ON THE RAMAN SPECTRA OF OXALATES IN SOLUTION AND THE STRUCTURE OF THE OXALATE ION.

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Plate XV.

ABSTRACT : In continuation of the author's previous work on formic acid and metallic formates,[1] where a difference between the Raman spectra of pure formic acid and formates and those of the aqueous solutions of these substances was observed, the Raman spectra of aqueous solutions of oxalic acid, potassium and ammonium oxalates have been examined. Similar changes have also been observed here, by which the behaviour of the carboxyl group before and after ionisation, as discussed in the said paper, have been confirmed.

INTRODUCTION.

The structural formulation of oxalic acid has been a subject of interest for some time past, particularly after the isolation of a new form of the acid by Wassilieff[2] by heating copper nitrate and benzene in sealed tubes at 170°-190° for several hours. On the basis of this work, Tschitschibabin[3] proposed a cis-trans type of isomerism of oxalic acid and tried to explain the various observations recorded in the literature regarding the properties of the acid with its aid.

The Raman spectrum of the acid has consequently been the subject of study of several workers. After the preliminary investigations by Krishnamurti[4], the substance has been reinvestigated by Rao[5] in the solid state and in the aqueous solution, by Angus and Leckie,[6] and with particular thoroughness by Hibben[7] in the solid state both in the form of the anhydrous acid and the crystalline dihydrate, and in solutions of water and methyl alcohol. The results of these workers are summarised in table I.

TABLE I.

Oxalic acid anhydrous (H)	Oxalic acid dihydrate		Oxalic acid in water			Oxalic acid in methyl alcohol (H)
	(H)	(A—L)	(R)	(H)	(A—L)	
		495	248(?)	395(m) 453(*m*)	493	403(m)
			480(m)			
			673(?)			
848(s)	847	854	845(s)	842(s)		850(s)
1370(d)	1365			1310(*w*)	1375	
	1471	1471	1430 ± 30(*wd*)	1460(d)		
1651(m)		1661(*b*)	1656(d)	1645(*d*)	1647 1684	
1740(?)		1759	1744(*s*)	1740(*m*)	1749	1755(s)

H = Hibben.[7]
A—L = Angus and Leckie.[6]
R = Rao.[5]

It is immediately apparent from the data tabulated above that the variance in the results obtained by the workers are beyond the limits of experimental error. For example, Angus and Leckie find in the crystalline dihydrate, the lines 1661 and 1759 cm^{-1} s, "as strong as the corresponding frequencies in the aqueous solution," which are not recorded by Hibben; while a strong line at 848 cm^{-1} obtained by Rao and by Hibben have not been recorded by the said authors. Whatever may be the results obtained with solids, which usually give strong continuous spectrum, the results obtained for aqueous solutions are too discordant to escape attention. The aqueous solution has therefore been re-examined, and in view of the previous work on formic acid and metallic formates done by the present author[1], the soluble oxalates of potassium and ammonium were examined in aqueous solutions, with a view to verifying the interpretation on the behaviour of the carboxyl group on ionisation, put forward in the said paper.

EXPERIMENTAL.

Saturated aqueous solutions of oxalic acid, potassium oxalate, and ammonium oxalate were examined. The chemicals were of reagent quality, once recrystallised. The crystals were washed once with dust-free distilled water (redistilled in vacuum) to remove all mother liquor from the crystals. This simple procedure materially diminishes the continuous background usually observed with aqueous

solutions. After dissolution, the solution was filtered through a well washed glass-sintered Gooch crucible (No. 4) before final introduction into the Wood's tube. A solution of m-dinitrobenzene in benzene was used to cut off 4046Å group of Hg lines, and the water band excited by it. The time of exposure is usually 24-30 hours. The results are tabulated below.

TABLE II.

| Oxalic acid solution in water (satd.)	Potassium oxalate solution (satd.)	Ammonium oxalate solution (satd.)
	175 (1)	
	294 (1)	
450 (2)	452 (2)	442 (1)
847 (4)	808 (4)	895 (3)
1372 (4b)	1306 (4)	1302 (3)
1459 (1)	1460 (3)	1460 (2)
	1485 (3)	1485 (2)
1631 (2b)	1600 ± 30 (3b)	1610 ± 30 (3b)
1740 (4)		

DISCUSSION OF RESULTS.

