

# Molecular Orbital Theory of the Hydrogen Bond.

## XV. Ring Closure and Proton Transfer in Formic Acid Dimer and $\beta$ -Hydroxyacrolein

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**Abstract:** Ab initio SCF calculations with a minimal STO-3G basis set have been performed in this study of hydrogen bonding and proton transfer in formic acid dimer and  $\beta$ -hydroxyacrolein. The computed structure and stabilization energy of the formic acid dimer are in good agreement with experimental data, except for an underestimation of the intermolecular distance. Changes which occur in intramolecular coordinates in this dimer are small, but significantly larger than changes observed in dimers stabilized by a single hydrogen bond. The  $C_s$  and  $C_{2v}$  forms of  $\beta$ -hydroxyacrolein are predicted to be energetically similar, with the  $C_s$  form being slightly more stable by approximately 6.6 kcal. Potential curves for the transfer of hydrogen-bonded protons in these systems have been obtained. In the formic acid dimer, such curves show a dependence on the intermolecular distance, and on the mechanism of proton transfer.

Within the past several years, there have appeared in the literature many ab initio molecular orbital studies of hydrogen bonding. The great majority of these studies have dealt with the formation of a single hydrogen bond between a pair of interacting molecules. From the results of such studies, it has been possible to characterize the structures and energies of hydrogen-bonded dimers, and to identify those factors which influence dimer structures and stabilities. There is little doubt that our understanding of hydrogen bonding has greatly increased as a result of such investigations.

There are, however, some aspects of hydrogen bonding which by comparison have received little attention. Among these are questions related to ring closure due to the formation of more than one hydrogen bond or through intramolecular hydrogen bonding, and inter- and intramolecular proton transfer, which are important considerations in many chemical and biological systems. An ab initio study of the formation of multiple hydrogen bonds in the guanine-cytosine base pair, and in the cyclic formic acid dimer, has been reported by Clementi, Mehl, and von Niessen.<sup>1</sup> In that study, these authors generated potential curves for the simultaneous transfer of the two hydrogen-bonded protons in formic acid dimer, keeping the  $\text{HCO}_2$  fragments fixed at the experimental geometry. The data which they obtained will be used extensively for comparison with the results of the present study. The same procedure for investigating proton transfer in formic acid dimer was also used by Morokuma, Iwata, and Lathan in studies of symmetric proton transfer in the ground and some low-energy excited electronic states.<sup>2</sup> The formic acid dimer was also studied by Ady and Brickmann, who investigated the rearrangement between the two tautomers, again using the experimental geometry.<sup>3</sup> Ring closure through the formation of pairs of hydrogen bonds in some cyclic dimers has been discussed previously in earlier papers of this series.<sup>4,5</sup> Ring closure through the formation of a symmetric intramolecular hydrogen bond in the hydrogen maleate ion has been examined in ref 2. Finally, the question of whether or not the intramolecular hydrogen bond in  $\beta$ -hydroxyacrolein is symmetric was addressed by Roos et al., who carried out partial geometry optimization of the  $C_s$  and  $C_{2v}$  forms of this molecule.<sup>6</sup>

In this present study, hydrogen bonding in the cyclic formic acid dimer and in  $\beta$ -hydroxyacrolein has been investigated. These two systems present an opportunity to compare ring closure through inter- and intramolecular hydro-

gen bonding, and the energetics of inter- and intramolecular proton transfer. In this study, the structure of the formic acid dimer has been fully optimized, allowing for changes in both inter- and intramolecular coordinates, with the restriction of  $C_{2h}$  symmetry. It is of interest to examine the extent to which changes in intramolecular coordinates are predicted, since in dimers stabilized by the formation of a single hydrogen bond, only small changes in these coordinates have generally been found.<sup>7</sup> In addition, experimental data on the structure and stability of this dimer are available, and therefore comparisons of computed and experimental results may be made. Two different modes of symmetric proton transfer in this dimer have been examined, and corresponding potential curves obtained. These curves are compared to those of ref 1. Intermolecular proton transfer in the formic acid dimer may be compared to intramolecular proton transfer in  $\beta$ -hydroxyacrolein, where fully optimized  $C_s$  and  $C_{2v}$  structures have been determined, and the potential curve has been obtained for the interconversion of these two structures through proton transfer. Experimental data on the enol form of the related  $\beta$ -dicarbonyl compound acetylacetone are available, and comparisons of experimental and theoretical results are made.

