

## RAMAN EFFECT AND HYDROGEN BONDS

### Part VII. Study of a Few Typical Carboxylic Acids

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IN continuation of the study of the Raman spectra of acetic acid and its solutions in various solvents (Parts III, IV and V)<sup>1</sup> a few typical carboxylic acids have now been examined with a view to make the survey more comprehensive.

*Propionic acid.*—The Raman spectrum of this acid was investigated by a number of workers in the past.<sup>2</sup> They recorded only one broad line in the region of the C=O frequency. For our investigation pure dry propionic acid was prepared by redistillation of the acid kept over fused sodium propionate for a day. The following frequencies were obtained:—

290 (1) 480 (3) 610 (1) 846 (6) 1001 (3) 1080 (5) 1257 (2) 1420 (5) 1460 (4) 1668 (10*b*) 1710 (0) 1740 (0).

The two lines with (0) intensities were very distinct though very faint. They were not recorded by previous workers. Thus the spectrum of propionic acid bears a very close resemblance to that of acetic acid in the C=O region. The spectrum was quite unaffected in carbon tetrachloride solution. With a solution of the acid in water (1:1) the 1668 cm.<sup>-1</sup> line becomes almost extinct and the 1710 cm.<sup>-1</sup> line very intense; the 1740 cm.<sup>-1</sup> line was not recorded at all. A dioxan solution (1:1) gave the three lines with almost equal intensity due to the first having become weaker and the other two much stronger. If the proportion of acid to dioxan was 1:3, the first line vanished, the other two persisting. The 1740 cm.<sup>-1</sup> line was more intense than the 1710 cm.<sup>-1</sup> line. Thus the behaviour of these solutions is also parallel to that of acetic acid solutions. Consequently the mechanism of the changes is the same as described in the case of acetic acid, the three entities involved being (1) ring dimers, (2) open dimers and (3) monomers; (2) and (3) take part in complex formation with the solvents employed.

*Formic acid.*—This acid is known to differ from its homologues in a number of respects, the most important being its marked strength as an acid and its reducing properties. An explanation of these characteristics was given in a note to *Current Science*.<sup>3</sup> Hence it was felt necessary to study the Raman spectrum of pure formic acid and of its solutions in certain select solvents.

The Raman spectrum of formic acid has been studied by several workers in the past<sup>4</sup>; but the records are not entirely in agreement. The following gives the complete spectrum of a sample carefully purified by repeated distillation as obtained by us:—

190  $\pm$  80 (8) 675 (3) 700 (1) 1048 (2) 1205 (2) 1400 (10) 1670 (8b) 1725 (4b) 2963 (7).

The broad and bright band at 190  $\text{cm}^{-1}$  is remarkable since it is present only in the spectrum of formic acid and not in those of its homologues. It has been previously noted by Parthasarathy<sup>5</sup> and by Ganesan and Venkateswaran<sup>6</sup> but was not reported by Dadiou and Kohlrausch.<sup>7</sup> In the region of the C=O frequency Parthasarathy (*loc. cit.*) reported 1672 and 1724  $\text{cm}^{-1}$  lines and Kohlrausch, Koppel and Pongratz<sup>8</sup> 1675 and 1728  $\text{cm}^{-1}$  lines. But Koteswaram could get only a broad frequency at 1702  $\text{cm}^{-1}$ .

An aqueous solution of formic acid was first studied by Parthasarathy. He noticed that the band at 189  $\text{cm}^{-1}$  underwent a slight shift and narrowing. In the place of the two C=O lines of the pure acid he obtained a diffuse line with a maximum at 1697  $\text{cm}^{-1}$ . These changes were attributed to the formation of hydrates. Koteswaram observed a shift of the maximum of the broad line at 1702  $\text{cm}^{-1}$  towards higher frequencies and attributed it to simple depolymerisation.

