

A Study of the Influence of Deuterium Substitution on the Hydrogen Bond of Dimeric Formic Acid

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In a search for a possible isotope effect on the hydrogen bond, the gas electron-diffraction technique has been used to study the structure of formic acid dimer where the hydroxyl hydrogen has been substituted by deuterium, and the results compared with those of earlier structure determination of formic acid.¹

The experimental data were obtained from the Oslo electron-diffraction apparatus,² and the computing work was based upon the standard methods of this laboratory.^{3,4} The nozzle-to-plate distances were approximately 48 cm and 20 cm, and four plates from each distance were used. The intensity data were combined to cover the s range from 1.875 to 44.0 Å⁻¹.

The experimental conditions were so chosen as to avoid contribution from monomeric acid and from decomposition products. The nozzle temperature was kept at 26 ± 2°C during the experiments. The final electron-diffraction analysis showed that the amount of extraneous molecular species present, if any, was negligible.

The molecular intensity function obtained after final subtraction of the background was visually indistinguishable from that of the corresponding light formic acid.¹ Because of the experimental precautions taken it was not necessary to correct for the presence of CO as in the case of (HCOOH)₂; the difference between the experimental and theoretical radial distribution curve has no peak at about 1.1 Å.

The structure parameters were determined by least squares refinement. The results are presented in Table 1. The refinement was based upon the assumption that the substitution of hydrogen by deuterium in the hydroxyl group has no influence on the C—H bond. Consequently, the corresponding bond distance and u value were kept constant and equal to the values found in the light acid. Further,

Table 1. Parameters for (HCOOH)₂ and (HCOOD)₂.

	a	b	c
C=O	1.220 Å	1.220 Å	0.003 Å
C—O	1.323 Å	1.332 Å	0.003 Å
O—H	1.036 Å	1.058 Å	0.017 Å
O—H...O	2.703 Å	2.722 Å	0.007 Å
∠O=C—O	126.2°	125.5°	0.48°
∠C—O—H...O	108.5°	107.8°	0.42°
O...O	2.268 Å	2.268 Å	0.004 Å

a. Distances and angles for (HCOOH)₂.

b. Distances and angles for (HCOOD)₂.

c. Standard deviations of the parameters of column *a*.

the angle H—C=O, the u value of the C=O bond, and the u values of the longest C...O, O...O, and C...C distances were assumed to be the same as in (HCOOH)₂. These parameters were also kept constant during the refinement. The C—O distance was refined together with its u value keeping the C=O distance constant and then refined together with the C=O distance keeping u_{C-O} constant. This was repeated alternately until there was no change in the parameters. All the parameters listed in Table 1 except the O...O distance are independent parameters.

The distances and angles listed in the table are obtained by least squares refinement with an experimental diagonal weight matrix. The standard deviations obtained for distances and angles of (HCOOH)₂ are also listed. The two parameters that ought to be determined with the highest degree of accuracy are the C=O bond distance and the O...O distance within the same carboxyl group. These two parameters are found exactly the same in the two molecules. This finding indicates that there is no scale difference in the two investigations.

For the valency angles listed in the table and for the O—H bond length no unexpected difference is found, the standard deviations taken into account. The two parameters for which relatively large differences occur are the C—O bond distance and the hydrogen bond distance. For the C—O bond distance the value for (HCOOD)₂ is found 0.009 Å larger than for the (HCOOH)₂. If the standard devia-

tions found in $(\text{HCOOH})_2$, for this parameter are taken also for the $(\text{HCOOD})_2$, the difference may seem close to significant. There are, however, reasons to question the value of the standard deviation for the C—O distance in $(\text{HCOOH})_2$. When the standard deviations for the structure parameters of light formic acid were estimated, the effect of correlation between neighbouring points in the observed intensity data was not estimated for each individual parameter. General experience is in favour of a greater standard deviation for the C—O bond length than for the C=O bond length due to a larger u value for the former. For $(\text{HCOOD})_2$, a number of least squares refinements were carried out using an experimental non-diagonal weight matrix. This refinement increases the standard deviation for the C—O bond length by approximately 30 %, reducing the apparent significance.

Turning now to the hydrogen bond length, the value for $(\text{HCOOD})_2$ is found 0.019 Å larger than that of $(\text{HCOOH})_2$. For the hydrogen bond there seems to be no systematic error in the estimate of the standard deviation. The value of 0.019 Å is approximately twice as large as the standard deviation of the difference.

The observed value of the isotope effect on the hydrogen bond length is in good agreement with that observed by Delaplane and Ibers on α -oxalic acid dihydrate.⁵ They find an isotope effect of approximately 0.02 Å, and they conclude that the isotope effect is about the same in weak and strong hydrogen bonds. The hydrogen bond of dimeric formic acid must be considered as a rather weak one. Hydrogen

bond lengths between carboxyl groups range from 2.45 Å in symmetric hydrogen bonds up to approximately 2.75 Å. The hydrogen bonds in the gaseous dimeric formic acid, acetic acid,⁶ and propionic acid⁷ are certainly significantly longer than the hydrogen bonds of chain structured solid acids.^{8,9}

For the scale comparison all distance parameters of Table 1 are given as $r_a = r_g(1)$, and the scale is based upon gold diffraction. If reference is made to gaseous CO_2 as customary in this laboratory, all distance values should be reduced by about 0.25 %.

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