Short-lived Subtle Bond of Formic Acid

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Abstract: *The subtle bond between oxygen atom and hydrogen atom of formic acid is presented.*

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1. INTRODUCTION

In previous papers [1],[2]the subtle bond was presented on the example of equal atoms of the same molecule. In this paper we will try to include the unequal adjacent atoms, too, and explain the topicon the example of formic acid.

2. THE SUBTLE BOND BETWEEN ADJACENT ATOMS
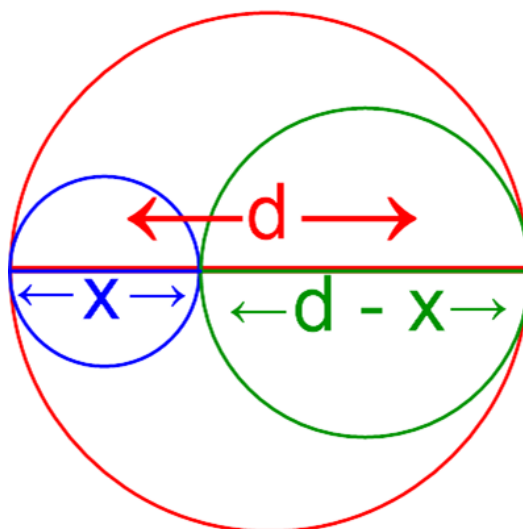
Figure1. *Individual ant bonding orbits inside common bonding orbit*

Subtle bond is a lasting attraction on the double surface between the adjacent atoms on the distance d(diameter of red circle) providing the movement of pair of electrons on one half of more stable common subtle bonding orbit of length $\frac{s(\pi d)}{2}$ (half of red circle) and cancelling the movement on one half of two less stable individual subtle anti bonding orbits of length $\frac{s(\pi x)+s(\pi(d-x))}{2}$ (half of blue and half of green circle) between adjacent atoms. Since on the double surface the subtle bonding length $s_{bonding}$ (half of red circle) is always shorter than the subtle anti-bonding length$s_{antibonding}$ (half of blue and half of green circle)regardless of the size ratio of the two inscribed inner circles:

$$s_{bonding} \ = \frac{s(\pi d)}{2} < s_{antibonding} \ = \frac{s(\pi x) + s(\pi(d - x))}{2}, \ for \ 0 < x \le \frac{d}{2}. \tag{1}$$

And the corresponding subtle bonding energy $E_{bonding}$ is lower than the subtle anti-bonding energy$E_{antibonding}$:

$$E_{bonding} \ = -\frac{Ry\alpha^{-1}}{\frac{s(\pi d)}{2}} < E_{antibonding} \ = -\frac{Ry\alpha^{-1}}{\frac{s(\pi x)+s(\pi(d-x))}{2}}, \ for \ 0 < x \le \frac{d}{2}. \tag{2}$$

So, at forming a subtle bonding the energy is released (signed negative):

$$\Delta E_{forming} = E_{bonding} - E_{antibonding} = Ry.\,\alpha^{-1}\left(-\frac{1}{\frac{s(\pi d)}{2}} + \frac{1}{\frac{s(\pi x)+s(\pi(d-x))}{2}}\right) < 0. \qquad (3)$$

And for disconnecting the subtle bonding (forming the anti-bonding) the energy is consumed (signed positive):

$$\Delta E_{disconnecting} = -\Delta E_{forming} > 0. \qquad (4)$$

It can be seen that the length of less stable subtle anti-bonding orbits is the shortest when one inner orbit is missing and the remaining inner circle covers the outer one, since at $x = 0$ holds:

$$\frac{s(\pi x) + s(\pi(d-x))}{2} = \frac{0 + s(\pi d)}{2} = \frac{s(\pi d)}{2}. \qquad (5)$$

And the length of less stable subtle anti-bonding orbits is the longest when both inner orbits are equal, since at $x = \frac{d}{2}$ holds:

$$\frac{s(\pi x) + s(\pi(d-x))}{2} = \frac{s(\pi\frac{d}{2}) + s(\pi\frac{d}{2})}{2} = \frac{2s(\pi\frac{d}{2})}{2} = s\left(\pi\frac{d}{2}\right). \qquad (6)$$