### Method and Procedure

**Basis Set.** The wave functions for the monomers and dimers have been expressed as single Slater determinants, constructed from doubly occupied molecular orbitals. Each molecular orbital (MO)  $\psi_i$  is written as a linear combination of atomic basis functions  $\phi_\mu$  (the LCAO approximation)

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}$$

with the expansion coefficients determined by solving the Roothaan equations.<sup>8</sup> The atomic orbital basis set used in this work is the minimal STO-3G basis set with standard scale factors.<sup>9</sup> It has been demonstrated that ab initio MO calculations with the STO-3G basis set are capable of satisfactorily reproducing molecular geometries.<sup>10,11</sup> Moreover, where comparisons with experimental data can be made, it appears that dimer structures and energies are also reasonably reproduced with this basis set, except for an underestimation of the intermolecular distance by about 10%.<sup>12,13</sup> Use of the STO-3G basis set in this study has made tractable the computational task of full geometry optimization of the formic acid dimer and of both the  $C_s$  and  $C_{2v}$  forms of

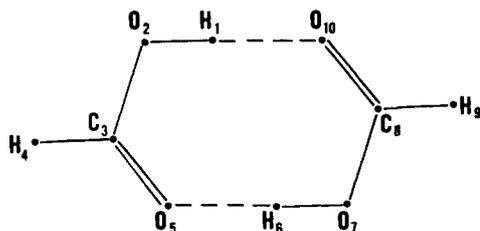


Figure 1. The formic acid dimer.

$\beta$ -hydroxyacrolein. The results obtained with this basis will be compared with those of related studies employing larger atomic orbital basis sets.

**Geometry Optimization.** The optimized STO-3G geometry of formic acid has been reported<sup>11</sup> and used in the initial part of this study in which the dimer geometry was optimized subject to the constraints of  $C_{2h}$  symmetry (which is consistent with experimental data) and rigid monomers. Under these restrictions, only two geometrical parameters, a distance and an angle, remain. Optimization of this dimer was carried out to  $\pm 0.01$  Å in  $R$ , the intermolecular  $O_2-O_{10}$  distance (see Figure 1), and  $\pm 1^\circ$  in  $\theta$ , the  $H_1-O_2-O_{10}$  angle, which measures monomer rotation about an axis perpendicular to the dimer symmetry plane at the hydroxyl oxygen,  $O_2$ . At  $\theta = 0^\circ$ , the  $O_2-H_1$  bond is colinear with the  $O_2-O_{10}$  line, and thus  $\theta$  is a convenient measure of the linearity of the  $O_2-H_1 \cdots O_{10}$  (and by symmetry the  $O_7-H_6 \cdots O_5$ ) hydrogen bond. This dimer was then reoptimized allowing for changes in both inter- and intramolecular coordinates. Geometry optimization was again carried out to  $\pm 0.01$  Å in  $R$  and the intramolecular bond lengths, and to  $\pm 1^\circ$  in  $\theta$  and the intramolecular bond angles, subject to the constraint of  $C_{2h}$  symmetry.

The molecule  $\beta$ -hydroxyacrolein (enolic malondialdehyde) was geometry optimized in two forms. In the first,  $C_s$  symmetry was assumed. Bond lengths were optimized to  $\pm 0.01$  Å, and bond angles to  $\pm 1^\circ$ , except for the angles  $C_3-C_4-H_8$  and  $C_5-C_4-H_8$  (see Figure 2), which were optimized to  $\pm 0.5^\circ$ . In the second form,  $C_{2v}$  symmetry was assumed, and optimization of bond lengths and bond angles was carried out to  $\pm 0.01$  Å and  $\pm 1^\circ$ , respectively. The position of the hydrogen-bonded proton  $H_1$  was optimized to  $\pm 0.01$  Å along the  $C_2$  symmetry axis, measured from the midpoint of the  $O_2-O_6$  line. All calculations were performed in double precision on an IBM 370/145 computer.

## Results and Discussion

**Formic Acid Dimer.** In the formic acid dimer constructed from the rigid optimized monomers (to be called the constrained dimer), optimized values of the intermolecular coordinates  $R$  and  $\theta$  of 2.64 Å and  $1^\circ$ , respectively, were found. Thus, essentially linear  $O-H \cdots O$  hydrogen bonds are predicted. The intermolecular energy of the constrained dimer, computed as the difference between the total dimer energy and the energy of two isolated monomers, is 12.4 kcal, which compares with the experimental value of  $14.8 \pm 0.5$  kcal.<sup>14</sup>

With the constrained dimer as a starting point, the formic acid dimer was reoptimized in all inter- and intramolecular coordinates with the restriction of  $C_{2h}$  symmetry. The structure of this equilibrium dimer (called the fully optimized dimer) is shown in Figure 1, and reported in Table I, along with the experimental structure.<sup>15</sup> In this fully optimized dimer, the intermolecular distance has decreased from the constrained dimer value of 2.64 to 2.54 Å, which is somewhat less than the experimental value of 2.73 Å. The hydrogen bonds in this dimer remain essentially linear, with

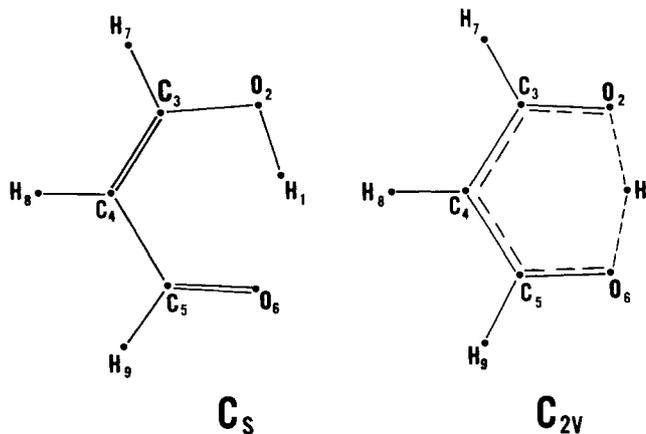


Figure 2.  $C_s$  and  $C_{2v}$  forms of  $\beta$ -hydroxyacrolein.

