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The Crystal Structure of Formic Acid*

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The crystal structure of formic acid has been determined at $-50\pm5°$ C., using single-crystal X-ray diffraction techniques. The unit cell is orthorhombic with $a = 10{\cdot}23\pm0{\cdot}02$, $b = 3{\cdot}64\pm0{\cdot}01$, and $c = 5{\cdot}34\pm0{\cdot}01$ Å. There are four molecules per unit cell. The space group is *Pna*.

Bond lengths have been determined using Fourier projections on (010) and (001). The C–O bond length is $1{\cdot}26\pm0{\cdot}03$, C=O $1{\cdot}23\pm0{\cdot}03$ Å and the O–C=O angle $123\pm1°$. The molecules are arranged in the form of infinite chains in the crystal, each molecule being linked to two neighbors by hydrogen bonds. The length of the hydrogen (O–H · · · O) bond is $2{\cdot}58\pm0{\cdot}03$ Å.

Introduction

Although the structure of the carboxyl group has been extensively investigated by X-ray (Robertson & Woodward, 1936; Brill, Hermann & Peters, 1942; Dunitz & Robertson, 1947*a*, *b*; Booth, 1947), electron diffraction (Karle & Brockway, 1944; Schomaker & O'Gorman, 1947) and spectroscopic methods (Williams, 1947), considerable uncertainty still exists concerning that interesting group. The simplest molecule containing the carboxyl group is formic acid, (HCOOH). Our knowledge of its structure is derived principally from electron diffraction and spectroscopic studies of the molecule in the gas phase. Results of these measurements are listed in Table 1.

An X-ray diffraction investigation of formic acid was carried out by Gibbs (1924), using powder techniques. Only one line was observed on the diagram. No single-crystal X-ray diffraction study of formic acid has been reported prior to this investigation. However, detailed X-ray analyses have been made of other carboxylic acids which are crystalline at room temperature. (Formic acid and the next eight members of the mono-carboxylic acid series are liquid at room temperature.) There are marked differences between the results of measurements of the carboxyl group reported in these X-ray studies and those listed in Table 1. In general, the X-ray results indicate much smaller differences between the two carbon–oxygen bonds than do either the electron diffraction or spectroscopic measurements. These comparisons, of course, involve different acids in different physical environments. It is not known, therefore, to what extent these discrepancies, which appear to be well in excess of the probable errors of measurement, reflect either differences between formic and other carboxylic acids, or changes in the structures in going from the vapor to the solid phase. In this paper the results of a single-crystal X-ray study of formic acid are presented. These make possible a direct comparison of X-ray diffraction measurements of bond lengths in formic acid with results obtained by other means.

Experimental

Reagent-grade formic acid was re-crystallized several times and distilled in vacuo into a thin-walled glass capillary tube (0·3 mm. in diameter) which was subsequently sealed. The low-temperature single-crystal oscillation camera used in this investigation has been described previously (Post, Schwartz & Fankuchen, 1951). A simple adaptation of this apparatus to the precession camera made it possible to utilize the full 30° precession angle of the instrument at low temperatures.

Single-crystal oscillation diagrams using Cu $K\alpha$ radiation and precession diagrams using Mo $K\alpha$ were obtained at $-50\pm5°$ C. Lattice constants were computed from single-crystal oscillation and precession diagrams. The specimen-to-film distance in each case had been calibrated with a quartz standard. Single-crystal diagrams were indexed on the basis of an orthorhombic unit cell with:

Table 1. *Bond lengths and angles of formic acid*

Reference	C=O (Å)	C–O (Å)	O–C–O angle (°)
Karle & Brockway, 1944	1·24 ±0·03	1·42 ±0·03	117 ±2
Karle & Brockway, 1944*	1·25 ±0·03	1·36 ±0·03	121 ±2
Schomaker & O'Gorman, 1947	1·213±0·026	1·368±0·034	123·5±3
Williams, 1947	1·225±0·02	1·41 ±0·02	125 ±1

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$$a_0 = 10{\cdot}23 \pm 0{\cdot}02,\quad b_0 = 3{\cdot}64 \pm 0{\cdot}01,\quad c_0 = 5{\cdot}34 \pm 0{\cdot}01\ \text{Å}\,.$$

There are four molecules per unit cell. The calculated X-ray density is $1{\cdot}5_2$ g.cm.$^{-3}$. This is in reasonable agreement with the values obtained by extrapolation of the known density of the liquid at 20° C. (1·24 g.cm.$^{-3}$) to that of the solid at −50° C. as estimated by the observed contraction upon freezing.

Reflections of the following type were systematically absent from single crystal diagrams: ($h0l$) with h odd, ($0kl$) with $k+l$ odd. The most probable space groups are therefore C_{2v}^{9}–Pna and D_{2h}^{16}–$Pnam$.