A comparative study of the results given in the two preceding tables reveals the facts that, (1) the line 1740 cm^{-1} which is known to be due to the group $C=O$ is absent in aqueous solutions of potassium and ammonium oxalates; and is also considerably weak in the anhydrous acid; (2) a pair of lines near 1650 cm^{-1} and (1300-1400) cm^{-1} is present with fairly large intensities in the aqueous solution of the oxalates and in the anhydrous acid; (3) in the methyl alcoholic solution of oxalic acid, the line 1750 cm^{-1} becomes very intense while the lines 1310 cm^{-1} and 1650 cm^{-1} are totally absent; (4) the line at 1370 cm^{-1} observed in the anhydrous acid is shifted to 1305 cm^{-1} in the aqueous solutions of the salts.

The difficulty in interpreting the origin of the line 1310 cm^{-1} observed by Hibben in an aqueous solution of the acid was pointed out by him. This line can neither be attributed to the deformation oscillation of $C-H$ in CH_2 group, for the latter group is absent in oxalic acid, nor with any degree of certainty to $C-OH$ grouping, for the more fundamental frequencies attributed to this grouping, which lie in the region of (1050-1090) cm^{-1}, are absent. In extension of the views of Kohlrausch[8] discussed in a previous paper by the author,[1] this line and the line 1650 cm^{-1} can be interpreted to have their origin in the antisymmetric and

symmetric vibrations of the Hantzsch's model of the COOH group. The extreme parallelism in the nature of this pair of lines in potassium and ammonium oxalate solutions with the lines 1329 cm^{-1} and 1667 cm^{-1} in sodium trichloracetate solution[1], both as regards the character and relative intensities, strongly suggest that the origin of this pair of lines in each of these substances is the same. The diminution in the frequency shift of the line 1370 cm^{-1} in anhydrous oxalic acid to 1305 cm^{-1} in oxalate solutions, which is similar to the change observed in the case of formic acid when the latter is converted into aqueous solutions of metallic formates, goes to confirm the view put forward by Peychès[9] that the angle between the two C—O bonds increases when the H of the COOH group is replaced by a metal which ionises in aqueous solutions.

The acid in the anhydrous state, thus appears to have the structure
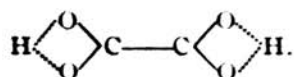
In a molecule having such a structure, the vibration O—H is expected to be greatly hampered, since either of the H atoms is bound between two O atoms, and is therefore not free to oscillate against one oxygen atom. The absence of the OH frequency which is normally strong, as pointed out by Hibben, is thus clearly intelligible from this formulation.

On dissolving in water, the molecule undergoes marked changes in structure. It was pointed out previously by the author[1] that in a carboxylic acid, the conversion of the group to the normal form seems to be a precursor as well as a measure of the strength of the acid.* Oxalic acid, being a strong acid, is converted to a large extent to the normal form in an aqueous solution. The small percentage of molecules of the normal form which only ionise to H$^+$ and oxalate ions, gives rise to two lines in positions similar to those due to the Hantzsch's model of the molecule, in which the angle between the two C—O bonds is somewhat less than that in the oxalate ion, as previously pointed out. In consequence, the line near 1310 cm^{-1} observed by Hibben loses its sharpness in oxalic acid solution, owing to the presence of two lines 1310 cm^{-1} and 1360 cm^{-1} side by side, the latter being caused by the antisymmetric oscillation of the residual number of molecules of Hantzsch's structure still persisting in the aqueous solution. Such complications, however, disappear when the acid is

