A Reinvestigation of the Structure of Monomer and Dimer Formic Acid by Gas Electron Diffraction Technique

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The purpose of the present work was to make a careful structural comparison of an unengaged carboxyl group as found in the monomer of gaseous formic acid, with the carboxyl group in the corresponding dimer where well defined hydrogen bonds are formed. The unsymmetric arrangement of the carboxyl group in the dimer is confirmed, and the two carbon-oxygen bonds are found to be essentially double and single bonds as in the monomer. However, there are significant changes in the structure of the carboxyl group due to the hydrogen-bond formation. No significant change in the $C=O$ bond distance can be claimed, but the $C-O$ bond length is found significantly shorter and the $\angle O=C-O$ is found larger in the dimer than in the monomer. Also the $O-H$ bond length seems different in the two cases. The hydrogen bond in the ring structured dimer is 2.703 Å (standard deviation 0.008 Å). This distance value corresponds to a rather unsymmetric hydrogen bond. The other structure parameters are summarized in Tables 2 and 4.

The present study was inspired by the beautiful and important work on hydrogen bonds being carried out at the University of Uppsala by Dr. Ivar Olovsson and his coworkers. The work of the Uppsala group has resulted in a large series of publications, only a few of them being quoted in this work.[1-5] It was felt that the well defined molecular species HCOOH and $(HCOOH)_2$ in the gaseous phase deserved a comparative reinvestigation. The gaseous monomer exhibits the simplest existing unengaged carboxyl group. Further, the ring structure of the gaseous dimer contains a well-defined hydrogen-bond system, free of the complicating intermolecular engagements that have to be accounted for in crystal work.

The present work is being supplemented by a corresponding study on acetic acid and propionic acid carried out by J. Derissen at the University of Utrecht and also based upon data collected in Oslo.

An early electron-diffraction study by Pauling and Brockway[8] demonstrated the ring structure of the dimer formic acid in the gaseous phase. The ring contains two hydrogen bonds, and thus all oxygen atoms of the

molecule are engaged in hydrogen bonding. From electron-diffraction evidences and from resonance considerations Pauling and Brockway drew the conclusion that the dimer molecule had a D_{2h} symmetry with four equivalent oxygen atoms. Later electron-diffraction studies [9-11] confirmed the ring structure, but rejected the symmetric model. They all favoured a ring model with more or less conventional double and single carbon-oxygen bonds.

The molecular structure of monomeric formic acid has been thoroughly studied by various techniques as electron diffraction,[9,12,13] microwave,[14-16] infrared spectroscopy,[17] and NMR.[18] In the mass of structural information that may be extracted from these studies, there is a certain inconsistency. Further we have made it a point to make a simultaneous comparative investigation of the monomer and the dimer.

The fact that four bond distances occur in the region from approximately 1 to 1.35 Å, limits the accuracy by which each individual distance may be determined. It is necessary to take advantage of the last years improvement in the method of gas electron diffraction and also to include the information that may be obtained by introducing spectroscopically calculated mean amplitudes of vibration into the electron-diffraction refinement.

EXPERIMENTAL

The experimental data were collected using the Oslo electron-diffraction equipment.[6] The data deduction and computing work are based upon the standard methods of the Oslo laboratory.[7]

The pressure and temperature conditions were so chosen to avoid mixture of dimer and monomer and at the same time to avoid decomposition products. For the monomer exposures the bath temperature defining the "pushing pressure" was kept at 13°C, while the oven and the nozzle were heated to 175°C and kept within a temperature range of $\pm 10°$ during the experiments. For the dimer the bath was kept at 10°C, and the nozzle temperature was kept at 12°C$\pm 2°$. The container holding the liquid material in the bath was a glass container while the oven-nozzle system was all brass. The final electron-diffraction analysis shows that the amount of monomer at the low nozzle temperature as well as the amount of dimer at the high nozzle temperature must be negligible. However, for the high temperature experiments it can be shown that decomposition must have taken place. The decomposition products, as it can be seen from the electron-diffraction experiments, most probably contain carbon monoxide, but no indication of the presence of carbon dioxide is found. There are therefore reasons to believe that the kind of decomposition that takes place, must be the well known HCOOH$\rightarrow$ CO+H$_2$O,[19] though water cannot be detected directly in our experiments because of its low diffraction power. The least squares refinement indicates that there is about 9 mole % dissociation to CO+H$_2$O in the gas mixture at the high temperature experiments. Even at the low temperature the electron diffraction analysis indicate presence of decomposition products. 4.4 % per carboxyl groups is found dissociated to CO+H$_2$O. Whether the presence of carbon monoxide is due to decomposition that has taken place during the time interval between the last purification and the experiment or has been taking place during the experiment itself, is difficult to say for sure. Probably the decomposition takes place in the oven and at the nozzle. It is customary to let the gas flow go for a while before the diffraction takes place to get rid of possible volatile impurities or reminiscent air. If CO had been present in the main liquid container it would probably have disappeared during this gasing out period.