Relative intensities of reflection were estimated visually. Multiple-film techniques were used in the case of oscillation diagrams. Each precession diagram was exposed for a series of fixed time intervals. The spots were compared with a set of standard density strips in order to estimate intensities. Lorentz and polarization corrections were applied to the estimated intensities.

Determination of structure

It was evident, in view of the short b axis of the unit cell, that the (010) projection would show maximum resolution of the atoms. A Patterson (010) projection yielded little information. Evaluation of a sharpened Patterson (1935) for this projection, however, showed three clearly resolved peaks which appeared to correspond to the following intramolecular interactions: C–O$_{\text{I}}$, C–O$_{\text{II}}$, O$_{\text{I}}$–O$_{\text{II}}$. The atomic positions indicated by the sharpened Patterson are inconsistent with the space group $Pnam$. The space group was therefore taken to be Pna.

The approximate structure indicated by the sharpened Patterson projection was refined by successive Fourier syntheses computed for the non-centrosymmetric (010) projection, using axial subdivisions equal to $a/60$ (0·17 Å) and $c/30$ (0·18 Å). When successive syntheses ceased to show significant changes ($>$ 0·005 Å) in atomic locations, a 'back shift' correction, described by Shoemaker *et al.* (1950), was applied to compensate for series-termination errors. The contributions of hydrogen atoms were considered in computing phases and structure factors and in determining F_c for comparison with F_o. The value of

$$r = \Sigma ||F_o| - |F_c|| \div \Sigma |F_o|$$

for the ($h0l$) zone is 9%, using F_c obtained from the atomic locations listed in Table 2.

Table 2. *Atomic parameters*

		($hk0$)	($h0l$)	Mean value
O$_{\text{I}}$	x	0·089	0·089	0·089
	y	0·140	—	0·140
	z	—	0·000	0·000
C	x	0·154	0·159	0·157
	y	0·306	—	0·306
	z	—	0·161	0·161
O$_{\text{II}}$	x	0·275	0·276	0·276
	y	0·337	—	0·337
	z	—	0·147	0·147

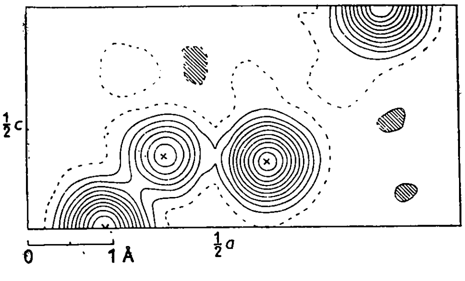

Fig. 1. Electron-density projection along the b axis. Contours drawn at intervals of 1 e.Å^{-2}, the unit contour line being broken. Regions of negative electron density are shaded.

The electron-density map is shown in Fig. 1. Contour lines were plotted at intervals of 1 e.Å^{-2}. Regions in which the electron density is negative are shaded. The largest negative value is 0·2 e.Å^{-2}. The final positions assigned to carbon and oxygen atoms are shown by crosses. It is interesting to note that a small maximum may be observed about 1 Å from the carbon atom. The location of this maximum is very close to the expected position of a carbon-bonded hydrogen atom.

Patterson and electron-density maps were then computed for the centrosymmetric (001) projection. Successive Fourier syntheses were refined in the usual way untll no further changes in signs of structure factors occurred. A 'back shift' correction was then applied to compensate for series-termination errors. The final ($hk0$) electron-density map is shown in Fig. 2. Atomic locations are indicated by crosses. For this zone the discrepancy coefficient was 10·5%. The atomic parameters derived from the two projections are listed in Table 2. The two projections, of course, provide independent determinations of the x parameters of the atoms. As can be seen, these agree very well in the case of the two oxygen atoms. The only significant discrepancy is found in the x parameter of the carbon atom (0·159 from ($h0l$) data and 0·154 from ($hk0$) data). The arithmetic mean of the two values was taken as the parameter of the carbon atom (0·157).

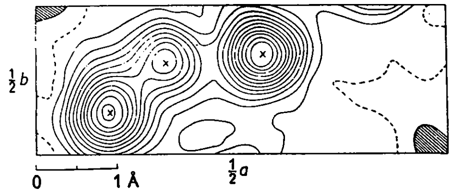

Fig. 2. Electron-density projection along the c axis. Contours are drawn at intervals of 1 e.Å^{-2}, the unit contour being broken. Regions of negative electron density are shaded.

