to β_{AB} but can instead be obtained from the observed moments of suitable molecules. These values can then be used for the calculation of charge distribution in other molecules containing the same links.

Smith *et al.* list values for β_{AB} for a number of bonds and also for γ_{AB} for the CF, CCl, CBr, and CI links. These values have been adopted for this work except that slight alterations have been made in the γ_{AB} figures because of the more accurate values for the dipole moments of the methyl halides now available.[17] Since the values of γ_{AB} depend on

[15] Mizushima, Shimanouchi, Ichishima, Miyazawa, Nakagawa, and Araki, *J. Amer. Chem. Soc.*, 1956, **78**, 2038.

[16] Smith, Ree, Magee, and Eyring, *ibid.*, 1951, **73**, 2263.

[17] "Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," N.B.S. Circular No. 537, Nat. Bur. Stand., Washington, 1953.

the value of μ_{OH} in methane, the set corresponding to $\mu_{C^+H^-}$ 0·3 D have been chosen. γ_{OO} was calculated from the molecular dipoles of formaldehyde and carbonyl chloride, and the β parameter for the C–C bond was that suggested by Smith and Mortensen.[18]

TABLE 2.

Bond AB	β_{AB}	$\gamma_{AB} \times 10^{10}$ (e.s.u.)	Bond AB	β_{AB}	$\gamma_{AB} \times 10^{10}$ (e.s.u.)	Bond AB	β_{AB}	$\gamma_{AB} \times 10^{10}$ (e.s.u.)
H–C	0·13	−0·418	Cl–C	0·71	−2·40	I–C	1·29	−2·865
F–C	0·25	−1·91	Br–C	0·91	−2·55	O=C	0·45	−3·023

By using the constants in Table 2, the charge distributions for a number of RR'CO compounds were evaluated, and from these, the dipole moment of the C=O bond and, in some cases, the molecular dipole were deduced. The results are shown in Table 3 together with the observed molecular dipole, where available. It will be seen that this approach leads to resonable values for individual bond dipoles and that in the cases where the molecular dipole moment is known, the agreement between the observed and calculated values is good.

TABLE 3. (*All substances measured in the vapour phase.*)

Substance	μ_{CO} (D), calc.	$\mu_{molecular}$ (D): calc.	$\mu_{molecular}$ (D): obs.	ν_{CO} (cm.$^{-1}$): obs.	ν_{CO} (cm.$^{-1}$): mass-corr.	Substance	μ_{CO} (D), calc.	$\mu_{molecular}$ (D): calc.	$\mu_{molecular}$ (D): obs.	ν_{CO} (cm.$^{-1}$): obs.
CH$_2$O ...	2·45	2·31	2·34	1744 ^{a}	1771	CF$_3$·COF ...	1·97	0·34	—	1901 ^{b}
COF$_2$	1·68	0·10	—	1928 ^{a}	1916	CF$_3$·COCl ...	2·16	1·07	—	1810 ^{b}
COCl$_2$ ...	2·09	1·18	1·19	1827 ^{a}	1822	CF$_3$·COBr ...	2·23	1·53	—	1838 ^{b}
COBr$_2$ ...	2·23	1·25	—	1826 ^{b}	1825	CF$_3$·COI	2·34	2·35	—	1812 ^{b}
COHF ...	2·01	1·77	—	1837 ^{f}	1850	CF$_3$·CHO ...	2·35	1·53	—	1788 ^{c}
COClF ...	1·93	1·23	—	1868 ^{a}	1860	CF$_3$·CO·CH$_3$	2·50	2·58	—	1780 ^{d}
CH$_3$·CHO	2·61	2·67	2·72	1752 ^{b}		CF$_3$·CO·CF$_3$	2·26	0·32	—	1825 ^{e}
(CH$_3$)$_2$CO	2·75	2·85	2·88	1740 ^{b}						

^{a} Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377. ^{b} This work. ^{c} Husted. ^{d} Whiffen. ^{e} R. N. Jones. ^{f} Wilkinson and Price, personal communications.

Frequencies of groups in the infrared region are usually sensitive to changes both in the electrical nature and in the mass of substituents. However, in the case of R'R'CO group Halford[19] has recently shown for all masses greater than about 12 when R is polyatomic, that the CO frequency is mass-insensitive and he has also supplied correction formulæ for when R is monatomic. Table 3 gives the observed carbonyl frequency and also the mass-corrected frequency when this is significantly different.

When the bond dipoles are plotted against the carbonyl frequencies, a simple relation is found (see Figure), as would be expected if the frequencies were directly related to the inductive effect of substituents on the carbonyl. The acetyl halide series has also been studied and gives a line parallel to that of the COX$_2$ line. However, the position of this line is sensitive to the choice of the sign of μ_{OH} in methane, lying below or above the COX$_2$ line for the two extremes of $\mu_{OH} \pm$ 0·3 D.

The CO bond dipoles of the trifluoroacetyl halide series in Table 3 have been calculated solely on the basis of induction through the bonds. It will be seen from the Figure that this line is diplaced from the basic carbonyl line by about 0·2 D, which we attribute to the intramolecular field effect from a fluorine atom in the *cis*-position to the carbonyl-oxygen atom.

It is possible to estimate the magnitude of the induced dipoles which would arise in this way. By taking the calculated CF and CO bond dipoles as 1·51 and 2·35 D, respectively, and the CF and CO longitudinal bond polarisabilities as 0·96 × 10^{-24} and 1·99 × 10^{-24} c.c. and assuming that point dipoles are located in the fluorine and oxygen atoms, it can be shown that μ_{CF} would be lowered by about 0·15 D and μ_{CO} by about

[18] Smith and Mortensen, *J. Amer. Chem. Soc.*, 1956, **78**, 3932.
[19] Halford, *J. Chem. Phys.*, 1956, **24**, 830.

0·19 D as a result of the dipolar interaction. The good agreement obtained is probably fortuitous, as the calculation is very much an approximation and takes no account of the likely influence of the other halogen atoms in *gauche* configurations. Nevertheless, it
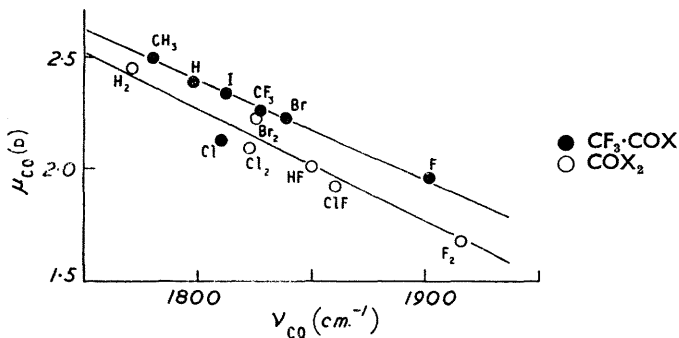
indicates that a field effect of the type postulated would be likely to lead to frequency shifts of the general order of magnitude which is observed.

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