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Spectral correlations for α, β-unsaturated acid halides

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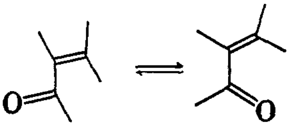
Abstract—The infrared spectral behaviour of alkyl substituted α,β-unsaturated acid fluorides, chlorides and bromides is reported. The ratio r^i of the integrated band intensities of the C=O and C=C stretching vibrations is measured and correlated with the preferred conformation (S-*cis* and S-*trans*) of the molecules. These results are compared with others obtained for the related carbonyl compounds.

Introduction

A number of papers have been published on the infrared spectra of α,β-unsaturated ketones, many of which deal with the conformations of the molecules [1]. In this paper the results of the related acid halides are reported and an attempt has been made to assign the preferred conformation of the type:



S-*trans* (transoid) S-*cis* (cisoid)
Ia Ib

Temperature dependence studies by Katon and Feairheller [2, 3] of the i.r. spectra of acrylyl chloride and bromide, and methacrylyl and crotonyl chlorides showed that the rotational equilibrium Ia ⇌ Ib could be detected from the carbon–halogen stretching vibrations between 500–800 cm^{-1}. Similar studies on the i.r. spectra of acrylyl fluoride showed that if the above rotational equilibrium does exist, as pointed out by Koster [4] on the basis of n.m.r. study, there is a very small difference between the spectra of the two forms [5]. Furthermore, the i.r. results of fumaryl chloride and fumaryl and maleoyl fluorides have been reported [6].

In α,β-unsaturated ketones, it has been pointed out that the preferred S-*cis* and S-*trans*, conformations can be obtained from the ratio r^i of the integrated band intensities of the C=O and C=C stretching vibrations. The ratio is low in the cisoid and high in the transoid conformation [7, 8].

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EXPERIMENTAL

Substituted α,β-unsaturated acid fluorides [9] and bromides [10] were prepared by the reaction of the corresponding acid chlorides with SbF_3 and PBr_3 respectively, and acrylyl and methacrylyl chlorides by the reaction of their carboxylic acids with benzoyl chloride STEMPEL *et al.* [11]. Other substituted α,β-unsaturated acid chlorides were prepared by conventional means using thionyl chloride. The acid halides, purified by fractional distillation (Table 1), were cooled and pumped under reduced pressure before recording the i.r. spectra. In addition, their spectra were scanned against the corresponding carboxylic acid which might be formed by hydrolysis.

Table 1. Boiling points of substituted α,β-unsaturated acid halides

R	COF	COCl	COBr
$CH_2{=}CH$	34–34·5	75–76	82–83
$CH_2{=}C(CH_3)$	58–60	96–97	114–116
$CH_3CH{=}CH$ (*trans*)	80–82	122–123	146
$CH_3CH{=}C(CH_3)$ (*trans*)	102–104	144–145	158–160
$(CH_3)_2C{=}CH$	106–108	146–147	161

The i.r. spectra of the compounds were recorded in solution (CCl_4) employing a Beckman IR12 spectrophotometer. Cells with KBr windows and 0·1 cm path length were used. The integrated band intensities were calculated using a planimeter and tabulated in arbitrary planimeter units. The frequency values are recorded in cm^{-1} and the ε_{max} in $l.\ mol^{-1}\ cm^{-1}$.

RESULTS AND DISCUSSION

The results show that the lowest and highest r^i values are obtained for the β,β-dimethyl and α-methylacrylyl halides respectively (Tables 2–4). The values

Table 2. Infrared spectra of α,β-unsaturated acid flourides

Acid fluorides	C=O			C=C			$\Delta\nu$	r^i
	ν_{max}	ε_{max}	A	ν_{max}	ε_{max}	A		
$CH_2{=}CHCOF$	1828	758·2	141·9	1632	33·2	4	196	35
$CH_2{=}C(CH_3)COF$	1815	800	123	1646	26·3	3·1	169	39
$CH_3CH{=}CHCOF$	1821	897	146·8	1659	181·5	20·5	162	7
$CH_3CH{=}C(CH_3)COF$	1808	921·3	133·2	1656	105	12·7	152	10
$(CH_3)C{=}CHCOF$	1808 1838(sh)*	684·3	115·7	1648	253	52·5	160	2·3

* Could be due to the first overtone of the strong absorption at 919 cm^{-1}.

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Table 3. Infrared spectra of α,β-unsaturated acid chlorides

Acid chlorides	C=O in CCl_4			C=C in CCl_4					ν in $CHCl_3$		
	ν_{max}	ε_{max}	A	ν_{max}	ε_{max}	A		r^i	$\nu_{C=O}$	$\nu_{C=C}$	ν_{C-Cl}*
$CH_2=CHCOCl$	1767 1778 (sh)	517	124·7	1615 1626	44 14	6·5	152	19	1762	1614 1625	610† 708‡
$CH_2=C(CH_3)COCl$	1748 1773§	307‖ 342‖	135	1626 1641	9·1 8·5	3·9	127	34	1743 1772	1625 1640	
$CH_3CH=CHCOCl$	1752 1772	134 617	147	1640 1652	147 55	22	116	6·7	1747 1768	1637 1650	610¶ 768**
$CH_3CH=C(CH_3)COCl$	1759	709	136	1637 1654	17·4 80·5	14	114	9·7	1753	1633 1649	
$(CH_3)_2C=CHCOCl$	1760 1789	192·8†† 220·7††	103	1626	302·7	52	149	2	1755 1788	1622	760

* Recorded as liquid film.