Table I. Structures and Energies of Formic Acid Dimers

Distances, Å	Constrained dimer <sup>a</sup>	Fully optimized dimer <sup>b</sup>
$C_3-O_5$	1.214	1.23 (1.25 $\pm$ 0.03)
$C_3-O_2$	1.386	1.35 (1.36 $\pm$ 0.04)
$C_3-H_4$	1.104	1.11
$O_2-H_1$	0.991	1.01
$O_2-O_{10}$	2.64	2.54 (2.73 $\pm$ 0.05)
Angles, deg		
$O_5-C_3-H_4$	125.9	122
$O_2-C_3-O_5$	123.7	126 (121. $\pm$ 2.)
$C_3-O_2-H_1$	104.8	108
$\theta$	1	1
Stabilization energy, kcal	12.4	15.1 (14.8 $\pm$ 0.5) <sup>c</sup>

<sup>a</sup> Intramolecular coordinates are those of the optimized monomer, taken from ref 11. <sup>b</sup> Experimental values in parentheses, taken from ref 15. In the fully optimized dimer, the  $O_5-C_3-C_8$  angle has a value of  $58^\circ$ , which is in excellent agreement with the experimental value of  $58^\circ \pm 1^\circ$ . <sup>c</sup> Reference 14.

$\theta$  equal to  $1^\circ$ . The predicted stabilization energy of 15.1 kcal is in excellent agreement with the experimental value of 14.8 kcal. A stabilization energy of 16.2 kcal was obtained in ref 1 with a "9/5 plus polarization" basis set.

It is interesting to examine the changes in the intramolecular coordinates in the equilibrium dimer. As evident from Table I, the optimized monomer carbonyl C-O distance increases from 1.21 to 1.23 Å upon dimer formation, while the C-O single bond distance decreases from 1.39 to 1.35 Å. Since a correlation is generally found between bond distance and bond order, the above changes suggest that the carbonyl C-O bond loses some of its double-bond character, while the C-O single bond gains double-bond character. The change in the double-bond length is less than that in the single bond, which is consistent with the larger force constants for double bonds. The  $O_2-H_1$  bond length in the dimer increases as anticipated from 0.99 to 1.01 Å. These changes in bond distances are also accompanied by changes in bond angles. The more significant of these are the increases in the O-C-O and C-O-H bond angles from 124 and  $105^\circ$  in the monomer, to 126 and  $108^\circ$ , respectively, in the fully optimized dimer. It is important to note that the  $O-H \cdots O$  hydrogen bonds are essentially linear in the constrained dimer, and remain linear in the fully optimized dimer. However, a rather significant result of the changes in the intramolecular coordinates is the reduction of the  $O_2-O_{10}-C_8$  and  $O_7-O_5-C_3$  angles from  $132^\circ$  in the constrained dimer to  $127^\circ$  in the fully optimized dimer. This

**Table II.** Mulliken Gross Electron Populations (Formic Acid)

Atom	Monomer		Constrained dimer		Fully optimized dimer	
	Total	$\pi$	Total	$\pi$	Total	$\pi$
H <sub>1</sub>	0.793		0.746		0.728	
O <sub>2</sub>	8.285	1.879	8.319	1.850	8.327	1.811
C <sub>3</sub>	5.745	0.900	5.726	0.851	5.718	0.838
H <sub>4</sub>	0.793		0.746		0.728	
O <sub>5</sub>	8.251	1.221	8.289	1.299	8.304	1.351

change is in the direction which approaches the idealized value of 120° for a proton acceptor carbonyl group, the value which has been associated with a directed carbonyl lone pair in the general hybridization model for the hydrogen bond.<sup>5</sup> In an absolute sense, the changes in the intramolecular coordinates are small, but they are significant when compared to intramolecular coordinate changes in dimers stabilized by a single hydrogen bond.<sup>7</sup> In the fully optimized dimer, the destabilization of the monomers is compensated by the formation of two stronger hydrogen bonds which result as lone pairs of electrons become more properly oriented for hydrogen bond formation, and the H<sub>1</sub>-O<sub>10</sub> and H<sub>6</sub>-O<sub>5</sub> distances decrease. Even when the intermolecular distance in the fully optimized dimer is lengthened to the experimental distance of 2.73 Å, the resulting dimer has a stabilization energy of 12.8 kcal, and is therefore slightly more stable than the constrained dimer, which has a stabilization energy of 12.4 kcal, at the shorter intermolecular distance of 2.64 Å. Finally, a comparison of the computed and experimental data in Table I shows that the computed structure of the equilibrium dimer is generally in good agreement with available experimental data, except for the usual underestimation of the intermolecular distance.

