Carbonyl Stretching Frequencies of Carboxylic Acids Dissolved in Sulphuric Acid

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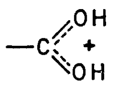
Summary Two bands assignable to stretching modes of carbon–oxygen bonds have been found in the i.r. spectra of carboxylic acids dissolved in 100% H_2SO_4 or D_2SO_4.

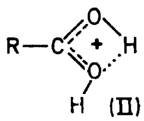
CONFLICTING assignments of the carbonyl stretching frequencies of the protonated carbonyl group (I) have appeared in the literature.[1,2] With the hope of resolving this difference of opinion, and in order to provide a basis for other work involving carboxylic acids in H_2SO_4, we have recorded the infra-red spectra of a number of such systems, both in H_2SO_4 and D_2SO_4.

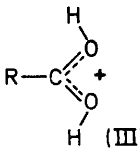
In all cases the carbonyl stretching band characteristic of the parent acid is absent, and two new bands appear at lower frequency. Both bands are strong, but that at higher frequency is always the stronger of the two. It is unlikely that these are the antisymmetric–symmetric stretching modes of (I), since no corresponding bands occur in the Raman spectrum of acetic acid in H_2SO_4[1,2] where the symmetric mode should absorb strongly.

N.m.r. studies[3,4] of carboxylic acids dissolved in HSO_3F–SbF_5–SO_2 at about −60° reveal two resonances attributable to acidic OH protons with a small chemical shift between them. These were assigned as the OH proton resonances of the structure (II).

It is likely that a similar situation exists in H_2SO_4, though rapid exchange of the labile hydrogen in the system prevents the observation of separate OH resonances in the n.m.r. spectrum. The great preponderance of (II) compared with (III) reported in reference 4 indicates that stabilisation of (II) must occur. It has been suggested[3] that hydrogen bonding occurs as indicated by the dotted line in (II), and if this is so, it follows that the frequency of the CO band involved in the hydrogen bond will be lowered. Also, since this CO group is affected by both hydrogen atoms, the effect on it of replacing hydrogen with deuterium should be greater than on the other CO group. That this is so is clearly demonstrated by the figures for the band frequencies in D_2SO_4 (Table). The shift to lower frequency is about 12 cm^{-1} for the high frequency band, and about 38 cm^{-1} for the low frequency band. For comparison, the corresponding frequencies of acetone are also listed in the Table. In this case the shift is comparable with that of the high frequency band of the acids, as expected.


(I)


(II)


(III)

It seems clear, therefore, that in sulphuric acid, saturated carboxylic acids do exist in the form represented by (II).

I.r. frequencies of protonated carbonyl species between 1500 *cm*$^{-1}$ *and* 2000 *cm*$^{-1}$

Solute	In H_2SO_4	In D_2SO_4	Δ, cm^{-1}
Acetic acid	1618, 1552	1607, 1514	11, 38
Propionic acid	1608, 1542	1595, 1505	13, 37
Butyric acid	1611, 1542		
Isobutyric acid	1601, 1542	1588, 1503	13, 39
Pivalic acid	1580, 1540	1570, 1501	10, 39
Valeric acid	1611, 1543		
Stearic acid	1607, 1540		
Acetone	1609	1599	10

Preliminary work has shown that esters in sulphuric acid also exhibit two bands similar to those found with carboxylic acids. For example, ethyl acetate has bands at 1611 cm^{-1} and 1500 cm^{-1} in H_2SO_4 which are lowered to 1602 cm^{-1} and 1493 cm^{-1} respectively, in D_2SO_4. Again these results can be accommodated by postulating a structure for the protonated ester similar to (II) in which the added proton, though formally attached to the carbonyl oxygen atom, also interacts with the acyl oxygen atom.

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