

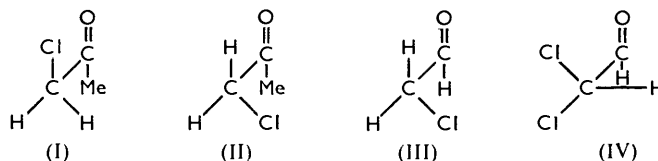
698. *Infrared Spectra and Polar Effects. Part IX.* Field Effects in α -Halogenated Aldehydes and Acid Chlorides.*

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The effects of α -chlorine substitution in aldehydes and acid chlorides are compared. In aldehydes the most stable rotational isomer is probably that in which the chlorine occupies a position well away from the oxygen atom. This is due to the low steric repulsion of the aldehyde hydrogen atom. In acid chlorides the situation is reversed, as the steric effect is then large and is reinforced by electrostatic repulsions between the chlorine atoms. Some apparently anomalous carbonyl frequencies are observed in the acid halide series and the origin of these is discussed.

SUBSTANTIAL results are now available on the spectroscopic behaviour of α -halogenated ketones: the carbonyl frequency rises when the halogen and oxygen atoms are close together but remains unchanged when they are not.¹ This has been attributed to an intramolecular field effect and many otherwise anomalous frequencies can be satisfactorily explained on this basis. When CH_2Cl or CHCl_2 groups are adjacent to the carbonyl group, rotational isomerism leads to two carbonyl absorptions. These can be assigned to the more and the less polar conformation on the basis of the observed frequencies, and the results obtained agree well with previous assignments based on dipole moments and similar results.

In chloroacetone the two conformations are close to (I) and (II), and the carbonyl frequency in the former is raised whilst in the latter it is unchanged. Mizushima *et al.* suggested² that the relative stabilities of these conformations are determined by the resultant of the electrostatic repulsion between the oxygen and the chlorine atom which operates in one



direction, and of the steric repulsion between the methyl group and the chlorine atom which operates in the other. We have therefore studied α -chlorinated aldehydes in which the steric repulsion is reduced to a minimum, and α -chlorinated acid chlorides in which the steric effect is much increased and is reinforced by an electrostatic repulsion between the two halogen atoms.

α -Halogenated aldehydes do not appear to have been studied previously, but Mizushima *et al.*³ discussed the spectra of chloroacetyl chloride, bromoacetyl chloride, and bromoacetyl bromide. On the basis of a normal co-ordinate treatment they conclude that the

* Part VIII, *J.*, 1958, 2463.

¹ Bellamy, Thomas, and Williams, *J.*, 1956, 3704; Bellamy and Williams, *J.*, 1957, 4294; Jones, Forbes, and Mueller, *Canad. J. Chem.*, 1957, **35**, 504.

² Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shindo, *J. Chem. Phys.*, 1953, **21**, 815.

³ Nakagawa, Ichishima, Kuratani, Miyazawa, Shimanouchi, and Mizushima, *ibid.*, 1952, **20**, 1720.

more stable form in the solid state is that with the more polar conformation, and that this form is responsible for the higher of the two carbonyl frequencies of the liquid. This is in accord with the assignment which would be made on the basis of field effects. However, in chloroacetyl chloride both the carbonyl frequencies in the liquid state are reported at values which are lower than that of acetyl chloride and this also appeared to merit further investigation.

Experimental.—Samples were examined in a Grubb-Parsons S.3.A. double-beam spectrometer with a sodium chloride prism, or in a Grubb-Parsons G.S.2. double-beam grating instrument with a 2400 line/inch N.P.L. grating. The carbonyl frequencies of all the compounds measured with the prism spectrometer were checked against a standard run at the same time, and all frequencies are thought to be accurate within ± 1 cm^{-1} . Acetone in carbon tetrachloride (1719 cm^{-1}) or acetyl chloride vapour (1821 cm^{-1}) were used as standards depending on the expected frequency range. Solutions were studied in 0.1 mm. cells while vapours, etc., were examined in 10 cm. cells. The acid chlorides studied were prepared by the reaction of the appropriate acid with benzoyl chloride. The product was then fractionally distilled and finally kept *in vacuo* to remove any alkyl halide which might have been formed by decomposition. Chloral was prepared by distilling chloral hydrate with concentrated sulphuric acid, dichloroacetaldehyde by depolymerisation of the commercially available material by vacuum-distillation, and monochloroacetaldehyde by repeated distillation of the semihydrate through anhydrous copper sulphate.