The total and  $\pi$  electron densities obtained from Mulliken population analyses<sup>16</sup> are reported in Table II. The total electron densities of the hydroxyl and carbonyl oxygen atoms increase in going from monomer, to constrained dimer, to fully optimized dimer, while the electron densities of the hydrogen-bonded protons and of the carbon atoms decrease in the same order. The fact that both the carbonyl and hydroxyl oxygens gain electron density may be somewhat surprising at first, especially when considered in light of the changes in the C-O bond distances in the fully optimized dimer. However, the changes in the oxygen electron densities are quite consistent with electron density changes observed previously for atoms X and Y which form the X-H...Y hydrogen bond,<sup>5</sup> and occur through distinctly different mechanisms. As part of the proton donor group, the hydroxyl oxygen (X) experiences an increase in negative charge due to an increase in electron density in the  $\sigma$  electron system, produced primarily by electron flow through the O-H bond toward the hydroxyl oxygen. On the other hand, the increase in the electron density of the proton acceptor carbonyl oxygen (Y) is due to an increased polarization of the  $\pi$  electrons toward this oxygen. This increased polarization compensates for the  $\sigma$  electron density loss at this atom.

**$\beta$ -Hydroxyacrolein.** A relatively simple system in which intramolecular hydrogen bonding may occur is  $\beta$ -hydroxyacrolein (the enol form of malondialdehyde). The question of whether the proton is symmetrically positioned between the two oxygen atoms in this molecule has been addressed in ref 6, where ab initio calculations with partial geometry optimization of the  $C_s$  and  $C_{2v}$  forms have been reported, using a small Gaussian basis set. In that study, it was concluded that the  $C_s$  form is more stable than the  $C_{2v}$  form by approximately 11.5 kcal. Unfortunately, no structural data

**Table III.** Structures of the  $C_s$  and  $C_{2v}$  Forms of  $\beta$ -Hydroxyacrolein

Distances, Å	$C_s$	$C_{2v}$ <sup>a</sup>
O <sub>2</sub> -H <sub>1</sub>	1.00	1.168 <sup>b</sup> (1.26)
O <sub>2</sub> -C <sub>3</sub>	1.36	1.29 (1.287)
C <sub>3</sub> -C <sub>4</sub>	1.33	1.40 (1.405)
C <sub>4</sub> -C <sub>5</sub>	1.48	1.40
C <sub>5</sub> -O <sub>6</sub>	1.23	1.29
C <sub>3</sub> -H <sub>7</sub>	1.09	1.10
C <sub>4</sub> -H <sub>8</sub>	1.08	1.07
C <sub>5</sub> -H <sub>9</sub>	1.10	1.10
Angles, deg		
H <sub>1</sub> -O <sub>2</sub> -C <sub>3</sub>	104	102.4 <sup>b</sup> (88.4)
O <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	125	121 (123.2)
H <sub>7</sub> -C <sub>3</sub> -C <sub>4</sub>	122	121
C <sub>3</sub> -C <sub>4</sub> -H <sub>8</sub>	121.5 <sup>c</sup>	122.5 (120.9) <sup>d</sup>
H <sub>8</sub> -C <sub>4</sub> -C <sub>5</sub>	119.5 <sup>c</sup>	122.5 (120.9) <sup>d</sup>
C <sub>4</sub> -C <sub>5</sub> -H <sub>9</sub>	117	121
C <sub>4</sub> -C <sub>5</sub> -O <sub>6</sub>	122	121

<sup>a</sup> Experimental data for acetylacetone given in parentheses. <sup>b</sup> In the  $C_{2v}$  form, the distance from H<sub>1</sub> to the O<sub>2</sub>-O<sub>6</sub> line has an optimized value of 0.22 Å. <sup>c</sup> In the  $C_s$  form, the C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub> angle is 119°. <sup>d</sup> In the  $C_{2v}$  form, the C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub> angle was optimized to  $\pm 1^\circ$ . The computed value is 115°, compared to the experimental value of 118.3°.

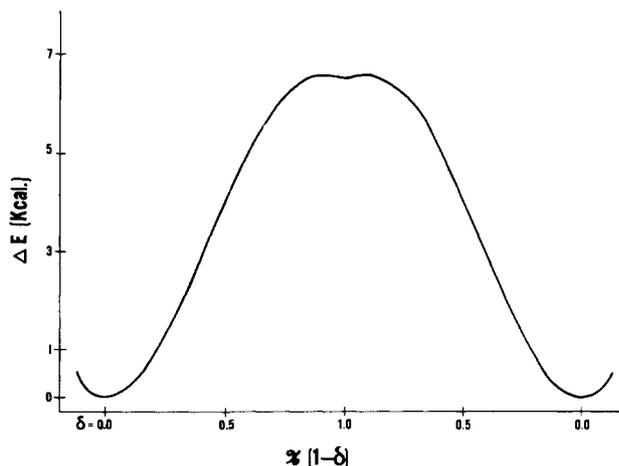
for  $\beta$ -hydroxyacrolein exist, although structural data for acetylacetone and other related  $\beta$ -dicarbonyls have been reported, and are summarized in ref 6. Electron diffraction studies of acetylacetone suggest that this compound has  $C_{2v}$  symmetry.<sup>17</sup> The experimentally determined values of intramolecular coordinates which correspond to intramolecular coordinates in  $\beta$ -hydroxyacrolein are given in parentheses in Table III. However, an ir study of the same compound has suggested that acetylacetone does not have  $C_{2v}$  symmetry.<sup>18</sup> Thus, the equilibrium structure of this compound has not been unequivocally established.

