

THE RAMAN SPECTRA OF SOME FORMATES AND THE CONSTITUTION OF FORMIC ACID.

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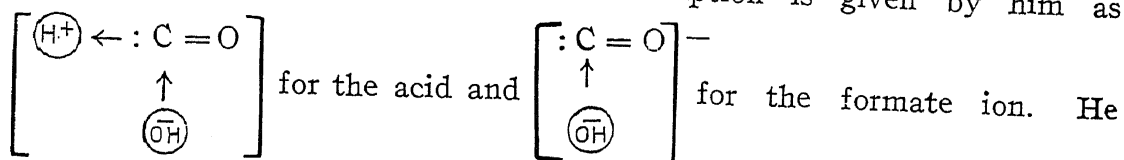
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1. Introduction.

THE most interesting among the fatty acids is formic acid on account of the striking differences between its chemical properties and those of its higher homologues. The most important among its exceptional properties is that it is about twelve to twenty times stronger as an acid than acetic or propionic acids; it is, unlike the latter, easily oxidisable and does not form a chloride or an anhydride corresponding to acetyl chloride or anhydride. Some of these properties have been explained on the basis of the older hypothesis that an aldehyde group COH, is present in the molecule. In a recent note to *Nature*¹ Sir P. C. Ray has put forward the suggestion, based on the experimental work of P. B. Sarkar, that the anomalous behaviour of formic acid is due to a difference in its chemical constitution, namely, that "the ionisable hydrogen in it is not the hydrogen of the hydroxyl group, as in the case of the other fatty acids but the hydrogen attached to the carbon atom". The electronic conception based on this assumption is given by him as



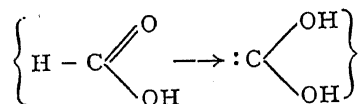
establishes the identity of the former with the well-known electronic configuration of the nitrite ion $\left[\begin{array}{c} : \text{N} = \text{O} \\ \searrow \\ \text{O} \end{array} \right]^-$ and finds support for it in the possibility of preparing mixed crystals of formates and nitrites of a few metals.

Exception to this suggestion has, however, been taken by T. R. Seshadri² who has pointed out that it is wholly unjustifiable from other important

¹ Ray, P. C., *Nature*, 1934, 133, 646.

² Seshadri, T. R., *Current Science*, 1935, 3, 383.

chemical considerations. This author has explained the classical synthesis of formates, the reducing power of the formate ion and other exceptional properties on the assumption "that the carboxyl group in the acid is linked to a hydrogen atom (aldehyde group) whereas in its homologues the carboxyl is linked to the alkyl groups and in the course of certain reactions formic acid is capable of undergoing isomeric change to dihydroxymethylene."



Thus according to the suggestions of Sir P. C. Ray, the formate ion does not contain the CH group, whereas Seshadri presumes that it is present in it, just as in the case of acetates, etc. This issue is capable of being decided by the method of the Raman effect where the presence of the CH group in the metallic formates could be detected directly by experiment. At the suggestion of Dr. Seshadri, the author has investigated this problem and the present paper deals with the results obtained with the formates of sodium, calcium, cadmium and lead both as crystals and aqueous solutions. The measurements give indication of the existence of the CH group in the compounds studied.

2. Experimental Technique and Results.

The experimental arrangement was essentially the same as that described by the author in the previous communications.³ Extra-pure crystals of sodium, calcium and cadmium formates were prepared and kindly lent to the author by Dr. Seshadri of the Andhra University, Waltair. Lead formate crystals were the extra-pure variety supplied by Kahlbaum. Since sodium formate is hygroscopic it was kept sealed in an evacuated tube during exposure. Cadmium formate was cooled during exposure by water circulation in order to avoid the loss of water of crystallisation. Using specially backed Ilford "golden isozenith" plates H. and D. 1400, the time of exposure was about twelve hours for the crystal powders and twenty-four hours for the aqueous solutions. The plates were measured on a Hilger comparator, alongside of an iron-arc spectrum and the results are set out in Table I. The Raman lines due to CH are indicated in the enlarged photograph of the spectra of 42% aqueous solution of sodium formate and of the crystals of lead formate which are reproduced in the accompanying Plate. In order to provide a comparison, the spectrum of formic acid* enlarged to the same scale, has also been reproduced.

³ Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, 1, 850; 2, 119.