Mixtures of formic acid with various solvents have now been investigated. The significant results are given below:

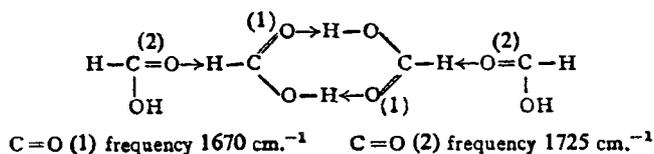
*Water mixtures.*—190  $\text{cm}^{-1}$  band narrowed down, the 1670  $\text{cm}^{-1}$  line decreased in intensity and the 1725  $\text{cm}^{-1}$  line increased in intensity. In a solution having acid and water in the proportion 1 : 3, the 1670  $\text{cm}^{-1}$  line became very faint though it did not disappear altogether.

*Dioxan mixtures.*—Formic acid and dioxan in the proportions 1 : 1 and 1 : 3 were employed. The 190  $\text{cm}^{-1}$  band narrowed down; the 1670  $\text{cm}^{-1}$  line decreased in intensity with a corresponding increase in the 1725  $\text{cm}^{-1}$  line. In the more dilute solution the first line was more faint and the second much stronger.

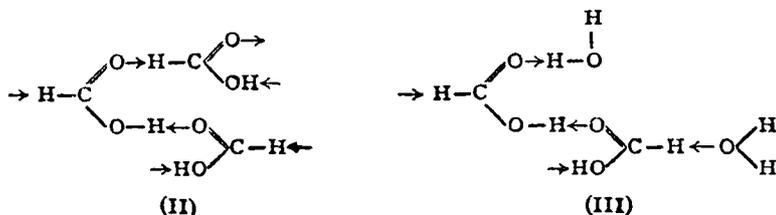
*Acetal, acetone and ethyl acetate mixtures.*—The solutions in acetal behaved very similar to those in dioxan. In acetone solutions C=O frequencies could not be studied due to the existence of the strong C=O frequency of acetone falling in this region. But the narrowing of the band at 190  $\text{cm}^{-1}$  was observed. The changes in ethyl acetate mixtures were again similar to those taking place in dioxan. But how far the C=O frequency of the ester (1740  $\text{cm}^{-1}$ ) could have rendered the observation inexact could not be gauged. The narrowing down of the 190  $\text{cm}^{-1}$  band is, however, significant in this case also.

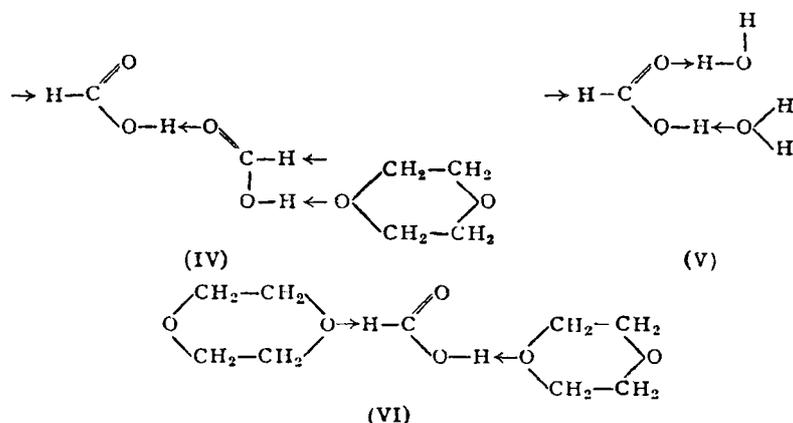
*Discussion of results.*—There is ample evidence for the existence of formic acid in the polymeric form. The presence of ring dimers has been proved by the method using electron diffraction.<sup>10</sup> The changes taking place in mixtures with water and other kationoid and anionoid solvents may be expected to be somewhat similar to those found in the case of acetic and propionic acids. But there are obviously marked differences arising from the very nature of the formic acid molecule and the complications that it may give rise to. The chief item to be noted is the capacity of H of the CH in formic acid to form H bonds in addition to the OH of the carboxyl. This naturally introduces complications that have to be taken account of. The changes in  $190\text{ cm.}^{-1}$  band are in some manner connected with depolymerisation of formic acid aggregates and formation of heteromolecular associates. The smallness of the frequency shift appears to suggest that we are here concerned with a phenomenon involving aggregation only less in size compared with crystal aggregates. But the exact correlation is not clear.