Results and Discussion.—The results are set out in the Table.

α -Halogenated aldehydes. Acetaldehyde itself absorbs at 1745 cm^{-1} in the vapour state, at 1730 cm^{-1} in CCl_4 , and 1723 cm^{-1} in acetonitrile. The monochloro-derivative also shows only a single absorption band in the vapour (1752 cm^{-1}), in CCl_4 (1742 cm^{-1}), and in acetonitrile (1738 cm^{-1}). Unfortunately this compound could not be studied in the crystalline state owing to the great ease of hydration. The appearance of only a single

Carbonyl frequencies (cm^{-1}).

Compound	Vapour	In CCl_4	In MeCN
$\text{CH}_3\cdot\text{COCl}$	1821	1806	1807
$\text{CH}_2\text{Cl}\cdot\text{COCl}$	1835, 1798	1821, 1785	1817, 1786
Intensity ratio *	1.6	4.9	> 8.5
$\text{CHCl}_2\cdot\text{COCl}$	1823, 1790	1810, 1779	1805, 1783
Intensity ratio *	0.66	0.96	> 2.0
$\text{CCl}_3\cdot\text{COCl}$	1815	1803	1803
$\text{CH}_3\cdot\text{CHO}$	1745	1730	1723
$\text{CH}_2\text{Cl}\cdot\text{CHO}$	1752	1742	1738
$\text{CHCl}_2\cdot\text{CHO}$	1761	1748	1744
$\text{CCl}_3\cdot\text{CHO}$	1778	1768	1761

* The intensity ratio figures represent the ratio of the apparent max. extinction coeff. for the high- and the low-frequency CO bands respectively.

carbonyl band in solution is in marked contrast to the behaviour of chloroacetone and indicates that only a single rotational isomer is present. The frequencies in various solvents are all somewhat higher than for acetaldehyde but the shifts are much smaller than would have been expected for a conformation with an eclipsed chlorine-oxygen grouping. Trichloroacetaldehyde, for example, absorbs at 1778 cm^{-1} in the vapour state. Free rotation would lead to much broader bands than are found, so that it seems that the chlorine atom is predominately in a position such as (III), well away from the oxygen atom. This accords with Mizushima's hypothesis. The frequency shift must then be ascribed to residual inductive effects.

The results for dichloroacetaldehyde are also not as clear cut as those for α -chloroacetone. Only a single carbonyl band is shown in the vapour and in solution, again indicating the predominance of one rotational isomer. The frequencies are now intermediate between the values which might be expected for conformations which respectively

have and have not eclipsed chlorine–oxygen atoms, and it is possible that some skew form such as (IV) is involved. No definite decision is possible from the data but it is significant that only one form is present and that this absorbs at a lower frequency than does the trichloro-product.

In trichloroacetaldehyde the carbonyl absorption is at 1778 cm.^{-1} for the vapour and at 1768 cm.^{-1} in CCl_4 . In this form one chlorine must be eclipsed by the oxygen atom, or two chlorine atoms must lie in the vectorially equivalent conformation in which they are at 60° to the carbon–oxygen plane. The substantial frequency rise over the value for acetaldehyde is, therefore, to be expected on the basis of field effects.

The results for chlorinated aldehydes as a whole are not conclusive but the stabilisation of a single rotational isomer throughout, and the lower frequencies of the partially chlorinated members, provide some support for the view that the reduction in steric hindrance on passing from ketones to aldehydes leads to a stabilisation of conformations in which the chlorine is twisted away from the oxygen atom wherever possible.