To obtain the electron-diffraction intensity curve for the monomer 11 sectored plates were used. Three plates from the 48 cm nozzle-to-plate-distance experiments were chosen, covering the s interval from 1.0 to 20.25 Å^{-1}. Further four 38 cm plates were

used covering the s interval from 3.0 to 25.75 Å^{-1}, and finally four 15 cm plates were used, covering the s range from 10.0 to 55.5 Å^{-1}.

For the dimer a total 11 plates were chosen, six 48 cm plates, covering the s range from 1.0 — 19.4 Å^{-1} and five 19 cm plates, covering the s range from 8 — 46 Å^{-1}.

A standard photometer procedure was applied including oscillation of the plates. The intensity data obtained after final subtraction of the background are shown in Fig. 4 (monomer) and Fig. 7 (dimer).

STRUCTURE ANALYSIS

Already the radial distribution curves based upon undamped molecular intensity data indicate a larger difference between the two carbon-oxygen bond distances in the monomer than in the dimer. Fig. 1 reproduces the
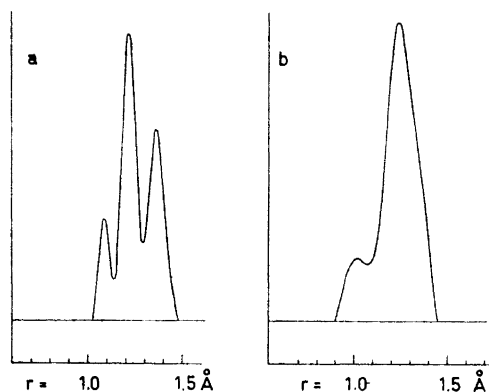

Fig. 1. First experimental radial distribution curves for the inner peak complex. k in $\exp(-ks^2)$ is equal to 0. a) monomer, b) dimer.

inner top complex of the radial distribution curve ($k=0$) for the two molecules. The curve for the monomer has two peaks corresponding to carbon-oxygen distances at about 1.21 Å and 1.35 Å, while the dimer curve is not resolved in the carbon-oxygen bond-distance region. Certainly no final conclusion should be based upon these observations. The obvious defects in the outer part of the experimental intensity curve for the monomer obscure the undamped intensity curve (Fig. 4). However, the structural difference indicated by the two curves of Fig. 1 appears to be independent of the defect of the outer part of the intensity curve. The structural difference is clearly demonstrated by the final least squares analysis in which the effect of the outer part of the intensity curve has been strongly reduced.

A large number of least squares refinements were carried out keeping some structure parameters constant and varying others, going systematically through all combinations deemed necessary.

LEAST SQUARES REFINEMENT OF THE STRUCTURE OF THE MONOMER

It was not possible to refine all structure parameters simultaneously. Even if theoretical vibrational amplitudes of the O—H and C—H bonds were applied and kept constant the bond lengths did not refine in the first attempt. It was therefore necessary to start out the refinement with assumed values for the bond distances involving hydrogen and for the corresponding vibrational amplitudes. Following values were assumed: $r_{O-H}=0.97$ Å, $r_{C-H}=1.10$ Å, $u_{O-H}=0.068$ Å, and $u_{C-H}=0.077$ Å. The two u values were calculated by Cyvin.[20] Under these assumptions the remaining five geometric parameters were refined as well as the u values of the carbon-oxygen bond distances and that of the oxygen-oxygen distance. The result is given in Table 1 with the standard deviations as they come out of the refinement. The weight factor was kept equal to 1 in the s range from 4.5 Å^{-1} to 36.0 Å^{-1} and damped down exponentially to 0.3 at $s=1.5$ Å^{-1} and to 0.01 at $s=55.25$ Å^{-1}.

Table 1. Parameters refined for HCOOH before correcting for the presence of decomposition products and using assumed values for r_{C-H}, r_{O-H}, u_{C-H}, and u_{O-H}.

	a	b	c	d
C=O	1.213 Å	0.00099 Å	0.035 Å	0.0010 Å
C—O	1.361 Å	0.0015 Å	0.045 Å	0.0013 Å
∠O=C—O	123.6°	0.28°		
∠H—C—O	110.3°	6.1°		
∠H—O—C	107.5°	2.2°		
O···O	2.270 Å		0.056 Å	0.0021 Å

a. Distances and angles. b. Standard deviations as they come out of the least squares refinement. c. Refined u values. d. Standard devations for the u values.