The  $1670\text{ cm.}^{-1}$  line and the change it undergoes seem to be common to all the aliphatic acids. It is therefore right to attribute it to the C=O groups existing in ring dimers. Instead of the two lines of acetic and propionic acids ( $1710$  and  $1740\text{ cm.}^{-1}$ ) which change markedly on admixture with other solvents, formic acid has only one broad line at  $1725\text{ cm.}^{-1}$  which is fairly strong even in the pure acid and brightens up in the mixtures. Obviously in the case of this acid no un-co-ordinated C=O is possible under any circumstances and the  $1725\text{ cm.}^{-1}$  line corresponds to a linearly co-ordinated C=O. This leads us to the inference that in the pure acid there is an appreciable proportion of C=O groups linearly co-ordinated and that this increases in the mixtures. The following tentative structures are suggested to exist in the pure acid (I, II) and in mixtures (others).

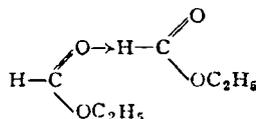


(I)





In this connection may be mentioned a similar peculiarity noted with ethyl formate. Whereas ethyl acetate and esters of other aliphatic acids have a sharp  $C=O$  frequency at  $1740\text{ cm.}^{-1}$ , formates have a rather broad line at  $1715\text{ cm.}^{-1}$ . The low value of this frequency and its breadth may be due to association of the ester molecules by means of hydrogen bonds. This point requires careful verification by other methods and is being studied.



*Benzoic acid.*—The Raman spectra of benzoic acid in solvents such as benzene, ether and alcohol were studied by Dadiou and Kohlrausch.<sup>11</sup> The  $C=O$  frequencies recorded were  $1648$ ,  $1716$  and  $1689\text{ cm.}^{-1}$  respectively. Koteswaram studied the molten substance and its solutions in benzene and water. He recorded  $1654\text{ cm.}^{-1}$  for the free acid and benzene solutions and  $1728\text{ cm.}^{-1}$  for the aqueous solutions at  $100^\circ\text{ C}$ . Sunanada bai<sup>12</sup> has noted the  $C=O$  frequency of the molten acid as  $1660\text{ cm.}^{-1}$

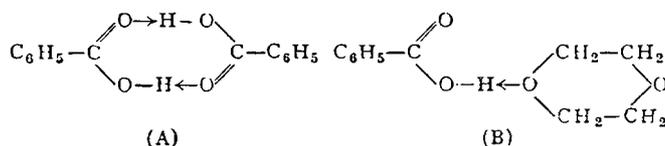
The following is the spectrum of the pure molten acid as observed by us:

160 (1) 172 (3) 422 (3) 480 (?) 625 (6) 648 (0) 800 (4) 820 (0) 999 (10)  
1016 (2) 1030 (0) 1109 (1) 1176 (1) 1270 (3) 1560 (8) 1598 (4).

The  $C=O$  line remained practically unaffected in the benzene solution. On the other hand in ether this disappeared and a new  $C=O$  frequency was recorded at  $1710\text{ cm.}^{-1}$  and this was more prominent than the original line at  $1650\text{ cm.}^{-1}$ . A solution in dioxan gave the same result, *i.e.*, new  $C=O$  line was at  $1715\text{ cm.}^{-1}$  and the original one at  $1650\text{ cm.}^{-1}$  was absent. In acetal solution (1:1) besides the  $1715$  line, the  $1650\text{ cm.}^{-1}$  line could be observed

faintly. It however disappeared when 1:3 (acid:acetal) solution was employed.

