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X-ray Analysis of Hydrogen Bonding in the Structure of Oxalic Acid Dihydrate.

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X-ray intensities in the {*h*0*l*} zone of oxalic acid dihydrate have been measured by means of a Geiger-counter diffractometer with sufficient accuracy to give significant hydrogen peaks on the difference map of electron density. The results show that the water molecules do not enter into appreciable combination with the acidic hydrogen atoms to form oxonium ions, and thus confirm the results of proton resonance and optical experiments.

Introduction

For some time it has seemed that proton magnetic resonance and neutron diffraction offered the most promising opportunities of advancing exact knowledge of the location of hydrogen atoms in crystals and their role in forming chemical bonds between electronegative atoms. Because of their lower accuracy, X-ray and electron diffraction from single crystals have at present perhaps only a confirmatory value, and we have often had to be content to identify hydrogen bonds only by their lengths. Further improvement of experimental accuracy can, however, enable these techniques to yield the more detailed information of which they are theoretically capable, and in favourable cases to solve problems of exact location of hydrogen and of electron distribution. One of these problems is to ascertain how far a given hydrogen atom has been displaced from its position in the isolated molecule, and whether it then occupies a median position in the bond or the more probable unsymmetrical position discussed by Bernal & Megaw (1935). This unsymmetrical bond may appear with a double peak in structures determined by diffraction methods, if there are two chemically possible locations for the hydrogen atom. In oxalic acid dihydrate this possibility takes a particular form. The earliest structure determinations, such as those by Zachariasen (1934) and by Robertson & Woodward (1936), indicated that the water molecule was bound to the hydroxyl group and to two neighbouring carbonyl groups. What remained uncertain was whether a more or less symmetrical oxonium ion was thereby formed, as Zachariasen had proposed and Bernal & Megaw (1935) afterwards disputed. Subsequently, Richards & Smith (1951) showed, by proton resonance, that the oxonium structure exists in other solid acid hydrates, but were led to conclude that such a structure is not correct for oxalic acid dihydrate. Their conclusion has subsequently been confirmed by proton resonance experiments on single crystals by Itoh, Kusaka, Kiriyama & Yabumoto (1953). Finbak & Norman (1948), using the then existing X-ray data, reached the opposite conclusion, though it is now clear that this was hardly warranted by their results, and a critical study of the bond lengths by Ahmed & Cruickshank (1953), based on the same data, again favoured the true hydrate structure. The ionic structure has therefore been generally discredited in its simple form though Gallagher, Ubbelohde & Woodward (1954) hold to it as a partial structure to explain the exceptional properties towards isotopic substitution of the short hydrogen bond in acetylene dicarboxylic and oxalic acids, originally noticed in the latter by Robertson & Ubbelohde (1939*a*, *b*). The ionic structure is pictured as occurring at localized lattice sites to form a kind of chemical defect. The results of the present experiments, while confirming the hydrate structure, would not exclude the occurrence of the ionic structure at a small minority of sites, though they give no positive support to this hypothesis. The experiments were begun in order to explore some of the possibilities of accurate X-ray intensity determination by using Geiger counters. Luzzati (1953*a*, *b*) has meanwhile demonstrated the existence of the oxonium ion, in nitric acid trihydrate, by using accurate photographic methods in circumstances which he describes as favourable for the determination of hydrogen atoms, but the accuracy of photography is generally somewhat too low for this purpose. By counter measurement a fairly clear qualitative picture of the hydrogen atoms is obtained in the present case, but finer detail, such as electron density in the chemical bonds, is not clearly shown up.