Using the thus refined parameters together with the assumed ones, the first theoretical radial distribution curve was calculated. This curve is given in Fig. 2 together with the experimental radial distribution curve. The difference between experimental and theoretical curve is also presented. The damping constant [k in $\exp(-ks^2)$] is here 0.0025 Å^2. The most striking feature of the difference curve is the peak at approximately 1.11 Å suggesting the presence of impurities. As mentioned the most probable source of impurity would be from decomposition of formic acid to carbon monoxide and water. The presence of water is not expected to be detectable. Another possible decomposition product would be carbon dioxide. However, the radial distribution curve does not suggest such an impurity. It would require a maximum in the difference radial distribution curve at 2.32 Å in contrast to what is observed.

From this on the fraction of dissociated molecules (α) was included as a parameter in the least squares refinement, and now it appeared possible also to refine the bond distances to hydrogen. As the structure parameters of the
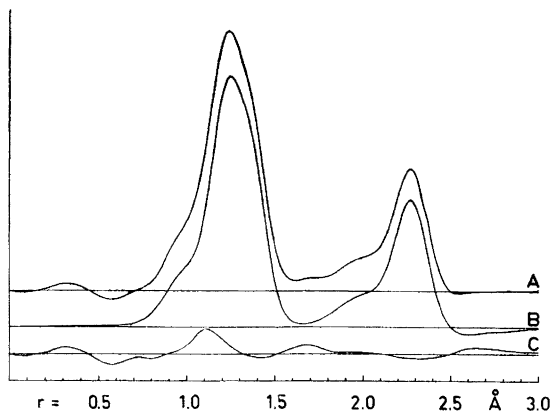
Fig. 2. Experimental (A), theoretical (B), and difference (C) radial distribution curve for the monomer before correction for the effect of the decomposition products. ($k = 0.0025$).

dissociation products can certainly not influence the structure parameters of the formic acid molecule to any intelligible amount, they were kept constant during the refinement. Following values were used: $r_{C-O} = 1.1282$ Å,[21] $u_{C-O} = 0.0337$ Å,[22] $r_{O-H} = 0.958$ Å,[21] and $u_{O-H} = 0.0677$ Å.[22] The vibrational amplitudes of the C—H and the O—H bonds in the formic acid molecule were kept constant as earlier. A small background correction was made in order to eliminate the error features seen in the experimental radial distribution curve in the interval from 0 to 0.5 Å. The weight function was also slightly changed in the inner part of the intensity curve, bringing it up to 0.5 at $s = 1.5$ Å^{-1}.

At first the already refined parameters were kept constant. r_{O-H} and r_{C-H} of formic acid were refined together with α, and afterwards these three parameters were kept constant and the other parameters were re-refined. The u values of the non-bonded distances to hydrogen were not refined but kept constant equal to 0.09 Å. Likewise u_{O-H} and u_{C-H} of formic acid were kept constant as earlier. However, the effect of possible errors in these u values was included in the error estimate of the most vulnerable parameters. The hydrogen-hydrogen contribution is too small to be used for determining the torsional situation around the C—O bond. The hydroxyl hydrogen is during the refinement kept in *trans* position relative to the other hydrogen atom.

The result of these refinements is given in Table 2. All the parameters listed except $r_{O...O}$ are independent parameters. For the distance parameters four different sets of standard deviations are listed. The first set (column b, Table 2) contains the values as they come out of the least squares calculation. The second set (column c, Table 2) includes the effect of correlation between the sets of parameters that were not simultaneously refined. It also includes the effect of possible errors in the assumed u values. In the third set of standard deviations (column d, Table 2) our empirical scale uncertainty is further

Table 2. Parameters refined for HCOOH. The effect of the decomposition products is included.

	a	b	c	d	e	f	g	h
C=O	1.217 Å	0.00072 Å	0.0010 Å	0.0020 Å	0.0026 Å	0.032 Å	0.0008 Å	0.0010 Å
C—O	1.361 Å	0.0011 Å	0.0014 Å	0.0023 Å	0.0030 Å	0.042 Å	0.00098 Å	0.0014 Å
O—H	0.984 Å	0.009 Å	0.019 Å	0.019 Å	0.024 Å	0.068 Å spec.		0.016 Å
C—H	1.106 Å	0.012 Å	0.019 Å	0.019 Å	0.024 Å	0.077 Å spec.		0.062 Å
∠O=C—O	123.4°	0.21°	0.23°		0.46°			
∠H—C—O	109.1°	2.5°	4.4°		8.8°			
∠H—O—C	107.3°	1.7°	2.2°		4.4°			
O···O	2.271 Å	0.002 Å	0.002 Å	0.0037 Å	0.0048 Å	0.054 Å	0.0016 Å	0.0018 Å

a. Distance and angles.
b. Standard deviations of the parameters of column a as they come out of the refinement.
c. Same as in b but correlations between parameters included.
d. Same as in c with scale error included.
e. Same as in d with the correlation of neighbouring points in the intensity included.
f. Refined u values.
g and h. Standard deviation for the u values corresponding to those of columns b and c.