In this present study, both the  $C_s$  and  $C_{2v}$  forms of  $\beta$ -hydroxyacrolein (see Figure 2) have been geometry optimized, and the optimized structures are reported in Table III. The optimized value of the O-H bond length in the less stable  $C_{2v}$  form of  $\beta$ -hydroxyacrolein is 1.17 Å, which is longer than the O<sub>2</sub>-H<sub>1</sub> covalent bond distance of 1.00 Å in the  $C_s$  form, but significantly shorter than the 1.65 Å distance between H<sub>1</sub> and O<sub>6</sub>. The O-O distance decreases from its value of 2.56 Å in the  $C_s$  form to 2.29 Å in the  $C_{2v}$  form. These changes are consistent with structural changes which would be anticipated for the formation of a symmetric hydrogen bond in the  $C_{2v}$  form. It is interesting to note that the optimized values of the C-O and C-C bond distances in the  $C_{2v}$  form of  $\beta$ -hydroxyacrolein are the mean values of the corresponding C-O and C-C single- and double-bond distances in the  $C_s$  form. As shown in Table III, the optimized values of the intramolecular coordinates in the  $C_{2v}$  form of  $\beta$ -hydroxyacrolein are in good agreement with the electron diffraction results for corresponding bond lengths and bond angles in the enol form of acetylacetone, except for the O-H distance and the H-O-C angle. From the experimental data it was concluded that the proton lies along the O-O line, but the calculations predict that the proton is displaced approximately 0.22 Å from that line, hence the difference between the computed and experimental values of these two coordinates.

The STO-3G calculations which have been performed in this study predict that the  $C_s$  form of  $\beta$ -hydroxyacrolein is more stable than the  $C_{2v}$  form, but only by 6.6 kcal. Thus, both this study and ref 6 support the greater stability of the  $C_s$  form. However, these results have been obtained with small basis sets, and neither study has taken into account the correlation energy corrections, which would be greater

Table IV. Mulliken Gross Electron Populations ( $\beta$ -Hydroxyacrolein)

Atom	$C_s$		$C_{2v}$	
	Total	$\pi$	Total	$\pi$
H <sub>1</sub>	0.742		0.691	
O <sub>2</sub>	8.301	1.843	8.315	1.563
C <sub>3</sub>	5.896	0.894	5.846	0.796
C <sub>4</sub>	6.161	1.179	6.203	1.282
C <sub>5</sub>	5.854	0.860	5.846	0.796
O <sub>6</sub>	8.254	1.224	8.315	1.563

Figure 3. Potential curve for proton transfer in  $\beta$ -hydroxyacrolein.

in the  $C_{2v}$  form. Since the difference in the stabilities of the two forms is small, it may well be that the  $C_s$  and  $C_{2v}$  forms are easily interconverted, and that the equilibrium structure may also depend on the physical state. These features would account for the differences in the symmetry assignments which have been given to the equilibrium structures of the enol forms of related  $\beta$ -dicarbonyl compounds.

The total and  $\pi$  electron densities in the  $C_s$  and  $C_{2v}$  forms of  $\beta$ -hydroxyacrolein are reported in Table IV. Atoms O<sub>2</sub>, C<sub>4</sub>, and O<sub>6</sub>, which are negatively charged in the  $C_s$  form, become more negatively charged in the  $C_{2v}$  form. The carbon atoms C<sub>3</sub> and C<sub>5</sub> become more positively charged in the  $C_{2v}$  form, as does the hydrogen-bonded proton H<sub>1</sub>. A rather dramatic redistribution of  $\pi$  electron density occurs as the  $C_s$  form is converted to the  $C_{2v}$  form. The hydroxyl oxygen atom O<sub>2</sub> in the  $C_s$  form loses  $\pi$  electron density in the  $C_{2v}$  form, while the carbonyl oxygen O<sub>6</sub> of the  $C_s$  form gains  $\pi$  electron density. The  $\pi$  density at each oxygen in the  $C_{2v}$  form approaches the mean  $\pi$  density of the O<sub>2</sub> and O<sub>6</sub> atoms in the  $C_s$  form. It is evident from these data that the  $\pi$  electron density changes at the oxygens do not parallel the changes in total electron density as the  $C_s$  structure is converted to the  $C_{2v}$ .