Calculated and observed values of F are listed in Table 3. Calculated structure factors were adjusted in the usual way by multiplication by a temperature

Table 3. *Calculated and observed structure factors*

Centrosymmetric

$hk0$	F_c	$\|F_o\|$	$hk0$	F_c	$\|F_o\|$	$hk0$	F_c	$\|F_o\|$
200	−22·0	19·5	910	+ 3·8	3·7	130	− 3·1	2·5
400	− 7·2	6·5	10,1,0	+ 5·1	5·6	230	− 0·5	< 0·5
600	−12·8	13·8	11,1,0	+ 0·2	< 0·4	330	− 0·1	0·5
800	− 0·2	< 0·4	12,1,0	− 1·0	0·9	430	− 2·8	2·7
10,0,0	+ 0·7	< 0·5				530	+ 1·0	1·2
12,0,0	+ 4·2	3·0	120	+ 7·9	9·4			
			220	+ 5·8	5·2	630	+ 0·2	< 0·5
020	−13·0	13·0	320	−17·1	15·2	730	+ 6·0	7·0
040	− 3·0	3·4	420	+ 0·4	< 0·4	830	+ 1·6	1·8
			520	− 0·8	1·2	930	− 3·0	3·3
110	+11·6	9·5				10,3,0	+ 0·2	0·4
210	−19·2	18·2	620	− 0·2	< 0·5			
310	+ 2·1	1·3	720	+ 2·8	2·7	140	− 2·8	3·3
410	−11·0	10·4	820	0·0	< 0·5	240	+ 0·2	< 0·4
510	− 3·2	2·7	920	+ 3·4	3·6	340	+ 1·8	1·7
			10,2,0	+ 0·7	0·7	440	0·0	< 0·3
610	+ 9·7	9·6	11,2,0	− 0·4	< 0·4	540	+ 0·6	0·7
710	− 9·2	8·6	12,2,0	− 0·7	0·8	640	+ 1·8	1·7
810	− 3·8	3·6				740	− 0·6	0·6

Non-centrosymmetric

hkl	$\|F_c\|$	$\|F_o\|$	hkl	$\|F_c\|$	$\|F_o\|$	hkl	$\|F_c\|$	$\|F_o\|$
002	28·0	27·2	12,0,1	1·0	1·0	513	2·2	2·6
004	7·2	6·9	12,0,2	2·2	1·7	613	4·5	5·0
006	12·8	14·8				713	1·9	1·4
			011	41·2	39·9	813	0·9	1·4
201	25·2	23·7	111	11·4	14·8	913	1·1	1·1
202	25·2	26·0	211	18·0	16·3	10,1,3	2·2	2·2
203	8·8	8·8	311	15·4	15·6	11,1,3	0·4	0·4
204	13·1	13·4	411	4·8	4·4			
205	6·4	6·0	511	1·8	1·0	114	3·2	3·0
206	3·2	2·8	611	6·7	7·8	214	3·5	3·6
			711	2·7	2·3	314	0·2	< 0·6
401	16·7	18·8	811	0·7	1·3	414	2·2	2·5
402	12·1	12·8	911	2·7	3·2	514	3·4	3·2
403	7·4	9·2	10,1,1	1·6	1·3	614	2·5	2·9
404	7·0	7·0	11,1,1	0·3	< 0·4	714	1·1	< 0·6
405	2·5	1·6	12,1,1	1·4	1·2	814	4·5	4·7
406	2·3	1·8				914	1·0	1·0
			112	8·4	8·4	10,1,4	1·2	0·0
601	13·8	14·8	212	8·0	6·9			
602	11·2	13·1	312	1·3	1·6	015	5·9	6·4
603	6·3	7·3	412	6·9	7·2	115	2·5	2·8
604	5·4	5·1	512	6·5	6·5	215	3·5	3·8
605	4·0	3·6	612	5·8	6·0	315	2·0	1·6
606	1·5	0·9	712	3·6	4·0	415	1·9	1·7
			812	7·6	8·1	515	0·8	0·9
801	10·2	10·2	912	2·2	2·4	615	1·0	< 0·4
802	2·2	3·0	10,1,2	2·8	2·5	715	0·8	0·8
803	14·1	12·8	11,1,2	1·4	1·5			
804	1·6	2·6	12,1,2	0·6	0·0	116	0·8	< 0·4
805	5·7	4·1				216	2·0	2·0
			013	6·6	6·4	316	0·2	< 0·4
10,0,1	9·2	9·9	113	9·7	8·6	416	0·6	0·5
10,0,2	5·2	4·5	213	12·2	13·5	516	0·0	0·0
10,0,3	3·0	2·0	313	2·4	2·5	616	1·2	0·0
10,0,4	3·8	3·0	413	5·8	5·0			

factor exp $[-\beta \sin^2 \theta/\lambda^2]$. β was evaluated graphically from the slope of a plot of $\ln F_o - \ln F_c$ against $\sin^2 \theta/\lambda^2$. For the [010] zone $\beta = 2{\cdot}5$ Å^2; for the other zones $\beta = 4{\cdot}3$ Å^2. The value of the discrepancy factor for all structure factors listed in Table 3 is 9·8%.