Experimental

The structure of oxalic acid dihydrate is such that a reasonable solution of the problem could be expected with one projection. A set of measurements for the {*h*0*l*} zone was therefore obtained by means of the X-ray diffractometer devised by Beard & Pringle (unpublished). This instrument uses a Geiger counter to measure the integrated intensity directly, while the primary beam is monitored by means of a similar counter receiving a beam diffracted by transmission through mica. Copper radiation was used throughout these experiments. The crystals were needle-shaped, and various sizes down to about 0·1 mm. diameter were used in order to minimize extinction and subsequently to correct for it. Statistical errors were reduced to a low level by ensuring that in the stronger reflexions not fewer than 10^4 pulses were recorded, corresponding to errors of order 1%, but in weaker reflexions a larger percentage error was tolerated. The statistical error associated with monitoring the beam was normally relatively small. Generally we might assume that, with the alcohol-quenched argon-filled tubes used, more serious errors could arise from the uncertainty of dead-time corrections and other sources of non-linearity, as well as from the corrections for the background of scattered radiation. Dead-time corrections were fairly large since a quenching amplifier was used, as described by Cooke-Yarborough, Florida & Davey (1949) with a pre-set time of 300 μsec., but this was increased by the wave-form factor (Westcott, 1948) to approximately 1 msec. for the monitoring counter, and by a further factor for the main measuring counter when related to the mean rate of pulsation during the rocking motion of the crystal. These corrections were determined empirically. Background corrections were made by first measuring the spectrum of radiation in a strong reflexion. The curve so obtained, representing intensity of background weighted for counter sensitivity, could then be used to calculate the contribution from wavelengths other than that of $K\alpha$ for any reflexion. The largest such contribution was from wavelengths adjacent to $K\alpha$, varying in amount with the Bragg angle because of variation of the optical resolving power of the apparatus. Contributions from $\lambda/2$, $\lambda/3$ etc. were important only in a few reflexions as the X-ray tube voltage was fairly low and also because the counters are insensitive to these rays with shorter wavelengths. In a few cases corrections were applied for wavelengths such as $4\lambda/3$ or $4\lambda/5$. The final correction was for extinction. Most of the measurements were made on crystals which had been dipped several times in liquid nitrogen to reduce extinction. In one case, measurements were also made before chilling. The intensity values seemed to include a residual extinction error that was mainly a function of reflecting power and was probably due to secondary extinction, though the possibility of some residual primary extinction could not be ruled out. It is probable that the empirical procedure used in correcting for extinction and for dead time would help to eliminate systematic errors due to any other causes of non-linearity or due to incomplete allowance for the background. The remaining errors probably exceeded the permitted statistical errors of counting, except for the weakest reflexions. In view of this it is best to judge the accuracy of measurement by the agreement between independent sets of data; this leads to an estimate of 5% standard deviation in intensity for the mean derived from all sets, or $2\frac{1}{2}$% in structure factors. The mean index of agreement between observed and calculated structure factors is $5\frac{1}{2}$%, or 7% r.m.s., but it varies with θ in the manner of Fig. 1.

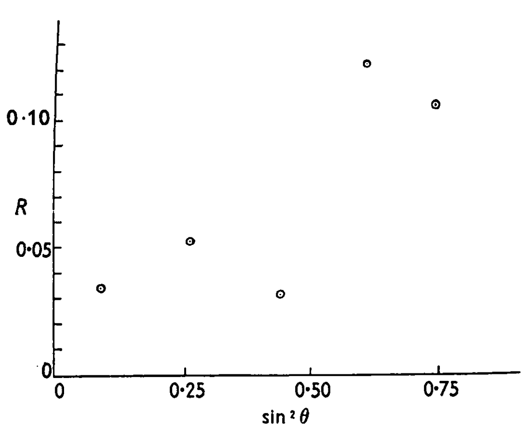


Fig. 1. Agreement index in different ranges of $\sin^2\theta$.

Interpretation of results

Crystallographic data and coordinates (Table 1) of the heavier atoms were practically as in Ahmed & Cruickshank's paper (1953). The small coordinate changes are well within the errors given by these authors, whose conclusions are unaffected by the new measurements. Calculated structure factors were redetermined, using spherically symmetrical atomic scattering factors based on those given by McWeeny (1951), and from these F_c's scale and temperature factors were deduced. The graph of $\log(\langle F_o^2\rangle/\langle F_c^2\rangle)$ against $\sin^2\theta$ was linear if the lower range of $\sin^2\theta$ was excluded. Departure from linearity in that range was different for different specimens and was attributed to extinction. An empirical correction to intensity-ratio I was therefore made from the formula $I' = I/(1-xI)$ by choosing the constant x for each crystal so as to make the new temperature plot straight, even including the lower range of $\sin^2\theta$. For this purpose it is desirable to check later with the hydrogen atoms inserted in the F_c, as these atoms influence chiefly the stronger low-index reflexions and their omission can obscure or falsify the correction for extinction. The corrected structure factors are given in Table 2, together with Robertson & Woodward's values after these are similarly corrected for extinction. The photographic values differ from F_c for the 49 reflexions measured by 11% s. d., not much more than for the

Table 1. *Oxalic acid dihydrate coordinates and temperature factors*

Atom	x/a	z/c	B (Å^2)	Estimate of s. d. (Å)
C	−0·0454	0·0514	1·7	0·0100
O_1	0·0852	0·1492	2·1	0·0087
O_2	−0·2187	0·0373	2·1	
$(H_2)O$	−0·4533	0·1793	2·2	
H_1	0·010	0·210	4·7	See p. 719
H_2	−0·1255	0·3355	4·7	
H_3	0·048	0·383	3·8	