Then the relation (1) becomes:

$$s_{bonding} = \frac{s(\pi d)}{2} < s_{antibonding} = s\left(\frac{\pi d}{2}\right). \qquad (7)$$

The relation (2) becomes

$$E_{bonding} = -\frac{Ry\alpha^{-1}}{\frac{s(\pi d)}{2}} < E_{antibonding} = -\frac{Ry\alpha^{-1}}{s\left(\frac{\pi d}{2}\right)}. \qquad (8)$$

And the relation (3) is

$$\Delta E_{forming} = E_{bonding} - E_{antibonding} = Ry.\,\alpha^{-1}\left(-\frac{1}{\frac{s(\pi d)}{2}} + \frac{1}{s\left(\frac{\pi d}{2}\right)}\right) < 0. \qquad (9)$$

As already seen in reference[1]for the energy of forming subtle bonding between equal atoms on the example of fluorine atoms of carbon tetra fluoride.

The relation (3) for the energy of forming subtle bonding between unequal atoms can be written also in the next way:

$$\Delta E_{forming} = E_{bonding} - E_{antibonding} = Ry.\,\alpha^{-1}\left(-\frac{1}{\frac{s(n)}{2}} + \frac{1}{\frac{s(n_1)+s(n_2)}{2}}\right) < 0. \qquad (10)$$

Where n is the number of the outer common orbit, and n_1 and n_2 are the numbers of inner individual orbitsof any size. With the restriction that only natural numbers and their half valuesn $= \frac{1}{2}$, $1, 1\frac{1}{2}$, $2, 2\frac{1}{2}$, $3, 3\frac{1}{2}$ ...come into consideration. Quartile values are of short breath due to the annihilation of orbit after doubling on the account of available kinetic energy. Let's introduce the theory on the example of the oxygen-hydrogen bond of formic acid.
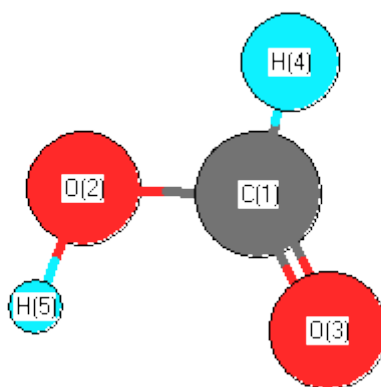
3. THE FORMIC ACID STRUCTURE

The structure of formic acid monomerH_2CO_2 and its cyclic dimer $H_4C_2O_4$ is presented in Figure 2:
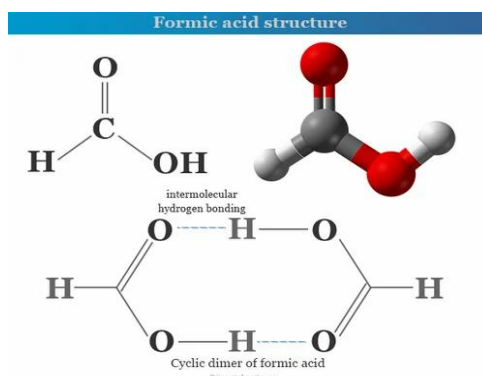
Figure2. *Formic acid structure[3]*

We will pay attention to the intermolecular $O - H$ bond present in both forms of formic acid.

4. THE FORMIC ACID MONOMER

Figure3. *The formic acid monomer[4].*

Let's take the needed data from reference[4].

4.1. The Subtle Bonding of Monomer

The distance between oxygen atom O (signed O(2)) and hydrogen atom H (signed (H5)) in formic acid monomer H_2CO_2 is $d = 97.20\ pm$ which expressed in Compton wavelengths of the electron equals $d = 40.061\lambda_e$. The orbit length is π- times longer yielding $s_{OH} = 125.855\ \lambda_e$. Its doubled value $2s_{OH} = 251.710\ \lambda_e$ is far from the geometrically stable orbit length $s(251\ \lambda_e) = 251,020\ \lambda_e$. The bonding orbit (red circle in Figure 1) in comparison with the anti-bonding orbits (blue circle and green circle in Figure 1) is energetically more stable (3) but geometrically unfavourable. The subtle bonding between the oxygen atom and hydrogen atom in the formic acid monomer is thus very short-lived.

