

RAMAN EFFECT AND HYDROGEN BONDS

Part V. Mixtures of Acetic Acid with Ethers (Dioxan and Acetal)

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Received March 23, 1942

THE Raman spectra of mixtures of acetic acid with a number of carbonyl compounds were reported in Part IV¹ and it was shown that anionoid solvents affect the molecular aggregation of acetic acid, though the breakdown of the ring dimers was not complete. The chief difficulty experienced in the above study was the interference from the carbonyl groups of the anionoid solvents with the result that only partial information could be obtained in each case. This may be contrasted with the use of water and phenol wherein all the three lines of acetic acid could be studied and complete information obtained. With a view to secure analogous conditions with anionoid solvents, types other than carbonyl compounds had to be examined. In this connection ethers as a group come in very handy and of these dioxan and acetal are the most convenient. Dioxan is a good solvent, has a conveniently high boiling point and has two anionoid oxygen atoms per molecule. In a similar way acetal is also good being the diethyl ether of the hypothetical acetaldehyde hydrate.

Though the Raman spectra of dioxan and acetal have been investigated in the past by a number of workers their usefulness as convenient solvents for the study of hydrogen bonds has been shown only by the present investigation. The spectra of these solvents purified by redistillation are given below:

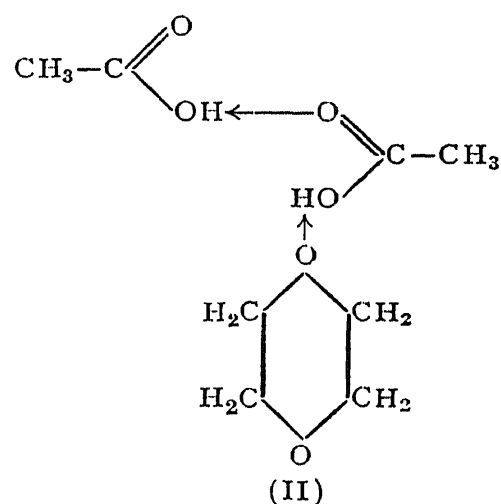
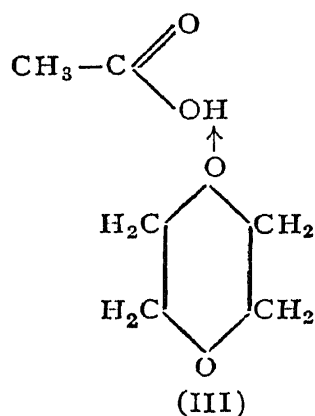
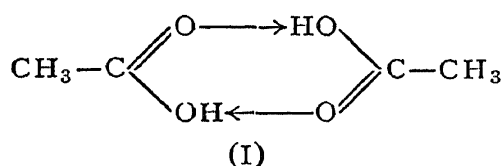
Dioxan.—180 (1) 435 (1) 483 (4) 837 (10) 850 (1) 1014 (6) 1107 (3) 1124 (1) 1214 (3) 1303 (6) 1332 (1) 1445 (8) 1459 (1) 2661 (0) 2719 (1) 2781 (1) 2858 (8b) 2889 (4) 2968 (9b).

Acetal.—350 (3) 450 (0) 530 (5) 660 (0) 810 (7) 850 (4) 919 (2) 1030 (3) 1063 (2) 1104 (4) 1150 (2) 1278 (4) 1340 (1) 1454 (10) 1486 (4) 2936 (5) 2982 (5).

Mixtures of acetic acid with dioxan.—Spectra of mixtures of acetic acid and dioxan in three proportions 1:1, 1:2 and 1:4 were studied. With the first mixture it was found that the three C=O lines of acetic acid namely 1670,

1710 and 1745 cm.^{-1} were of almost the same intensity. In the second mixture the 1670 cm.^{-1} line was weakened to the point of extinction and the 1710 and 1745 cm.^{-1} lines were fairly bright the latter being a little more intense than the former. In the third mixture containing 1 part of acetic acid and 4 of dioxan the 1670 cm.^{-1} line had vanished completely and of the other two lines 1710 and 1745 cm.^{-1} the latter was definitely brighter than the former. Thus progressive dilution with dioxan resulted in the disappearance of the first line and the brightening up of the other two of which the 1745 cm.^{-1} line became stronger.