* The author's thanks are due to Mr. R. Ananthakrishnan for his kind permission to reproduce his formic acid spectrum here for reference.

TABLE I.

Substance	Raman lines in cm. ⁻¹								Remarks
Sodium formate crystals	2834 (w,dif)	..	1717 (v.w)	1555 (v.w)	1397 (v.w)	1365 (m,sh)	..	
Sodium formate solution 42%	2834 (m,dif)	2734 (w,dif)	1353 (v.st,sh)	857 (w)	St. water band.
Calcium formate crystals	2973 (v.w)	2849 (w,dif)	..	1716 (w)	1550 (w)	1397 (m,dif)	1359 (w)	..	
Calcium formate solution 15%	2834 (m,dif)	2721 (w,dif)	1353 (st,sh)	..	
Cadmium formate crystals	2849 (w,dif)	..	1716 (w)	1550 (v.w)	1397 (w)	1359 (m,dif)	..	
Cadmium formate solution 3%	1353 (w)	..	
Lead formate crystals	2976 (w)	2847 (w,dif)	..	1717 (m)	1534 (m)	1397 (w)	1347 (v.st)	..	Line at 200 (doubtful)

The abbreviations in this and the following Table mean: v.st=very strong, st=strong m=medium intensity, w=weak, v.w=very weak, and dif=diffuse.

3. Discussion of Results.

Although the Raman spectra of formic acid⁴ and some of its esters⁵ have been studied by earlier investigators, the presence of the CH group in the formate ion can be established only from the Raman spectra of the metallic formates where the same group is not present in any other form. In Table II, the frequency shifts of formic acid and methyl formates are given along with the results obtained by the author for the metallic formates. Similar data are also given from Dr. Krishnamurti's work for acetic acid and sodium acetate. In general the metallic salts either in the solid state or as aqueous solutions, yield fewer lines than the acids. Among the four compounds studied (Table I) in the solid state, lead formate has given the most intense picture in spite of the fact that the other formates, especially the cadmium salt, were available in the form of better crystals. Similar observations with the acetates have also been made by Krishnamurti.⁶ Sodium formate

⁴ Ganesan, A. S., and Venkateswaran, S., *Ind. Jour. Phys.*, 1929, 4, 195.

Dadiou and Kohlrausch, *Physikal Z.*, 1929, 30, 384.

Parthasarathy, S., *Ind. Jour. Phys.*, 1931, 6, 287.

Kohlrausch, K. W. F., Koppl, F., and Pongratz, A., *Z. f. Phys. Chem.*, B, 1933, 21, 242.

⁵ Kohlrausch, K. W. F., and Pongratz, A., *Z. f. Phys. Chem.*, B, 1933, 22, 373.

⁶ Krishnamurti, P., *Ind. Jour. Phys.*, 1931, 6, 309.

TABLE II.

Formic acid	Methyl formate	Lead formate crystals	Sodium formate solution	Acetic acid (Incomplete)	Sodium acetate
189±80 (5)	334 (3b)	200 (?)		440 (3)	
673 (3b)	762 (2)			614 (5)	647 (1)
859 (½)	912 (10)		857 (1)	889 (6)	925 (4)
1050 (1b)	1030 (½)				
1200 (2)	1157 (1b)			1280 (1b)	
	1247 (½b)				
		1347 (5)	1353 (8)		1346 (3)
1398 (5)	1378 (3b)	1397 (1)		1368 (4b)	
	1445 (2v.b)			1432 (4b)	1411 (1b)
1672 (4)		1534 (2)			
1724 (2)	1717±6 (5v.b)	1717 (1)		1669 (4b)	1647 (1)
	2839 (3)	2847 (1)	2732 (2) 2834 (5)		
2963 (7b)	2955 (3)	2976 (½)		2940 (10b)	2934 (5b)
	3030 (2v.b)				

is the most soluble of the salts studied and a 40% solution of it has yielded a very intense spectrum. As can be seen from the accompanying Plate, the most prominent line in the crystal is the one at 1347 and it is followed by a faint companion at 1397 in the formates of sodium, cadmium and lead. In the case of calcium formate, the line at 1397 is stronger than the one at 1359. The corresponding line in formic acid falls at 1398. Parthasarathy⁷ has observed that it is followed by a wing to the violet side and as can be seen from the Plate the centre of this wing approximately coincides with the frequency shift 1347. If we assume that 1398 is the frequency in the unionised state, it follows that in the crystals of metallic formates there is a small percentage of the solid possessing covalent linkage giving rise to this line. In the calcium salt this percentage is considerably higher than in the