**Proton Transfer.** Proton transfer upon hydrogen-bond formation may occur in  $\beta$ -hydroxyacrolein as the  $C_s$  structure in which O<sub>2</sub> is the hydroxyl oxygen is converted to a second equivalent  $C_s$  structure in which O<sub>6</sub> becomes the hydroxyl oxygen and O<sub>2</sub> the carbonyl oxygen. The intermediate is the  $C_{2v}$  form. The potential curve corresponding to this conversion is shown in Figure 3. The abscissa  $\chi(1-\delta)$  is a single coordinate which smoothly converts the  $C_s$  form ( $\delta = 0.0$ ) to the  $C_{2v}$  form ( $\delta = 1.0$ ). The barrier to proton transfer (6.6 kcal) is of course the energy difference between these two forms. It is interesting to note that along this coordinate, a very shallow minimum surrounds the optimized  $C_{2v}$  form. The determination of whether or not this is a true minimum on the surface, or only a saddle point,

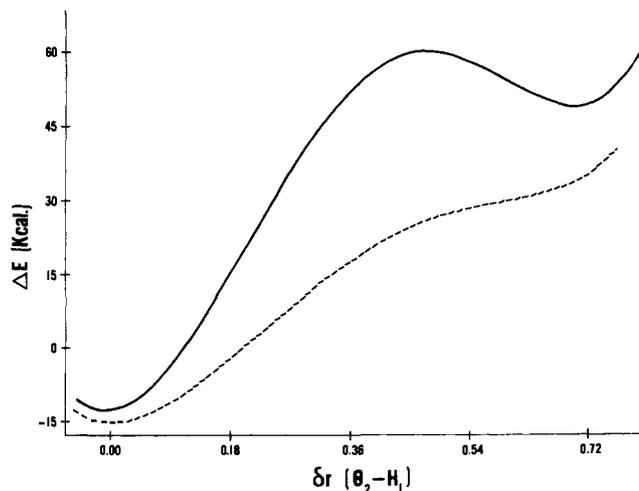


Figure 4. Potential curves for the symmetric transfer of hydrogen-bonded protons in formic acid dimer. HCO<sub>2</sub> fragments are held rigid, and  $C_{2h}$  symmetry maintained. Solid curve corresponds to an intermolecular distance of 2.73 Å, and dotted curve to a distance of 2.54 Å. (Limiting case I.)

would require a more complete investigation of the potential surface.

Intramolecular proton transfer in  $\beta$ -hydroxyacrolein may be compared with intermolecular proton transfer in formic acid dimer. It has been fairly well established that the transfer of a single proton in formic acid dimer does not give rise to a stable ion pair (the potential curve has only a single minimum),<sup>1</sup> and this process will not be investigated here. Rather, proton transfer in formic acid will be examined as the symmetric transfer of both hydrogen-bonded protons, H<sub>1</sub> to O<sub>10</sub>, and H<sub>6</sub> to O<sub>5</sub>. It is reasonable to expect that such a process would be accompanied by changes in both inter- and intramolecular coordinates in the dimer. However, the task of determining the optimal pathway for proton transfer on this multidimensional surface is a computationally unfeasible one. Therefore, two limiting cases will be considered, with (case I) and without (case II) monomer relaxation.

In the first case, proton transfer involves a simple coordinated motion of H<sub>1</sub> from O<sub>2</sub> to O<sub>10</sub>, and H<sub>6</sub> from O<sub>7</sub> to O<sub>5</sub>. For this process,  $\theta$  has been set to 0°, so that proton motion is along the O-O lines, the remaining HCO<sub>2</sub> fragments have been held rigid at their computed equilibrium positions, and  $C_{2h}$  symmetry has been maintained. It is important to note that the potential curve for this process is strongly dependent on the distance between monomers. Therefore, curves have been generated at the computed equilibrium intermolecular distance, and at the experimental O-O distance, and are shown in Figure 4. Corresponding potential curves have been reported in ref 1 and 2. As shown in Figure 4, the potential curve for symmetric proton transfer at the computed equilibrium distance of 2.54 Å exhibits only a single minimum. However, when the intermolecular distance is changed to the experimental O-O distance, the potential curve does exhibit a double minimum. It is informative to examine these results in light of the results obtained in ref 1. Clementi et al. found that the potential curve for symmetric proton transfer in formic acid dimer possessed a single minimum (but with a definite inflection point) when computed with a small 7/3 basis set. However, when larger basis sets (9/5 and 9/5 plus polarization functions) were used for the calculations, curves with double minima were produced at the experimental O-O distance. Morokuma also showed that an augmented "STO-3G + p" basis set produced a double minimum potential