Bond lengths and angles computed from the parameters listed in Table 2 are shown in Table 4.

Table 4. *Bond lengths and angles*

C–O$_{\text{I}}$	...	1·26±0·03 Å
C–O$_{\text{II}}$	...	1·23±0·03 Å
O–C–O	...	123 ±1°
C–O$_{\text{II}}$...O$_{\text{I}}'$	...	122 ±1°
O$_{\text{II}}$...O$_{\text{I}}'$–C′	...	114 ±1°
O–H–O	...	2·58±0·03 Å

Discussion of the structure

The arrangement of the formic acid molecules is shown in Fig. 3. The molecules are linked by hydrogen bonds at both ends to form infinite chains. This chain-like arrangement is in satisfactory agreement with recent measurements of the dielectric polarization of solid formic acid (Johnson & Cole, 1951). The results of that study have been interpreted as indicating that the values obtained are incompatible with a structure having dimeric molecules as the only units.

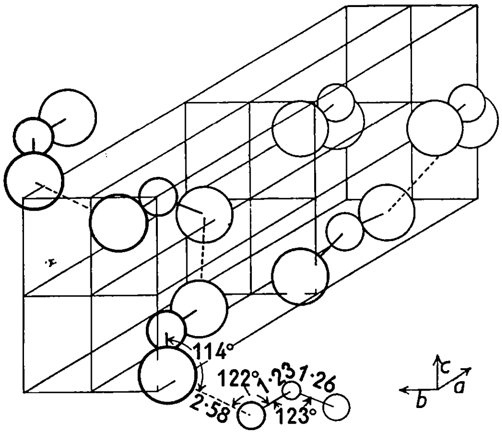

Fig. 3. Schematic drawing of the arrangement of formic acid molecules in the crystal. Broken lines represent hydrogen bonds. Bond lengths and angles are shown for a single molecule in the reduced image.

The length of the O–H · · · O bridge is 2·58±0·03 Å, compared with 2·51 Å in oxalic acid dihydrate (Brill, Hermann & Peters, 1942) and 2·56 Å in acetylene-dicarboxylic acid (Dunitz & Robertson, 1947*a*, *b*).

The tightly bonded chains of formic acid molecules appear to be held together in the crystal by ordinary van der Waals forces. Intermolecular distances are 'normal'; some of the closest intermolecular approaches are:

$$\text{O–O } 3{\cdot}28\text{ Å},\quad \text{O–C } 3{\cdot}18\text{ Å},\quad \text{C–C } 3{\cdot}75\text{ Å}.$$

Davies & Thomas (1950) have analyzed the most reliable X-ray measurements of the carboxyl group (based for the most part on studies of crystalline dicarboxylic acids). They list the range of the 'individual best values' as follows:

$$\text{C=O } 1{\cdot}20\text{–}1{\cdot}28\text{ Å},\quad \text{C–O } 1{\cdot}25\text{–}1{\cdot}31\text{ Å},$$
$$\text{O–C–O } 122\text{–}126^\circ.$$

In general, one C–O distance is found to be somewhat longer than the other. Brill, Hermann & Peters (1942) have reported values of 1·28 and 1·21 Å for oxalic acid dihydrate, while values of 1·28 and 1·26 Å have been computed by Booth (1947) from Robertson & Woodward's data (1936) for the same acid.

The bond lengths determined in this investigation (1·26 and 1·23 Å) are in reasonably good agreement with these values. These must, therefore, be reconciled with the longer bonds (especially the longer C–O bonds) found by means of electron diffraction and spectroscopic methods which have been listed in Table 1. Davies & Thomas (1951) have noted this divergence between X-ray and electron diffraction results and list two possible causes: "(1) There are very appreciable structural differences between formic acid and other carboxylic acids, or (2) marked changes (> 0·05 Å) occur in the C–O bond length on condensation from the vapour to the solid. (In that phase transition the principal structural changes will accompany the change from single (monomer) to double (dimer) molecules which can be studied in the vapour and in solution.)". Davies & Thomas further state that "at present the evidence does not allow an unequivocal decision between these alternatives but appears to favor (1)". The results of the present investigation, however, indicate clearly that the carboxyl group in formic acid is substantially like that in other carboxylic acids.

It is evident that if the electron-diffraction and X-ray measurements are both correct, the C–O bond length decreases by at least 0·1 Å during the transition from formic acid vapor to solid. Calculations by Davies & Sutherland (1938) indicate that a transition of this type might result in a decrease in the bond length of the order of 0·04 Å. It appears therefore that the difference in bond lengths cannot be attributed entirely to the vapor–solid transition. A redetermination of bond lengths in the vapor phase may help resolve this discrepancy.

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