⁷ Parthasarathy, S., *Loc. cit.*

others. The line at 1347 is evidently characteristic of the ionised group HCO, and shifts to a higher frequency as we pass from lead to sodium. The wing to the violet side in the acid is also to be attributed to a small percentage of dissociation in it. This line is also shifted to a slightly higher frequency in the aqueous solutions and is the strongest line in all cases. This line is attributed by Kohlrausch and his co-worker⁸ to the deformation oscillation of the CH in the aldehyde group HCO.

The valence frequency due to the CH binding appears in formic acid as a broad line at 2963 and as three lines at 2839, 2955 and 3030 in methyl formate. In the crystalline formates of lead and calcium two diffuse lines are clearly present at 2847 and 2986 but in the aqueous solution of the sodium and calcium salts they are replaced by two broad lines at 2834 and 2732. The possibility that these lines are excited by the 4358 radiations of the source is excluded on the consideration that the corresponding lines that would be excited by 4047 in such a case, do not appear in the region between 4358 and 4047. (See Sodium formate picture.) Thus, in the ionised state the line due to CH in the formates suffers a large shift of more than 130 wavenumbers towards lower frequency and coincides with the frequency shift of 2839 in methyl formate. In the case of acetates this change is considerably less. *These two lines, namely, 2834 representing the valence oscillation and 1347 representing the deformation oscillation of the HCO group, indicate beyond doubt the presence of this group in the formate ion.*

Another important feature of the spectra of the formates of which special mention may be made, is the presence of the line at 1534 which appears clearly in the spectrum of lead formate. This line is present very feebly in the other crystals also. But in the aqueous solutions, its presence could not be detected, for the water band excited by the 4046 radiations happens to fall in the region where it would appear. It may be inferred from Table II that no such line is present in formic acid or its esters or in acetic acid and acetates. This frequency is also too low to be attributed to the carboxyl group C = O and its origin is difficult to understand at this stage. But it is possible that it is in some way connected with the change of formic acid to the form dihydroxymethylene as suggested by Seshadri.

It is surprising that the frequency due to C = O appears only very weakly at 1717 in the spectra of the crystals. Due to a large number of feeble mercury lines in that region it could be identified only with great difficulty. In the spectra of the aqueous solutions this line, if present, would be superposed on the water band and hence could not be observed. Similar

⁸ Kohlrausch, K. W. F., and Koppl, F., *Z. f. Phys. Chem.*, 1934, 24, 370.

weakening of the carboxyl frequency has been previously noticed by Ghosh and Kar⁹ and Krishnamurti¹⁰ in metallic acetates and as is pointed out by the former authors, wherever C = O group forms part of the negative ion, it is considerably weakened. The weak line at 857 in the water solution of sodium formate is to be compared to the line at 859 in formic acid.

The influence of formates on the water bands is negligible. The well-defined minima separating the three bands in pure water are not clear in the solutions of formates and a slight narrowing of the bands is also observed.

In conclusion the author wishes to express his heartfelt thanks to Prof. Sir C. V. Raman for his interest in the work. The investigation was undertaken at the suggestion of Dr. Seshadri of the Andhra University, Waltair, to whom the author's best thanks are due.

Summary.

The Raman spectra of the formates of sodium, calcium, cadmium and lead have been investigated both as solid and as aqueous solutions and the following average frequencies have been obtained for the formate ion:— 2834, 2734, 1717, 1534, 1347 and 857 cm.^{-1} . The presence of the lines at 2834 and 2732 gives direct experimental evidence of the existence of CH group in formic acid. The solids have yielded faint lines also at 2976 and 1398. The frequencies are compared with those of formic acid and its esters and acetic acid and acetates. The presence of the line at 1534 seems to be characteristic of the formates.

⁹ Ghosh and Kar, *Jour. Phys. Chem.*, 1931, 35, 1735.