There is thus only one observable C=O frequency in the benzene solution. Since it is known from molecular weight determinations that the acid is associated (double) it may be concluded that the frequency of 1650  $\text{cm}^{-1}$  corresponds to the ring dimers of the type (A) and possibly the open dimers and monomers do not exist to any detectable extent. In dioxan and ether solutions and in the more dilute solutions in acetal again only a bright C=O frequency at 1715  $\text{cm}^{-1}$  exists. This may be said to correspond to monomer associates having free C=O groups as in (B). In justification of this may be mentioned that ethyl benzoate having an unco-ordinated C=O group exhibits a C=O Raman line at 1720  $\text{cm}^{-1}$ .



In less dilute solutions in acetal both lines appear though the 1650  $\text{cm}^{-1}$  line is very feeble indicating that both types of molecules exist simultaneously. It is remarkable that there is no indication of the presence of the intermediate stage of open dimers and their associates with the solvents employed. It may be tentatively suggested that in this case they are unstable and either undergo change into the ring dimers or into monomer associates with the solvents. The breaking up of the dimers of the acid through H bond formation seems to be more easy than in the case of the aliphatic acids.

*Cinnamic acid.*—The behaviour of the unsaturated acid, cinnamic acid is very similar to that of benzoic acid. The following is the Raman Spectrum of the molten acid:—

153 (2b) 615 (1) 675 (0) 875 (2) 990 (1) 1002 (8) 1027 (3) 1077 (1) 1110 (1) 1181 (5) 1194 (6) 1260 (7) 1490 (2) 1598 (7) 1624 (10b) 1654 (2b).

Of the last 3 lines 1598  $\text{cm}^{-1}$  frequency is attributed to the double bond of the benzene ring and 1624  $\text{cm}^{-1}$  to the extra nuclear double bond. The last line, 1654  $\text{cm}^{-1}$  is attributable to the C=O group of the acid. In benzene solution this line appeared at 1658  $\text{cm}^{-1}$  and obviously represents ring dimers. No other line was noted in the C=O region. In dioxan solution this disappeared and a new line appeared at 1708  $\text{cm}^{-1}$  thus indicating that complete break down into monomer associates with the solvent occurs. In support of the above contention may be stated (1) that cinnamic acid has double the molecular weight in benzene solution, (2) that the unco-ordinated C=O frequency should be at about 1708 since ethyl cinnamate has

the C=O line in this region and (3) the shift in the C=O Raman line due to formation of ring dimers (about 50 wave numbers) is according to expectation as judged from other cases. There is thus complete similarity between benzoic and cinnamic acids.

#### Summary and Conclusion

Raman spectra of (1) propionic acid, (2) formic acid, (3) benzoic acid and (4) cinnamic acid have been studied using the pure acids in the liquid or molten condition and solutions in various solvents, benzene (non-associating), water, ether dioxan, acetal, etc. (associating). The first closely resembles acetic acid both of them indicating the existence of ring dimers, open dimers and monomers, the last two forms being present to a very small extent in the free state and in increasing quantities (in association with solvents) in solution in associating liquids. The state of the molecules in formic acid seems to be more complex due probably to the capacity of H of the C-H group to form hydrogen bonds. There are 2 broad C=O lines equally strong in the pure liquid at 1670 and 1715  $\text{cm}^{-1}$ ; the former diminishes and the latter increases in solutions with associating solvents. The narrowing of the band at 190  $\text{cm}^{-1}$  is another characteristic. It seems to be possible that in this acid no molecular type having unco-ordinated C=O exists. Benzoic and cinnamic acids form a different type. The molten acids and benzene solutions give only one C=O line corresponding to ring dimers and in fairly dilute solutions in ethers monomer-associates alone containing unco-ordinated C=O groups exist. Thus they do not give indications of the intermediate open type of dimers.

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