included. The scale uncertainty of course does not influence the angle param-
eters. Finally in the fourth set (column e, Table 2) we have tried to include
the effect of correlation between neighbouring points of the observed intensity
data.[23] Results of least squares refinement with experimental non-diagonal
weight matrix [24] indicate that the standard deviations of distances as they
come directly out of the refinement may have to be multiplied by a factor
of about 2. If the scale uncertainty has been included on beforehand, the
factor is in most cases considerably smaller. The values in column e have been
obtained using the general experience from other molecules. For the u values
standard deviations are given only as they come out of the refinement (column
g, Table 2) and after the first kind of correction mentioned earlier (column h).
The standard errors of the geometric parameters as given in column e of
Table 2 ought to be fairly conservative. For comparison of distances within
the molecule itself they are probably too conservative as the scale factor
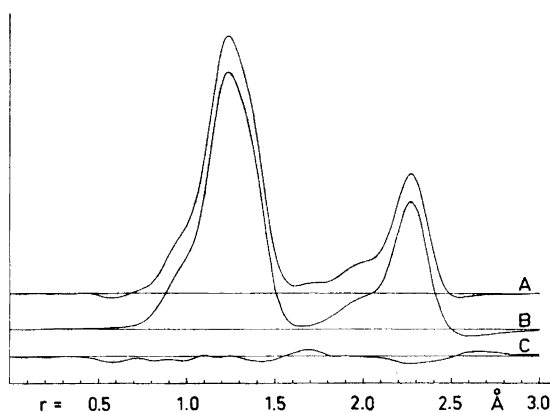should not change the ratio between the distances in the molecule.

Fig. 3. Experimental (A), theoretical (B), and difference (C) radial distribution curve for
the monomer after correction for the effect of the decomposition products. ($k = 0.0025$).

Fig. 3 gives a similar set of radial distribution curves as Fig. 2 but now
calculated from the data of Table 2. The contribution of the decomposition
products was now taken into account using the α value obtained by the least
squares refinement. The refined value for α was 0.09 with a standard devia-
tion varying from 0.015 to approximately 0.05 depending upon which type
of standard deviation is used. Now the peak in the difference curve at $r = 1.11$ Å
is removed. Fig. 4 shows the corresponding intensity curves.

The distance parameters are all $r_a = r_g(1)$, and our scale is based upon
evaporated gold diffraction. If reference is made to gaseous CO_2 according to
infrared data of Courtoy [25] and transferred to r_a by by Kuchitsu [26] all the
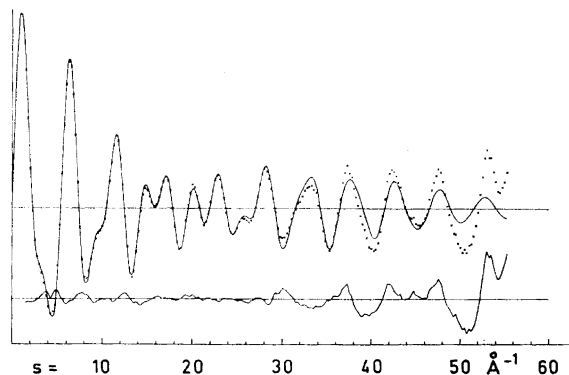distance values should be reduced by about 0.25 %.

Fig. 4. Intensity curves for the monomer. ———— calculated curve, + + + experimental data. Lower curve is the residual curve.

COMPARISON WITH EARLIER INVESTIGATIONS OF MONOMER FORMIC ACID

The two most recently published electron-diffraction investigations of the monomer are that of Schomaker and O'Gorman [12] and that of Karle and Karle.[13] The spectroscopic investigations are partly quite conflicting, the claimed accuracy taken into consideration. The latest micro-wave study by Kwei and Curl [16] is probably the most accurate of the spectroscopic investigations. It is based upon data from four different isotope species studied by Lerner, Dailey, and Friend [15] as well as on data from two additional species measured by Kwei and Curl themselves. In Table 3 the geometric structure parameters obtained in the various investigations are listed. The data in parenthesis are the error ranges except for the last column (this work) where the most conservative standard deviations are given. The three sets of electron-diffraction data certainly compare satisfactorily. The deviation between the distance values determined by Schomaker and O'Gorman (the assumed values disregarded) and those given by the present authors is 0.5 % or less. This is another example of the high quality of the old visual electron-diffraction work of Schomaker and his group. The high quality of the work is combined with a rather uncustomary modesty in error estimation that in retrospect may seem too cautious, though it certainly adds to the credulity.