Table 2. *Structure factors for h0l zone*

F_R Robertson & Woodward's values, corrected for extinction.
F_o Counter measurements based on four crystals, corrected for extinction.
F_c Calculated values allowing for hydrogen atoms and thermal anisotropy of oxygen atoms.

h0l	F_R	F_o	F_c
002	10·9	13·1	11·7
004	8·1	8·3	−8·1
006	29·0	29·2	28·7
008	16·3	14·5	−15·6
0,0,10	17·8	16·3	−16·7
0,0,12	5·0	4·9	−4·1
0,0,14	—	4·8	−4·5
101	27·4	27·7	29·2
103	27·4	28·1	28·1
105	13·2	13·1	13·2
107	22·2	21·4	20·6
109	< 5	2·0	−1·9
1,0,11	8·5	9·0	−8·3
1,0,13	—	4·9	3·8
$10\bar{1}$	18·4	22·7	19·8
$10\bar{3}$	4·0	5·2	4·1
$10\bar{5}$	37·8	42·4	−42·3
$10\bar{7}$	13·7	14·2	−14·1
$10\bar{9}$	8·5	7·0	−6·7
$1,0,\overline{11}$	21·4	20·8	−21·3
$1,0,\overline{13}$	< 5·5	1·9	1·7
200	24·6	25·0	26·0
202	47·4	41·6	−41·3
204	12·7	11·8	10·8
206	20·5	18·9	19·4
208	10·5	10·2	−9·9
2,0,10	< 6	2·1	2·0
2,0,12	—	4·3	4·5
$20\bar{2}$	5·0	5·1	−4·7
$20\bar{4}$	59·0	56·9	−57·8
$20\bar{6}$	3·0	3·4	−2·5
$20\bar{8}$	< 4·5	3·3	−2·5
$2,0,\overline{10}$	8·5	7·6	−7·5
$2,0,\overline{12}$	< 6·0	3·6	4·2
$2,0,\overline{14}$	—	5·6	4·5
301	11·1	8·8	−9·5
303	3·5	3·3	−3·5
305	< 5	3·1	−3·0
307	< 5	0	−0·4
309	8·0	9·6	−8·4
3,0,11	—	2·1	−2·3
$30\bar{1}$	4·0	4·1	−5·0
$30\bar{3}$	18·6	18·8	18·8
$30\bar{5}$	14·2	14·1	−12·7
$30\bar{7}$	5·6	5·2	−5·2
$30\bar{9}$	21·5	21·4	21·9
$3,0,\overline{11}$	< 5	2·6	−3·1
$3,0,\overline{13}$	< 5·5	1·3	0·8
400	11·1	9·9	9·1
402	6·5	6·5	−6·2
404	19·0	17·7	17·6
406	< 5	0	
408	7·5	10·0	−10·1
$40\bar{2}$	29·0	25·6	25·7
$40\bar{4}$	5·0	5·8	−6·4
$40\bar{6}$	< 5	1·0	−0·1
$40\bar{8}$	< 5	4·0	4·3
$4,0,\overline{10}$	< 5	2·3	−3·2
$4,0,\overline{12}$	< 5·5	2·4	−0·6
501	8·5	8·0	7·8
503	11·1	11·8	12·6
505	5·0	7·6	7·1
507	—	3·5	2·7
$50\bar{1}$	< 5	3·8	−3·8
$50\bar{3}$	9·0	7·9	8·4
$50\bar{5}$	6·1	6·1	−5·8
$50\bar{7}$	22·5	19·9	−20·2
$50\bar{9}$	< 6	2·4	2·2
$5,0,\overline{11}$	< 5·5	2·2	−2·2
$5,0,\overline{13}$	—	7·7	−6·3
600	6·5	8·1	−7·8
602	< 5·5	2·5	1·3
604	—	10·6	10·8
$60\bar{2}$	< 6	2·1	−1·5
$60\bar{4}$	8·5	10·0	−10·0
$60\bar{6}$	8·5	11·3	−10·4
$60\bar{8}$	< 5·5	3·5	−2·7
$6,0,\overline{10}$	—	0	−1·3
701	—	0	−0·7
701	—	8·7	−10·0
$70\bar{3}$	—	4·3	−4·5
$70\bar{5}$	—	1·6	1·2
$70\bar{7}$	—	6·8	−7·4