¹⁰ Krishnamurti, P., *Loc. cit.*

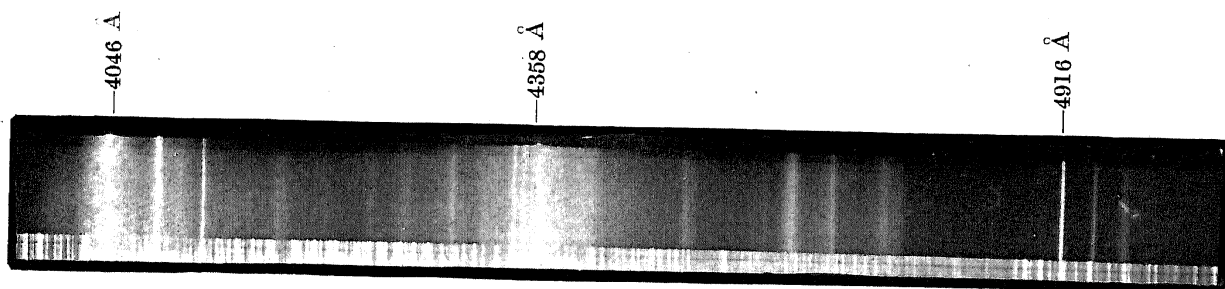


FIG. 1. Formic acid (liquid).

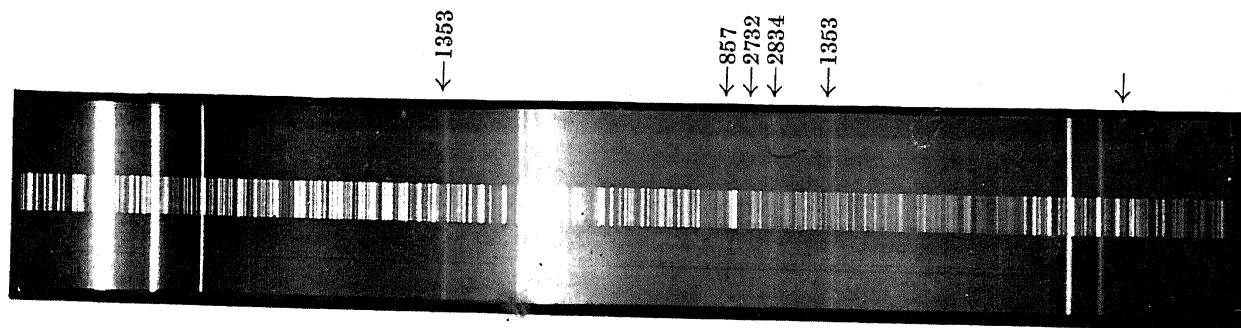


FIG. 2. Sodium formate (aq. soln.).

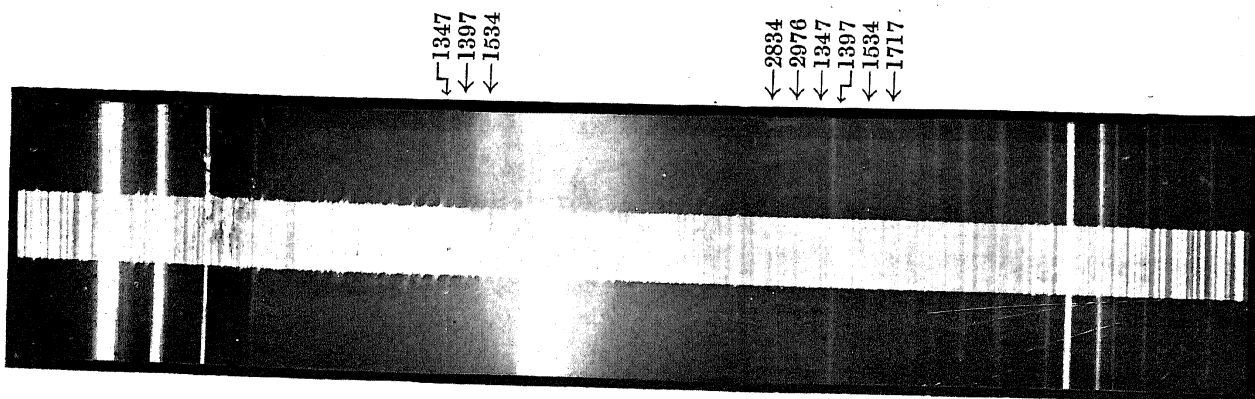


FIG. 3. Lead formate (crystals).

Raman Spectra.