Comparison of the three electron-diffraction sets of data with the most recent microwave result seems to reveal a scale difference. All the distances of the present work are larger than the corresponding microwave distances. The mentioned difference between the gold scale and the infrared CO_2 scale is too small to explain the discrepancy. Most probably the discrepancy is nothing but the difference one has to expect between r_s distances of microwave and the r_a distances of electron-diffraction.

Table 3. Geometric structure parameters obtained for HCOOH by several investigators. Values in parenthesis are error limits for column a—f. For g (present work) the most conservative standard deviations are given. (Distances in Å, angles in degrees).

|	a[12]	b[13]	c[17]	d[14]	e[15]	f[16]	g (present work)
C=O	1.213 (.026)	1.23 (.01)	1.225 (.02)	1.22	1.245 (.002)	1.202 (.01)	1.217 (.0026)
C–O	1.368 (.034)	1.36 (.01)	1.41 (.02)	1.34	1.312 (.002)	1.343 (.01)	1.361 (.0030)
O–H	0.97 ass.	0.97 (.05)	0.97 ass.	0.97	0.95 (.02)	0.972 (.005)	0.984 (.024)
C–H	1.09 ass.	1.09 ass.	1.08 ass.	1.09	1.085 (.02)	1.097 (.005)	1.106 (.024)
∠O=C–O	123.5 (3)	124.4 (1)	125 (1)	124.8	124.3 (.2)	124.9 (1)	123.4 (.46)
∠H–C–O		105 (10)		113.5	107.8 (1)	111 (2)	109.1 (8.8)
∠H–O–C				105.5		106.3 (1)	107.3 (4.4)
O⋯O	2.275 (.025)	2.27 (.005)		2.26	2.261 (.004)	2.257 (.005)	2.271 (.0048)
C–O	1.128	1.106	1.151	1.098	1.053	1.117	1.118
C=O							

LEAST SQUARES REFINEMENT OF THE STRUCTURE OF THE DIMER

Since the overlap in the bond distance range for the dimer is still more serious than for the monomer the determination of the parameters appears more problematic. However, a reconsideration of the symmetric ring molecule with four equivalent carbon-oxygen bonds is needless. From the radial distribution curve, as presented with no damping in Fig. 1 or with a damping constant of 0.0015 Å² in Fig. 5, it can readily be shown that the u value of a hypothetical one-type carbon-oxygen bond must be more than 0.08 Å which is a totally unacceptable value. Further theoretically calculated radial distribution curves based upon a symmetric molecule exclude this possibility.

Since it is impossible to refine all structure parameters simultaneously, one is faced with an uncomfortably large number of approaches. A large number of refinements were carried through. This presentation is restricted to the main steps of the refinement procedure.

The refinement was based upon the assumption that the u value of the C=O bond was about the same as in the monomer, at least probably not smaller. The theoretical u value of Cyvin [20] (0.035 Å) was therefore assumed. The three parameters $r_{C=O}$, r_{C-O}, and u_{C-O} were then refined consecutively. r_{C-O} was refined a series of times alternatively together with $r_{C=O}$ and u_{C-O}. This was repeated until no more change took place. The other parameters of the dimer were then refined successively. Some of the parameters connected to the hydrogen atoms were assumed. The best fit thus obtained without assuming the presence of any other molecular species than the ring shaped dimer is demonstrated in Fig. 5. The experimental and the calculated radial

Fig. 5. Experimental (A), theoretical (B), and difference (C) radial distribution curve for the dimer before correcting for the effect of the decomposition products. ($k=0.0015$).
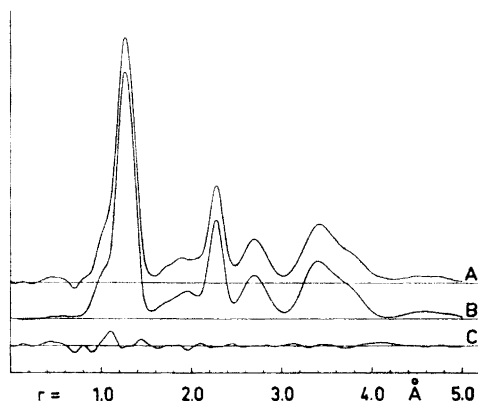
distribution curves are presented together with the difference between them ($k=0.0015$ Å²). The by far highest peak of the difference curve occurs at approximately 1.1 Å, suggesting the presence of carbon monoxide. However, the difference curve leaves no suspicion as to possible presence of the monomer, carbon dioxide or other dissociation products. The difference curve seems also to rule out possible contributions from other dimer conformations, at least any contribution that could obscure the further refinement. It thus

Table 4. Final parameters for $(HCOOH)_2$.