curve for proton transfer, again at the experimental distance.<sup>2</sup> This present study indicates that the minimal STO-3G basis set, unlike the small 7/3 Gaussian basis, does predict a double minimum in the potential curve for proton transfer in formic acid dimer at the experimental distance. With the 9/5 basis set, a barrier to proton transfer of 43 kcal and a depth of the second minimum of 13 kcal were computed. The 9/5 basis with polarization functions gave a barrier of 51 kcal and a depth of the second minimum of 15 kcal. With both basis sets, the potential maximum occurred at an O<sub>2</sub>-H<sub>1</sub> distance between 1.43 and 1.48 Å, and the second minimum was found at an O<sub>2</sub>-H<sub>1</sub> distance of 1.69 Å. With the STO-3G basis set, the predicted barrier to proton transfer is 73 kcal at an O<sub>2</sub>-H<sub>1</sub> distance of 1.48 Å. The second minimum has a depth of 11 kcal at an O<sub>2</sub>-H<sub>1</sub> distance of 1.69 Å. These results therefore are qualitatively similar to those obtained in ref 1 with much larger basis sets, although they are quantitatively different since the STO-3G basis set predicts a larger barrier to proton transfer and a more shallow second minimum. Since only a single minimum appears in the potential curve at the optimized O-O distance, it should be emphasized that the nature of this curve depends not only on the basis set, as shown in ref 1, but also on the intermolecular distance.<sup>19</sup> It is apparent, therefore, that although the computed structure of the formic acid dimer and the computed dimer energy obtained with the STO-3G basis set are in good agreement with experimental values, the underestimation of the O-O distance in the equilibrium dimer has a profound effect on the nature of the potential curve for symmetric proton transfer.

In the second limiting case (II), the symmetric transfer of H<sub>1</sub> and H<sub>6</sub> is accompanied by total inversion of the dimer structure. For this process, the proton motion is once again confined to the O<sub>2</sub>-O<sub>10</sub> and O<sub>5</sub>-O<sub>7</sub> lines ( $\theta$  has been set to 0°). As the protons move, all intramolecular coordinates change, and C<sub>2h</sub> symmetry is maintained. When proton transfer has been completed, a new structure results which is equivalent to the original. In the new structure, C<sub>3</sub>-O<sub>2</sub> is the carbonyl group, and atoms C<sub>3</sub> and O<sub>5</sub> are singly bonded. H<sub>1</sub> is covalently bonded to O<sub>10</sub> and hydrogen bonded to O<sub>2</sub>. In Figure 5, the inversion coordinate  $\chi(1-\delta)$  is the single coordinate along which the formic acid dimer is transformed from the original dimer ( $\delta = 0.0$ ) to a second equivalent dimer ( $\delta = 1.0$ ) through an intermediate of D<sub>2h</sub> symmetry ( $\delta = 1.0$ ). This process of proton transfer is similar to the process of intramolecular proton transfer in  $\beta$ -hydroxyacrolein. The potential curves for proton transfer through inversion of the dimer structure have also been obtained at the computed intermolecular distance of 2.54 Å and at the experimental distance of 2.73 Å, and are shown in Figure 5. It is obvious that the barrier to proton transfer in this case (II) is also distance dependent. At  $R$  equal to 2.54 Å, a barrier of 23 kcal is predicted, while at  $R$  equal to 2.73 Å, the barrier has increased to 56 kcal. Thus, the shorter intermolecular distance is more conducive to proton transfer through inversion of the dimer structure. In ref 3, the computed barrier for a similar process of proton transfer was 43 kcal, relative to the energy of the dimer at its experimental geometry. This barrier was also found to be lower than the barrier to proton transfer involving the motion of hydrogen atoms only.

The results of this work are in agreement with earlier studies in suggesting that simultaneous transfer of a pair of hydrogen-bonded protons (case I) gives rise to potential curves which most probably possess double minima. The height of the barrier to proton transfer and the depth of the secondary minimum are dependent on the intermolecular distance. Indeed, at short intermolecular distances, the second minimum may even disappear. The fact that the barrier

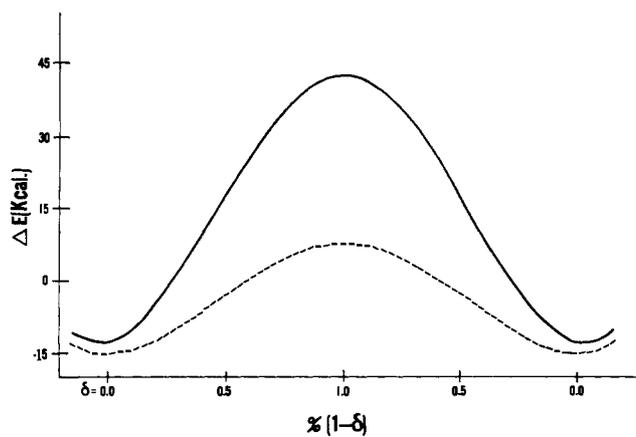


Figure 5. Potential curves for symmetric transfer of hydrogen-bonded protons through inversion of the formic acid dimer. Solid curve corresponds to an intermolecular distance of 2.73 Å, and dotted curve to a distance of 2.54 Å. (Limiting case II.)

to proton transfer through structural inversion (case II) is lower than the barrier to simple proton transfer (case I), and that the former barrier may be reduced as the intermolecular distance decreases, indicates that changes in both inter- and intramolecular coordinates would occur during such a concerted reaction. Because of the level of treatment in this study and the underestimation of the intermolecular distance, no attempt has been made to optimize the intermolecular distance in the D<sub>2h</sub> structure, or to quantitatively estimate populations of dimer vibrational states. However, the results which have been obtained suggest qualitatively that the barrier to proton transfer through structural inversion would be further reduced if proton transfer occurred during a vibration in which the intermolecular distance contracted.