†‡ Reported 607 and 703 cm^{-1} assigned as ν_{C-Cl} in S-*trans* and S-*cis* forms respectively [5].

§ May be due to first overtone of the strong band at 884 cm^{-1}, as $884 \times 2 = 1768\ cm^{-1}$.

‖ The relative intensity (ε_{max}) is $307/342 = 0{\cdot}89$ in CCl_4, where as $345/233 = 1{\cdot}48$ in $CHCl_3$.

¶** Reported 605 and 762 cm^{-1}, respectively.

†† The relative intensity (ε_{max}) is $192{\cdot}8/220{\cdot}7 = 0{\cdot}87$ in CCl_4, where as $203{\cdot}2/143{\cdot}3 = 1{\cdot}41$ in $CHCl_3$.

Table 4. Infrared spectra of α,β-unsaturated acid bromides

Acid bromides	C═O in CCl_4			C═C in CCl_4			r^i	ν in $CHCl_3$		ν_{C-Br}*
	ν_{max}	ε_{max}	A	ν_{max}	ε_{max}	A		$\nu_{C=O}$	$\nu_{C=C}$	
CH_2═CHCOBr	1773 1786 1805 (sh)	390 276	124·7	1606 1629	17	2·7	50	1769	1604 1628	590† 695‡
CH_2═C(CH_3)COBr	1770 1820	461 87	137	1620	5·4	1·6	86	1764 1819	1618	
CH_3CH═CHCOBr	1776 1805	244 97	77	1620 (sh) 1632	86	14·6	5·3	1767 1810	1629 1640 (sh)	580 740
CH_3CH═C(CH_3)COBr	1766	299	83	1632 1651	11 37	6·7	12·4	1758	1627 1646	
$(CH_3)_2$C═CHCOBr	1743 (sh) 1792	159	49	1619 1660 (vw)	109	20·2	2·4	1744 (sh) 1788	1615 1660 (vw)	732

* Recorded as liquid film.

†‡ Reported 585 and 695 cm^{-1}, assigned as ν_{C-Br} in S-*trans* and S-*cis* forms respectively [5].

range between 2–2·4 in the former while they are higher than 34 in the latter. In the lower frequency region the presence of one strong absorption at 760 cm^{-1} in β,β-dimethylacrylyl chloride could be attributed to the C—Cl stretching vibration of the S-*cis* form. This is based on the results obtained by KATON and FEAIRHELLER [3] for other related acid chlorides. Molecular models and scale diagrams of these molecules show that the S-*cis* conformation is adopted when the two β-hydrogens are substituted by methyl groups. Moreover, the α-methyl group destabilises the S-*cis* form and therefore the S-*trans* conformation is predominant. Similar predictions based on r^i values have been reported for the corresponding ketones (Table 5) [1].

Table 5. Values of r^i for different unsaturated carbonyl compounds (R—X)

R	X				
	CH_3	OCH_3	F	Cl	Br
$CH_2{=}CHCO$	7·8	20	34·5	19·2	46·2
$CH_2{=}C(CH_3)CO$	9	—	38·4	34·6	85·5
$CH_3CH{=}CHCO$	3·5	4·7*	7·2	6·7	5·3
$CH_3CH{=}C(CH_3)CO$	6	8·8	10·8	9·7	12·4
$(CH_3)_2C{=}CHCO$	0·7	2·6	2·2	1·97	2·4

* Ethyl ester was used [20].

Acrylyl halides have relatively high r^i values and therefore it is likely that they exist predominantly in the S-*trans* form (Tables 2–4). In the case of acrylyl chloride and bromide, the appearance of a shoulder at the high frequency side of the carbonyl absorption is due to the fraction of the S-*cis* form. This is verified by solvent effect studies (see later) in which the two absorptions collapse to give a single band at lower frequency values in changing the solvent from CCl_4 to $CHCl_3$ (Tables 3 and 4). These results are in good agreement with the observations made by KATON and FEAIRHELLER [3] and CARLSON *et al.* [5].