	a	b	c	d	e	f	g	h
C=O	1.220 Å	0.00062 Å	0.0014 Å	0.0022 Å	0.0029 Å	0.035 Å spec.	0.00070 Å	0.0021 Å
C−O	1.323 Å	0.00077 Å	0.0013 Å	0.0022 Å	0.0029 Å	0.043 Å spec.		0.0019 Å
O−H	1.036 Å	0.0079 Å	0.013 Å	0.013 Å	0.017 Å	0.068 Å spec.		0.015 Å
O−H···O	2.703 Å	0.0034 Å	0.0038 Å	0.0054 Å	0.0070 Å	0.126 Å	0.0040 Å	0.0045 Å
C−H	1.082 Å	0.010 Å	0.016 Å	0.016 Å	0.021 Å	0.077 Å spec.		0.034 Å
∠C−O−H···O	108.5°	0.15°	0.21°		0.42°			
∠O=C−O	126.2°	0.14°	0.24°		0.48°			
∠H−C=O	115.4°	1.45°	1.55°		3.1°			
O···O	2.268 Å	0.0013 Å	0.0015 Å	0.0034 Å	0.0044 Å	0.057 Å	0.0012 Å	0.0014 Å

a−h. Same meaning as for Table 2.

seemed justified to continue the refinement under the assumption of carbon monoxide and water as the only impurities. Again r_{O-H} and r_{C-H} of formic acid could be refined simultaneously with α (defined as the ratio of dissociated molecules per carboxyl group). Under these refinements u_{O-H} and u_{C-H} were kept constant and were given the calculated values of the monomer. The C—O and C=O parameters were also re-refined at this stage. The changes were negligible.

Finally the hydrogen bond distance, the three angles, and the u values of the two shortest oxygen-oxygen distances were refined. Other refinement sequences were tried without any change of the end result. Unfortunately the u values of the longest C···O, O···O, and C···C distances could not be refined. These distances all fall under the broad peak complex from 3 to 4 Å. By trial and error curve fitting of the radial distribution curve an estimate of 0.12 Å was assigned to each of the u values for these distances, and this value was used during the refinement. For lack of ability to determine the exact position of the hydroxyl hydrogen atom it was placed on the straight line between the two oxygen atoms.

The weight function was all the time equal to 1 in the s range from 3.0 to 37.0 Å^{-1} and fell off exponentially to either sides to obtain the value of 0.5 at $s=1.5$ Å^{-1} and the value of 0.01 at $s=44$ Å^{-1}.

The result of the least squares refinement is given in Table 4. The various sets of standard deviations are analogous to those presented in Table 2.

The α parameter was refined to a value of 0.044 with standard deviation somewhat smaller than the α value itself but of the same order of magnitude.

The question of possible deviation from planarity has been raised earlier, and arguments in favour of such a deviation were put forward.[10] In retrospect it can easily be seen that the apparent deviation from planarity was due to false estimation of the carbon-oxygen bond lengths that could not at that time be determined with any reasonable degree of accuracy. The present investigation does not indicate any deviation from planarity. The long inter-atomic distances are not found shorter than expected from a planar model, on the contrary, if anything, they are an idea longer.

After the final refinement the possibility of other molecular species than the ring dimer and carbon monoxide was reconsidered. The final radial distribution difference curve does not suggest any such other molecular species. A close analysis of the difference curve suggests that a possible monomer contribution must be less than 1 %. It is more difficult to set a limit for possible presence of non-ring dimers containing only one hydrogen bond. Such a molecular species would be expected to exhibit a high degree of torsional freedom around the hydrogen bond and thus have the long distance contributions washed out. In principle the residual maxima in the difference curve (Fig. 6) may be interpreted assuming such molecular species. If this be done the contribution of non-ring conformers of the dimer is still found less than a few per cent. It can therefore be concluded that possible presence of extraneous molecular species would hardly hazard any of the argumentation used in the refinement of the structure of the ring dimer.

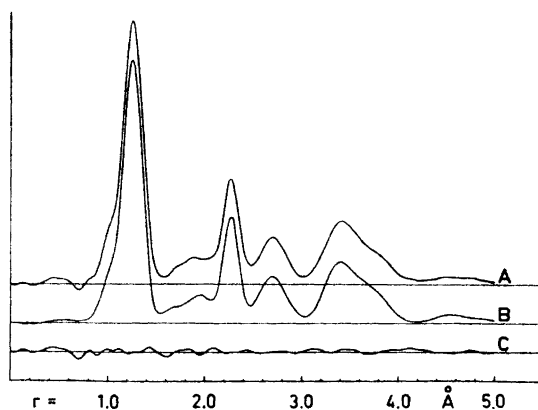Like in the monomer $r_a=r_g(1)$ values are used based upon evaporated gold as standard.