The implications which these results have in other more complex systems are noteworthy. The probable existence of double minima in potential curves for simple proton transfer in a pair of hydrogen bonds (case I) may be important in systems where inversion is not possible due to structural rigidity, or for proton tunneling. This latter phenomenon was originally proposed by Löwdin as a possible mechanism for proton transfer in biological systems.<sup>20</sup> For simple isolated cyclic dimers such as formic acid, these results suggest that in a concerted reaction, proton transfer accompanied by structural inversion (case II) is more favorable than simple proton transfer (case I) followed by vibrational relaxation.

### Summary

Ab initio SCF calculations with a minimal STO-3G basis set have been performed in this study of hydrogen bonding in formic acid dimer and  $\beta$ -hydroxyacrolein. The computed equilibrium structure of the formic acid dimer is in good agreement with the experimental structure, except for an underestimation of the intermolecular distance. The changes in the intramolecular coordinates which occur upon dimer formation are small in an absolute sense, but they are significantly larger than coordinate changes in dimers stabilized by a single hydrogen bond. The changes which occur maintain the linearity of the O-H...O hydrogen bonds, decrease the distance between proton and proton-acceptor atom, and provide for lone pairs of electrons which are more properly oriented for hydrogen bonding. These changes result in the formation of two stronger hydrogen bonds, thereby compensating for monomer destabilization. The computed dimer energy of 15.1 kcal is in agreement with the experimental stabilization energy of 14.8 kcal.

Optimized structures have also been computed for the  $C_s$  and  $C_{2v}$  forms of  $\beta$ -hydroxyacrolein. The calculations predict that the  $C_s$  form is more stable than the  $C_{2v}$  form, but by only 6.6 kcal. Since the energy difference between these two forms is small, it is reasonable to suggest that the equilibrium structures of this and related compounds may vary with physical state. Intramolecular proton transfer may easily occur leading to the conversion of one equivalent  $C_s$  form of  $\beta$ -hydroxyacrolein to the other, through an intermediate of  $C_{2v}$  symmetry. These features may account for the discrepancies in the symmetry assignments which have been given to structures of related enolic  $\beta$ -dicarbonyl compounds.

Two limiting cases of proton transfer in formic acid dimer have also been investigated. In the first case, symmetric transfer of both hydrogen-bonded protons occurs while the  $HCO_2$  fragments remain rigid. This process gives rise to potential curves, the characteristics of which depend on the intermolecular distance. At the computed equilibrium dimer distance, this curve possesses only a single minimum. However, at the experimental intermolecular distance, the potential curve for this process of proton transfer exhibits a double minimum, in agreement with the results of other studies which employed larger basis sets. It is obvious that the underestimation of the intermolecular distance with the STO-3G basis set is critical to the problem of proton transfer.

In the second case, proton transfer occurs in the formic acid dimer through inversion of the dimer structure. The barrier to this process is lowered as the intermolecular distance is reduced from the experimental distance to the computed equilibrium distance. Since, even at the experimental intermolecular distance, the barrier to proton transfer in this case is lower than it is in the first case, the approximation of rigid  $HCO_2$  fragments during proton transfer is not a realistic one. The results of this study suggest that in a concerted reaction, proton transfer accompanied by struc-

tural inversion is more favorable than simple proton transfer followed by vibrational relaxation.

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## Comparison of Equilibrium Reactions in the Gaseous and Liquid Phases. A New, Improved Theoretical Estimate

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**Abstract:** We have studied available data on four selected simple chemical equilibria: (1) cyclopentadiene  $\rightleftharpoons$  dicyclopentadiene, (2) ethanol + acetic acid  $\rightleftharpoons$  ethyl acetate + water, (3)  $NO_2 \rightleftharpoons N_2O_4$ , and (4) norbornene  $\rightleftharpoons$  nortricyclene. The enthalpy and entropy changes of each component on proceeding from the gas phase to the liquid phase were calculated with an equation that includes heat capacity corrections, but requires only the heat of vaporization, the molar volume, and the normal boiling point of each component. The agreement with experimental results in the liquid phase is improved appreciably over past calculations and was reasonable:  $\Delta G_r^\circ$  to within 1.5 kcal and  $K_{eq}$  to a factor of 10.

Recently Patrick<sup>1</sup> and Benson and Golden<sup>2</sup> published analyses of relationships expected between gas-phase and liquid-phase rates and equilibria. These followed earlier treatments of the subject by Martin,<sup>3</sup> Moelwyn-Hughes,<sup>4</sup> and Mayo.<sup>5</sup> In this paper we wish to examine certain equilibria for which enough data are available or calculable

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with sufficient accuracy to make a detailed analysis possible.

## Results and Discussion

The general form for our calculations is the thermodynamic cycle shown in Scheme I, below. Reagents at a standard state concentration of 1 M in the gas phase were transformed to a liquid concentration of 1 M through discrete