The acid fluorides show a single absorption in both the C=O and C=C stretching regions (Table 2), but the acid chlorides and bromides absorb as a doublet in most cases (Tables 2 and 3). The latter could be explained by either (i) the presence of a mixture of S-*cis* and S-*trans* conformers [12, 13], or (ii) Fermi resonance resulting from coupling between the C=O and C=C fundamental vibrations and others of different nature such as overtone or combination bands [14]. Since the C=O stretching frequency is usually decreased by changing the solvent from CCl_4 to $CHCl_3$, we used these solvents in our i.r. measurements of acid chlorides and bromides to obtain some information about the nature of the splitting. In α-methyl and β,β-dimethylacrylyl chlorides and bromides the low frequency component of the $\nu_{C=O}$ doublet is shifted by 5 cm^{-1} to lower values in $CHCl_3$, whereas the frequency

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of the higher component remains nearly constant. Therefore, the former bands are considered to be carbonylic in nature, while the latter are not. Such behaviour of the carbonyl doublet absorption is explained by Fermi resonance. Further evidence for this is found in α-methylacrylyl chloride by the presence of a strong absorption at 884 cm^{-1} which has a first overtone at 1768 cm^{-1}. In β,β-dimethylacrylyl chloride the two strong absorptions at 760 and 1001 cm^{-1} could combine to result in the absorption at 1789 cm^{-1}. Also we find an inversion of the relative band intensities (presented as ε_{max}) of the doublet on changing the polarity of the solvent (see footnotes ‖ and †† in Table 3), as has been reported for other carbonyl compounds [14, 15]. The presence of doublet C=C absorptions in some of the acid chlorides and bromides under study could be explained similarly and the examination of the corresponding deuterated compounds could possibly provide further information on this point.

In crotonyl chloride and bromide, the low frequency shift of both components of the $\nu_{C=O}$ doublet reflects the carbonylic nature of this absorption and points to the co-existence of S-*cis* and S-*trans* forms in equilibrium. The r^i values for these molecules are lower than for the preferred S-*cis* form of β,β-dimethyl halide and higher than for the preferred S-*trans* form of α-methylacrylyl halide. Recent temperature dependence studies on the i.r. spectra of related carbonyl compounds, including ethylidene acetone [16] and ethyl and methyl crotonates [17], showed that these molecules do exist as an equilibrium mixture of the S-*cis* and S-*trans* conformations.

In α,β-dimethylacrylyl halides, where the r^i values range between 9·7–12·7, the compounds still favour the S-*trans* conformation. These lower values, compared with α-methylacrylyl halides, might be explained by the opposing polarisation fields of the two methyl groups on the carbonyl group. Molecular models and scale diagrams of these molecules show that the S-*trans* form should predominate due to steric factors.

The relatively low $\nu_{C=O}$ and $\nu_{C=C}$ band intensities of the β-substituted acid bromides compared with the corresponding chlorides is attributed to steric factors exerted by the bromine atom.

GENERAL OBSERVATIONS

1. The effect of halogen substitution on the C=O stretching vibration frequency in α,β-unsaturated acid halides follows the same trend as in the corresponding saturated compounds [18]. The $\nu_{C=O}$ frequency decreases in the order: RCOF > RCOBr > RCOCl. Also a decrease in the average frequency difference ($\nu_{C=O}$(sat.)–$\nu_{C=O}$(unsat.)) from 34 to 30 cm^{-1} between RCOF and RCOCl is due to the conjugation effect (as indicated on page 271).

2. The number of alkyl groups and their positions has a much greater effect on integrated band intensity of the C=C than the C=O stretching vibration. The

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	R = CH_3 $\nu_{C=O}$ (cm^{-1})	R = Unsaturated $\nu_{C=O}$ (average) (cm^{-1})	$\Delta\tilde{\nu} = \nu_{C=O}$ (Sat.) $- \nu_{C=O}$ (Unsat.) (cm^{-1})
RCOF	1850	1816	34
RCOBr	1810	1777	33
RCOCl	1795	1765	30

most intense $\nu_{C=C}$ bands, in β,β-dimethylacrylyl halides, arise from the reinforcement of the β-methyl with the polarising influence of the C=O group. Not surprisingly, α-methyl substitution causes a slight decrease in the C=C band intensity. Similar observations were reported for some unsaturated ketones [19].

3. Generally the r^i values decrease in the order: α-methyl $>$ unsubstituted $>$ α,β-dimethyl $>$ β-methyl $>$ β,β-dimethylacrylyl halides. The same observation has been found for the related ketones [7] and esters [20] (Table 5). In α-methyl substituted compounds the S-*trans* form is favoured, whereas the β,β-dimethyl compounds exist mainly in the S-*cis* form.

4. The value of $\Delta\nu(\nu_{C=O} - \nu_{C=C})$ which has been considered as another factor besides the r^i ratio in distinguishing between the S-*cis* and S-*trans* forms in conjugated ketones [21] appears to have little structural significance in the compounds studied. The relatively high $\Delta\nu$ values in these compounds seem to be associated with a decrease of the C=C band intensities, by comparison with the corresponding values for conjugated ketones. This could be explained by a decrease in vibrational coupling between the C=O and C=C chromophores in acid halides. It has been mentioned that the degree of vibrational coupling is proportional to the band separation that results from it [15].

5. As unsaturated acid fluorides show single C=O and C=C stretching vibrations, the corresponding acid chlorides and bromides show multiple absorptions in these regions. The latter absorptions might give overtone and combination bands in the 1600–1800 cm^{-1} region.

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