Fig. 6. Experimental (A), theoretical (B), and difference (C) radial distribution curve for the dimer after correcting for the effect of the decomposition products. ($k = 0.0015$).

COMPARISON WITH EARLIER INVESTIGATIONS OF DIMER FORMIC ACID

The earlier structure analyses of the dimer are all based on electron-diffraction studies. In the old work of Pauling and Brockway (1934) [8] a hydrogen bond of 2.67 Å was found. The reinvestigation of Brockway and Karle (1944) [9] lead to a value of 2.73 Å, and the two Norwegian investigations gave the values 2.719 Å [10] and 2.680 Å.[11] In the oldest works the carbon-oxygen bond distances were more or less assumed, while the $O \cdots O$ distance over the $O-C=O$ angle was determined directly. The two Norwegian investigations gave the values 2.222 Å [10] and 2.251,[11] respectively. Though the Norwegian investigation of 1959 is not at the same level as the present one, mainly due to the dramatic change in computing facilities, the older values are compared with the present ones in Table 5. The deviation is not larger than should be expected. Even if the standard errors of the present work are assigned to the

Table 5. Comparison of earlier and new structure data for $(HCOOH)_2$.

	Present work	Earlier work [11]	Present work	Earlier work [11]
	Distances (Å) and angles (°)	Distances (Å) and angles (°)	u values	u values
C=O	1.220	1.224	0.035	0.037
C−O	1.323	1.315	0.043	0.050
C−H	1.082	1.10	0.077	0.079
O−H	1.036	0.99	0.068	0.050
O⋯O	2.268	2.251	0.057	0.050
O−H⋯O	2.703	2.680	0.126	0.104
∠O=C−O	126.2	125.0		
∠C−O−H⋯O	108.5	109.4		
∠H−C=O	115.4	117.5		

older data, which is hardly justified, the ratios between the deviations and the corresponding standard deviations for the nine geometric parameters listed in Table 5, assume quite acceptable values. There seems to be a slight scale difference. If the two sets of distances are compared using proper weights on each distance, there is a scale difference of 0.28 %, the present scale being the larger.

COMPARISON OF STRUCTURE PARAMETERS OF FORMIC ACID UNDER DIFFERENT CONDITIONS

Comparison of corresponding structure parameters in the monomer and the dimer should be rather favourable. The same method has been applied and the electron-diffraction diagrams of the two molecules have been taken during a short time interval. The last set of standard deviations including correlation effects and the long range scale fluctuation should therefore be rather realistic. We feel they are rather too large than too small. But it has to be admitted that in spite of conscientious study of the various sources of error the ultimate standard errors are not entirely free of subjective judgement.

It can immediately be concluded that the single bond carbon-oxygen distance is significantly larger in the monomer than in the dimer, as should be expected due to the effect of hydrogen-bond formation. The found difference between the two bond lengths is about 9 times larger than the combined standard deviations. Apparently the effect of hydrogen-bond formation on the $C=O$ bond length is considerably smaller than on the $C-O$ bond. This is to be expected because of the greater force constant of the double bond. The double bond is found slightly longer in the dimer than in the monomer as should be expected, but the deviation is certainly not significant being only 0.003 Å compared to a slightly larger combined standard deviation.

The $O=C-O$ angle is found 2.8° larger in the dimer than in the monomer with a standard deviation of the difference of about 0.7°. The angle should therefore be significantly larger in the dimer.

The $O-H$ bond is found larger in the dimer than in the monomer as should be expected, the difference being 0.052 Å. The effect of hydrogen-
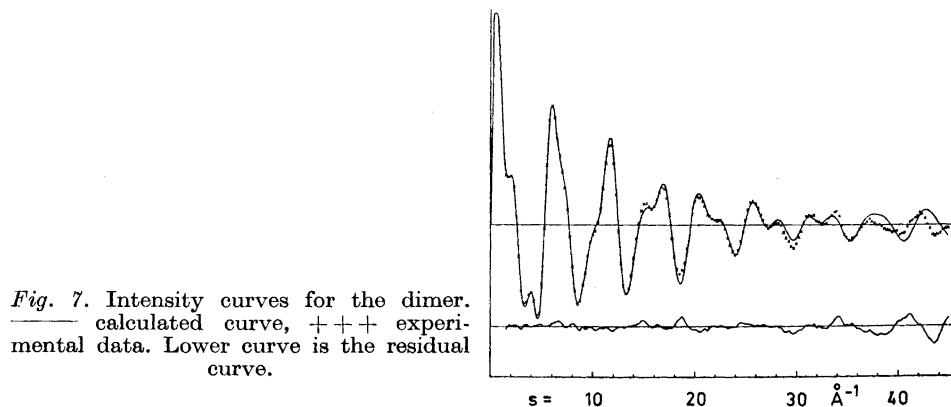

Fig. 7. Intensity curves for the dimer. ——— calculated curve, + + + experimental data. Lower curve is the residual curve.

s = 10   20   30 Å⁻¹ 40

bond formation should be larger on the O—H bond than on any other bond of the molecule. Unfortunately, the standard deviation for the difference is as large as 0.035 Å, leaving a certain probability of accidental deviation in the expected direction.