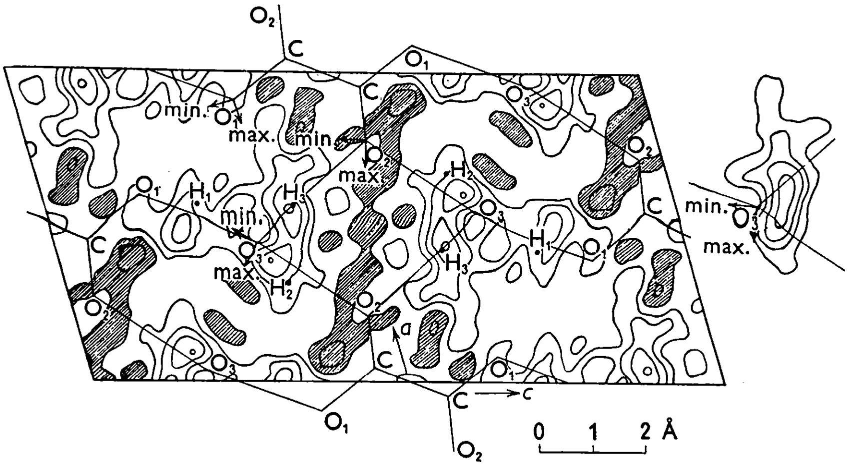


Fig. 2. The *h0l* difference density map of oxalic acid dihydrate, omitting hydrogen atoms from F_c. Dots represent protons as located by magnetic resonance (Itoh, *et al.*, 1953). Contour spacing 0·2 e.Å^{-2}.
Inset: Alternative water molecule (oxygen shift 0·012 Å).

counter measurements, but the number of reflexions is much smaller.

A difference map representing the Fourier transform of $(F_o - F_c)$, omitting hydrogen atoms from F_c, showed a marked anisotropic density distribution round the oxygen positions, but not round the carbon positions. The hydrogen peaks were revealed, but the electron cloud for those belonging to the water molecule appeared split into unequal parts, probably as a result of the anisotropy of the corresponding oxygen atoms. Most of the anisotropy disappeared from the difference map after F_c had been corrected on the basis of r.m.s. extreme amplitudes of thermal vibration of 0·18 Å and 0·14 Å, directed as shown in Fig. 2. This process would of course tend to obscure any real anisotropy of the oxygen electron cloud. The isotropy of the carbon vibrations may be peculiar to this projection and perhaps not complete in three dimensions.

The agreement index with only the heavier atoms in the calculation of F_c was 0·082. This was reduced to 0·055 on inserting the hydrogen atoms in the positions given in Table 1. The total number of reflexions measured was 83.

Location of hydrogen atoms: electron distribution

The difference map (Fig. 2) clearly shows that the arrangement of the three hydrogen atoms around the water oxygen atom is unsymmetrical and that the carboxyl group is intact. In this map the standard deviation given by Cruickshank's formula (1949) is 0·14 e.Å^{-2}, comparable with the contour separation of 0·2 e.Å^{-2}, so that most of the detail, except the hydrogen peaks, is false. The hydrogen atoms cannot be very accurately located, and the statistical part of the error, which is hard to estimate, is probably far exceeded by systematic errors due to the anisotropy of the nearby oxygen atoms. For comparison, the error of density in the difference map drawn by Finbak & Norman from data of Brill, Hermann & Peters (1939) was about 0·48 e.Å^{-2}, so that the reputed hydrogen peaks were probably not significant. Since Fig. 2 is only a projection, the interatomic distances involving hydrogen remain unknown; all one can conclude about them with any assurance is that the hydroxyl O–H bond is not shorter than about 1 Å, comparing reasonably with Cochran's (1953) value 1±0·1 Å for the corresponding bond in salicylic acid. The longer O · · · H distance (water–hydroxyl) appears to be not shorter than about 1·5 Å. This would agree with the conclusions of Richards & Smith since their values for the oxonium ion all lie close to 1 Å, whatever reasonable pyramidal angle is assumed. The proton positions suggested by Itoh *et al.*, from single-crystal proton resonance also agree qualitatively with Fig. 2. Finally, from Table 3 it will be seen that the Raman spectrum of oxalic acid dihydrate obtained by Weil (1954) has a closer affinity to the water spectrum than to the infra-red spectrum of the oxonium ion obtained by Ferriso & Hornig (1953). Weil favours a structure quite unlike the one given here, but it is doubtful whether valid conclusions of this sort can be drawn from the optical technique alone in its present state of development.