4.2. The Subtle Anti-bonding of Monomer

The length of anti-bonding orbits $s_{OH} = s_O + s_H$ between oxygen atom O and hydrogen atom H depends on the electronegativity e_O and e_H of individual atoms [5]. We have deal with an inverse proportion - higher the electro negativity of the atom closer the electrons to the atom- as written below:

$$\frac{s(n_2)}{s(n_1)} = \frac{s_H}{s_O} = \frac{e_O}{e_H} = \frac{3.44}{2.20} = \frac{\frac{3.44}{2.2+3.44}}{\frac{2.20}{2.2+3.44}} = \frac{\frac{3.44}{5.64}}{\frac{2.20}{5.64}} = \frac{0.61\ s_{OH}}{0.39\ s_{OH}}. \tag{11a}$$

At $s(n) = s_{OH} = 125.855\lambda_e \lambda_e$ (See section 4.1) we can write for oxygen individual orbit s_O:

$$s(n_1) = s_O = 0.39\ s_{OH} = 49.083\ \lambda_e\ (blue\ circle\ in\ Figure\ 1). \tag{11b}$$

And the length of hydrogen anti-bonding orbit $s_2 = s_H$ is according to (11c) the next:

$$s(n_2) = s_H = 0.61\, s_{OH} = 76.772\, \lambda_e\, (green\ circle\ in\ Figure\ 1). \tag{11c}$$

The length of oxygen anti-bonding orbit $s_O = 49.083\, \lambda_e$ is close to thegeometrically stable orbit length $s(49\, \lambda_e) = 49.100\, \lambda_e$. But the doubled value of hydrogen anti-bonding orbit length $2s_H = 153,544\, \lambda_e$ is close tothegeometrically unstable orbit length $s(153,5\, \lambda_e) = 153.532\, \lambda_e$. So, the oxygen anti-bonding orbit at the formic acid monomer is geometrically preferable what leads to free proton capable to react with the oxygen of adjacent molecule. The concerned subtle OH bond of formic acid monomer is thus unstable from energetic as well as geometric point of view.

5. THE FORMIC ACID CYCLIC DIMER
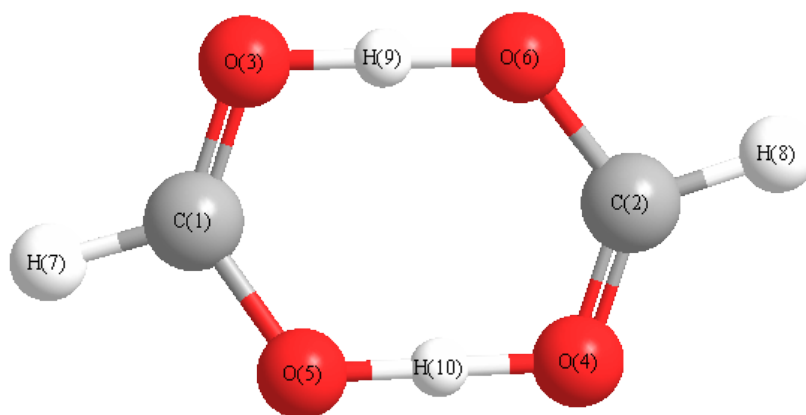
Figure4. *The formic acid cyclic dimer[4]*

Let's take the needed data again from reference [4].

5.1. The Subtle Bonding of Dimer

The distance between oxygen atom O(signed O (5)) and hydrogen atom$H$(signed (H10)) in cyclic formic acid dimer $H_4C_2O_4$ is now $d = 103.30\, pm$ which expressed in Compton wavelengths of the electronequals $d = 42.575\, \lambda_e$. The orbit length is π- times longer yielding$s_{OH} = 133.753\, \lambda_e$. Its doubled value $2s_{OH} = 267,506\, \lambda_e$ is close to the geometrically unstable orbit length $s(267.5\, \lambda_e) = 267.518\, \lambda_e$. The bonding orbit (red circle in Figure 1) in comparison with the anti-bonding orbits (blue circle and green circle in Figure 1) is energetically more stable (3) but geometrically unfavourable. The subtle bonding between the oxygen atom and hydrogen atom in the formic acid cyclic dimer is thus very short-lived.