α -Chloro-acid halides. Chloroacetyl chloride shows two carbonyl frequencies in the vapour, the liquid, and the solution state, and this has previously been established as due to rotational isomerism. Unlike the earlier workers we find that the higher of these two frequencies is appreciably above that of acetyl chloride, as would be expected from a field effect in the more polar *cis*-chlorine–oxygen conformation. The occurrence of two frequencies in the vapour state is in contrast to the situation with α -chloro-ketones which usually show only a single absorption under these conditions, corresponding to the less polar form. The presence of the second chlorine atom has therefore increased the stability of the *cis*-form, as would be expected from the steric and electrostatic repulsions between the chlorine atoms. As will be seen from the Table, dichloroacetyl chloride behaves similarly whilst trichloroacetyl chloride shows a single absorption as it can exist in only one form. These findings therefore further support Mizushima's hypotheses. However, their most interesting feature is the unusual behaviour of the carbonyl frequencies. The higher frequency band occurs at 1835 cm.^{-1} in chloroacetyl chloride (vapour), representing a shift of 14 cm.^{-1} from the frequency for acetyl chloride; for dichloroacetyl chloride this value falls to 1823 cm.^{-1} which is within 2 cm.^{-1} of that for the parent compound; for the trichloro-derivative, which must have a chlorine atom eclipsed with the oxygen, the frequency falls to 1815 cm.^{-1} , which is 6 cm.^{-1} below that for acetyl chloride. As these higher frequency bands correspond to the more polar form this behaviour represents a marked difference from that of the α -chloro-ketones and similar materials.

The lower-frequency bands, corresponding to the less polar conformation, are also anomalous. In α -chloro-ketones these usually occur very close to the frequencies of the parent compounds. However, for chloroacetyl chloride this band is 23 cm.^{-1} lower than that of acetyl chloride, and in dichloroacetyl chloride it falls even further.

The most logical explanation of these abnormalities is the possibility of field effects between two chlorine atoms, when one of them is at an angle of 120° to the oxygen, as well as the more normal effects between *cis*-chlorine–oxygen atoms. Although the two halogen atoms are further apart both are readily polarisable and some small interaction is to be expected. The high carbonyl frequencies of these compounds are determined primarily by the electronegativity of the element attached to the carbonyl group. The replacement of a methyl group of acetone by chlorine, for example, results in an upward shift of 81 cm.^{-1} which is much greater than the shifts which arise from field effects. A field effect between the two chlorine atoms would lead to a reduction in the electronegativity of both from induced charges, and even a small change would therefore be expected to result in appreciable lowering of the carbonyl frequency. Effects of this type would be essentially additive and the suggestion is well supported by the self-consistency of the results from this point of view. The figures suggest that a chlorine atom which is eclipsed by the carbonyl-oxygen atom raises the frequency by about 14 cm.^{-1} , and that when it is at an angle of 120° the frequency is reduced by about the same amount. Starting with

the observation that acetyl chloride absorbs at 1821 cm.^{-1} we can assess the remainder as follows:

	Form	ν (Calc.) (cm. ⁻¹)	ν (Found) (cm. ⁻¹)
CH ₂ Cl·COCl	Polar (1 <i>cis</i> -Cl)	$1821 + 14 = 1835$	1835
	Less polar (120° Cl)	$1821 - 14 = 1807$	1798
CHCl ₂ ·COCl	Polar (1 <i>cis</i> -, 1 120° Cl)	$1821 - 14 + 14 = 1821$	1823
	Less polar (2 120° Cl)	$1821 - 28 = 1793$	1790
CCl ₃ ·COCl	(1 <i>cis</i> -, 2 120° Cl)	$1821 + 14 - 28 = 1807$	1815

The postulate of additional field effects between the two chlorine atoms in suitable conformations therefore offers a reasonable explanation of these abnormal frequencies, and a compound such as chloroacetyl chloride provides an interesting example of a molecule in which different field effects occur in the two rotational isomers and operate there in opposite directions.

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