The above results are satisfactorily explained from the standpoint already described regarding the molecular aggregation of acetic acid. The anionoid oxygen of dioxan obviously attacks the hydroxylic hydrogen of the open dimers and the monomers forming complexes as represented below :



Of the three types of molecular aggregates (I), (II) and (III) the first contributes to the 1670 cm.^{-1} line only since all the $\text{C}=\text{O}$ groups are involved in H bonds of the ring type. Aggregate (II) should contribute equally to the two lines 1710 and 1745 cm.^{-1} as there is one unco-ordinated $\text{C}=\text{O}$ and one linearly co-ordinated $\text{C}=\text{O}$. On the other hand structure (III) should mean increase in intensity of the 1745 cm.^{-1} line only since the $\text{C}=\text{O}$ is unco-ordinated. In the 1 : 1 mixture since all the three lines are of the same intensity it may be concluded that (1) the breakdown of the ring dimers is only partial, (2) a considerable number of such molecules continue to exist, (3) aggregates of type II are mainly formed as a result of this mixture and (4) molecular aggregates of type III are probably not present

in any appreciable number. In the second mixture (1 : 2) most of the ring dimers should have been broken down since the 1670 cm.^{-1} line has been considerably reduced in intensity. From the fact that the 1745 cm.^{-1} line is the brighter of the other two it may be inferred that besides the predominance of aggregates of type II more of type III than before are formed. In the third mixture (1 : 4) the ring dimers have disappeared altogether and the mixture consists of types II and III only. The results are best explained even in the case of this dilute solution with the predominant occurrence of type II though the monomer aggregates (III) may be increasing with greater dilution.

It may be interesting to compare the results of the mixtures of acetic acid and water with those of acetic acid and dioxan. Though in both the cases the ring dimers are completely broken in dilute solutions, the fact that the 1670 cm.^{-1} line fades almost to extinction in aqueous solution even in 1 : 1 proportion shows that there is in this case almost complete breakdown of the ring form at comparatively high concentrations. Thus water seems to be far more effective than dioxan. Another point of difference between these cases is that in water the only line present is 1710 cm.^{-1} whereas in dioxan solution both 1710 cm.^{-1} and 1745 cm.^{-1} are present, the latter being the more intense of the two. This is due to the fact that in aqueous solutions the water molecules efficiently attack any unco-ordinated $\text{C}=\text{O}$ bonds and reduce their frequency whereas in dioxan solutions such a possibility does not exist.

Mixture of acetic acid and acetal.—In the spectrum of the mixture (1 : 1) the 1670 cm.^{-1} line was diminished in intensity and the other two lines became more intense (equal). Obviously the ether oxygen atoms of acetal serve the same purpose as those of dioxan. The results indicate that at moderate dilutions a considerable number of ring dimers break down to form aggregates of type II though this change is not so prominent as in the case of dioxan.

From the results obtained using mixtures of acetic acid with ethers and with carbonyl compounds it is definitely established that substances containing powerful anionoid centres such as $\text{C}=\text{O}$ or $\text{$\text{>O}$$ are capable of breaking down the molecular aggregates of acetic acid. It has already been shown that a powerful cationoid substance, phenol, has also considerable influence in regard to the above change. Hence the generalisation that both types of molecules can produce this effect, is quite valid. Water which possesses both the characteristics obviously acts in both capacities. This may account for the efficiency of water molecules in causing disruption of

ring dimers of acetic acid. It has been recorded that even in fairly concentrated aqueous solutions having limited amount of water the 1710 cm.^{-1} line alone exists. Molecules which have only one type of active group are not so satisfactory. Besides its dual character water may have other advantages. It is quite possible that its small size also counts since difficulties due to steric factors will then be at a minimum.

In our attempts to explain the spectra of aqueous solutions of acetic acid three types of molecular aggregates were postulated. Of these the existence of ring dimers had already been independently established by other physical methods such as electron diffraction method. Strong support for the existence of the open type of dimers has now been obtained from the study of mixtures with other solvents, the most conclusive evidence being obtained with the following mixtures: coumarin-acetic acid, dioxan-acetic acid and acetal-acetic acid. The existence of monomers of acetic acid in association with the solvents to some extent is definitely brought out in the spectra of the dioxan-acetic acid mixture.

Summary

Raman spectra of mixtures of acetic acid with donor solvents not having $\text{C}=\text{O}$ groups have been studied. The solvents chosen are dioxan and acetal. The results lend definite support to the mechanism described in previous papers (Parts III² and IV¹) of the progressive breakdown of the ring dimers of the acid into associates of the open dimers and eventually of the monomers with the solvent molecules. The extraordinary efficiency of water in bringing about the breakdown is attributed to its dual capacity to act as both donor and acceptor.

REFERENCES

1. Murty and Seshadri .. *Proc. Ind. Acad. Sci. (A)*, 1942, **15**, 238.
2. ————— .. *Ibid.*, 1942, **15**, 230.