Table 3. *Vibrational frequencies*

(Values in cm.$^{-1}$.)

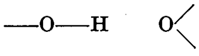
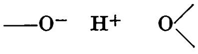
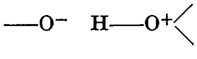
Water vapour	Oxalic acid dihydrate	$OH_3^+Cl^-$
1595	1635	1050
3650	3429	1700
	3440	2100
	3489*	2570
3750	3507	3200–3500

* OH valence vibration.

The process of refinement from the appearance of difference maps depends largely on judgment. By using slightly different coordinates and anisotropies one can alter the supposed hydrogen peaks considerably; an example is given with Fig. 2. Minor features must therefore be disregarded or interpreted cautiously. All the hydrogen atoms, however, do appear to lie fairly close to the O–O vectors. The water hydrogen peaks are not completely resolved in projection, and, either because of this overlap or because they lie off the O–O vectors in three dimensions, they appear closer than 1 Å to the parent oxygen atoms. On chemical grounds we might expect this distance to be larger than the bond length for isolated water molecules.

From the evidence now available it therefore seems that the structure proposed by Bernal & Megaw is substantially correct, though it now seems unnecessary to involve their hypothesis of a mechanism of simultaneous proton shuttling. This they introduced to explain the pseudo-symmetry of the structure which Zachariasen's results had tended to over-emphasize. Both the carbon–oxygen and water–oxygen pairs of bonds are now known to be unequal in length, and in fact the C=O distance is that of a typical pure double bond, according to Ahmed & Cruickshank's evaluation. There is therefore less to be explained than at that time, and less cause to postulate resonance phenomena.

In the case of resolved atoms we can estimate the associated electronic charge, and in the case of water the same can be done for the molecule as a whole. The result is that the carbon atoms have 6·1 electrons, hydroxyl oxygen atoms 8·3, carbonyl oxygen atoms 8·15 and hydrogen atoms only 0·5 electrons; the water molecule has 9·18 electrons; the s. d. is of order 0·1 in all cases. If we assume a superposition of three structures:

		2·5 Å	2·78 Å
(i)		(60%)	(65%)
(ii)		(28%)	(31%)
(iii)		(12%)	(4%)

as postulated by Danielsson (see Coulson, 1952), the structure (ii) would contribute, according to his calculations, about 28% of the total, corresponding to a hydrogen electronic cloud of order 0·7 electron. The low experimental value of 0·5, however, agrees better with that already measured by Cochran for hydrogen atoms in salicylic acid, i.e. 0·4 electron, and is more in accordance with earlier views of Bernal & Fowler (1933*a*, *b*). Bernal (1953) points out that the low electronic density around the acidic H atom in salicylic acid (in marked contrast to the charge of 0·8 electron around the benzenic H atoms in the same molecule) is in accordance with its chemical activity, and he surmises that in OH groups the screening effect of electrons around the proton will be found to increase with diminishing acidity; if this is so the electronic charge around the proton will diminish from about 0·6 for the weaker 'hydroxyl' bonds of length 2·75–2·85 Å to about 0·3 for the shorter bonds, 2·65–2·4 Å, occurring in the structure of strong acids. Correspondingly, he supposes that the O–H link may lengthen from 0·85 to 1·10 Å as the hydrogen bonds strengthen. Whether with still shorter bonds one can foresee the occurrence of a symmetrical type is not yet clear, as even in the intramolecular hydrogen bond of length 2·46 Å in maleic acid (Shahat, 1952), this stage has evidently not been reached.

Structures (i), (ii) and (iii) together would give the hydroxyl oxygen and water molecule charges of 0·4 and −0·1 electron respectively; the second value should presumably be diminished because of the two long hydrogen bonds also formed by the water molecule; these values are in reasonable agreement with 0·3 and −0·18 measured.

The small, hardly significant, measured negative charge on the carbon atoms does not support the suggestion of a positive charge made by Jeffrey & Parry (1952) in an attempt to harmonize any possible π-bond character in the C–C bond with its known normal single-bond length. A net negative charge on each COO group does not seem unreasonable, though the measured value of 0·55 electron may be too high. The observed charge on the oxalic acid molecule as a whole is insignificant.

My thanks are tendered to Prof. E. G. Cox, who suggested this work, and to Dr D. W. J. Cruickshank for discussion and for calculating structure factors on the Manchester computer, using programmes devised by Ahmed & Cruickshank. The apparatus used was provided in part by financial assistance from the Royal Society and Imperial Chemical Industries Ltd, to whom grateful acknowledgment is made.

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