* This view finds support in a recent work of Edsall (J. Chem. Phys., **4**, 1, 1936) who has shown that although in pure acetic and propionic acids, any line in the region of 1720 cm^{-1} is absent, dilute aqueous solutions of these acids of 30-35% concentration show the presence of a line at 1720 cm^{-1} in fairly large intensities.
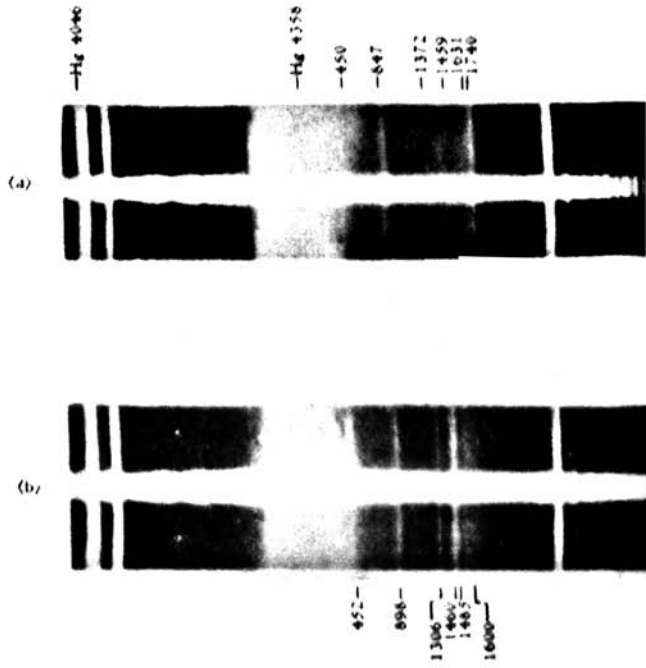
Raman Spectra.

(a) Saturated solution of oxalic acid in water.

(b) „   „   potassium oxalate.

converted into a metallic oxalate which dissociates freely in aqueous solutions leaving the oxalate ion in the form

$$\left(\begin{array}{c} O \\ O \end{array} \!\!\! \rangle C \!\!-\!\! C \!\! \langle \begin{array}{c} O \\ O \end{array} \right)^{- -}$$
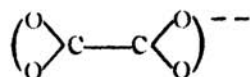
as depicted by Peychès ; the angle between the two $C - O$ bonds in each of the (COO) groups being greater than what it was in anhydrous oxalic acid, giving rise to a sharp line of smaller frequency shift (1305 cm^{-1}) than the line 1370 cm^{-1} in the anhydrous acid and a broad line in the region of 1620 cm^{-1}.

It is evident that under these conditions, no line due to $C = O$ can possibly appear. When the line due to $C = O$ near 1740 cm^{-1} will be prominent, the pair near 1310 cm^{-1} and 1620 cm^{-1} will lose their intensities. This is exactly what happens in a methyl alcoholic solution of oxalic acid examined by Hibben ; the line 1755 cm^{-1} is strong, while the lines 1310 cm^{-1} and 1645 cm^{-1} due to

$$C \!\! \langle \begin{array}{c} O \\ O \end{array}$$

have vanished altogether. It is interesting to note that the Raman spectrum of oxalic acid in methyl alcohol is examined under conditions similar to those for esterification of the acid, *viz.*, taking oxalic acid in an excess of methyl alcohol. Since the esters are all known to possess normal structures having $C = O$ grouping, the complete conversion of oxalic acid into the normal

$$C \!\! \langle \begin{array}{c} O \\ OH \end{array}$$

form from the Hantzsch's form in methyl alcohol can be anticipated.

The interpretation given above of the nature of the oxalate ion seems to have been confirmed by the X-ray analysis of ammonium oxalate crystals by Hendrick and Jefferson[10] who have shown that in these crystals, the angle between the two $(C - O)$ bonds in either of the (COO) groups is $129°$, which agrees approximately with the angle given by Peychès. It is noteworthy, however, that the distances of the two oxygen atoms from the carbon atom in either of the (COO) groups are not identical and that the two groups are not in the same plane

so that the configuration of $\left(\begin{array}{c} O \\ O \end{array} \!\!\! \rangle C \!\!-\!\! C \!\! \langle \begin{array}{c} O \\ O \end{array} \right)$ has not got the symmetry V_s

observed in the case of C_2H_4. The bond energy values for the two $C - O$ bonds in each (COO) group are consequently different, which should lead to extra lines. This might account for the presence of a doublet at 1460 and 1485 cm^{-1} besides the line 1305 cm^{-1} in the aqueous solutions of the oxalates.

7

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