The observed difference in the C—H bond is less than one half of that observed for the O—H bond and is certainly not significant. The angle parameters determining the hydrogen positions are not determined with sufficient accuracy for conclusions to be drawn.

The difference in the geometric structure parameters of the monomer and the dimer as found by electron-diffraction study is in good qualitative agreement with the results of Nakamoto and Kishida [27,28] deducing bond stretching force constants from spectroscopic observations of the molecules in the gas phase. Their data are given in Table 6. The approximately 11 %

Table 6. Bond stretching force constants. Nakamoto and Kishida.[27,28] Unit $10^5 \times$ dynes cm^{-1}.

	Monomer	Dimer
$K_{C=O}$	11.20	10.00
K_{C-O}	4.60	5.50
K_{O-H}	6.90	4.70
K_{C-H}	4.00	4.00
$K_{O\cdots H}$		0.36

reduction of the high force constants of the C=O bond when going from the monomer to the dimer is not accompanied by a dramatic increase in the bond length. For the C—O stretching force constant there is a 20 % increase when going from the monomer to the dimer, and for the O—H there is a 32 % decrease. The corresponding responds for the bond distances are a 0.038 Å decrease for the C—O bond and a 0.052 Å increase for the O—H bond.

The electron-diffraction structure parameters that in principle are most closely related to force constants, are the vibrational amplitudes. However, these parameters, if at all actually measured, are not determined with sufficient relative accuracy to justify a comparison. The vibrational amplitudes are not very sensitive to small changes in the force constants, and they are not too strongly correlated to the bond distances in an electron-diffraction study. For the determination of geometric structure parameters the insensibility of the amplitudes may often be an advantage as uncertainty in spectroscopically calculated amplitudes would in general not jeopardize accurate determination of internuclear distances. The difference between $u_{C=O}$ and u_{C-O} in both molecular species is worth noting. Further the finding of the unusual large vibrational amplitude for the hydrogen bond in the dimer is a valuable supplement to Nakamoto and Kishida's result of the small force constant for the O$\cdots$H stretching. A simple calculation correlating the force constants of Nakamoto and Kishida with our vibrational amplitudes and using their force constant for O$\cdots$H, suggests a u value for the hydrogen bond of 0.120 Å in excellent agreement with our measured value of 0.126 Å.

The X-ray crystallographic study of formic acid of Holtzberg, Post, and Fankuchen [29] dates back to 1952 when the low temperature technique for such study was fairly new and when the dramatic improvement in computing technique had not yet taken place. The bond lengths were determined using two Fourier projections. The $C=O$ bond-distance value (1.23 ± 0.03 Å) is in satisfactory agreement with our results. (The error estimates are given as "error limits" rather than standard deviations.) The $C-O$ bond distance (1.26 ± 0.03 Å) is not compatible with our results, and the $O=C-O$ angle agrees with our monomer result rather than with our dimer result. However, these discrepancies do not necessarily represent conflicting findings. The environment of the individual molecule is so different in the solid state from that of the dimer gas. In the crystal each molecule is linked to two neighbours by hydrogen bonds, thus forming endless chains. The hydrogen bond distance is 2.58 ± 0.03 Å, a value that is certainly significantly shorter than that in the dimer gas. It should be noted that a rather similar situation exists for acetic acid [30] where the molecules are linked together essentially the same way in the crystal as the molecules of formic acid. Also here the hydrogen bond is found considerably shorter (2.61 Å) than that found for the dimer of formic acid.

Nahringbauer and Larsson [5] have studied the 1:1 addition compound of formic acid with formamide. The formic acid molecules engage in hydrogen-bond formation with formamide molecules. The three major molecular parameters $C=O$ bond length, $C-O$ bond length, and $O-C=O$ angle are 1.202 Å, 1.320 Å; and 125.4°, respectively. The standard deviations for bond distances range from 0.002 Å to 0.003 Å, and the standard deviation of the angle is 0.2° to 0.3°. For the $C-O$ bond length and for the $O=C-O$ angle the correspondence is very satisfactory. Whether the apparently significant deviation between the values for the $C=O$ bond length represents conflicting findings or not, must remain unanswered. It may well be ascribed to different molecular environment or the inherit difference between X-ray data and electron-diffraction data.

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