5.2. The Subtle Anti-bonding of Dimer

The length of anti-bonding orbits s_{OH} between oxygen atom$O$ and hydrogen atom$H$ is according to the previous section 5.1 approximately the next:

$$s(n) = s_{OH} = s_O + s_H = 133.753\lambda_e. \tag{12a}$$

The length of oxygen anti-bonding orbit $s_1 = s_O$ is according to (11b) the next:

$$s(n_1) = s_O = 0.39\, s_{OH} = 52.164\, \lambda_e\, (blue\ circle\ in\ Figure\ 1). \tag{12b}$$

And the length of hydrogen anti-bonding orbit $s_2 = s_H$ is according to (11c) the next:

$$s(n_2) = s_H = 0.61\, s_{OH} = 81.589\, \lambda_e\, (green\ circle\ in\ Figure\ 1). \tag{12c}$$

The length of oxygen anti-bonding orbit $s_O = 52.164\, \lambda_e$ is close to thegeometrically stable orbit length $s(52\, \lambda_e) = 52.095\, \lambda_e$. And the doubled value of hydrogen anti-bonding orbit length $2s_H = 163,178\, \lambda_e$ is close tothegeometrically stable orbit length $s(163\, \lambda_e) = 163.030\, \lambda_e$. So, energetically less stable anti-bonding orbits (blue circle and green circle in Figure 1) are both geometrically more favourable than the bonding orbit (red circle in Figure 1).

6. THE FORMIC ACID CYCLIC DIMER AT SADDLE POINT

Key geometrical parameters are given now from reference [6] and presented in Figure5.[6]
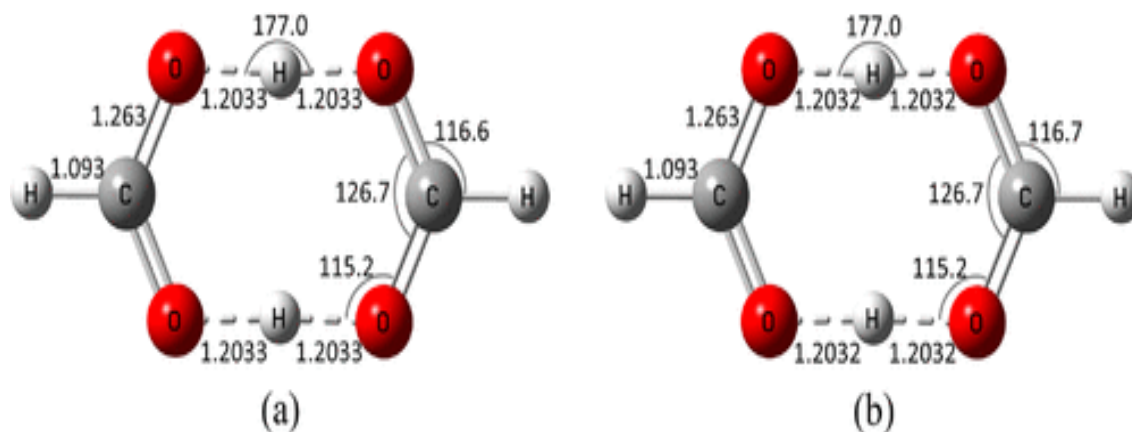
Figure5. *Key geometrical parameters of the saddle point of the formic acid cyclic dimer[6]*

The data [6] are given from the DLPNO-CCSD(T)/AVTZ calculations (a) and the NN PES (b).Bond lengths are given in angstroms and angles in degrees.

6.1 The Subtle Bonding of Dimer at Saddle Point

Regardless of the intermolecular or intra molecular origin of the bond between oxygen atom$O$ and hydrogen atom$H$, its length is at the saddle point the same. The middle value of given distance is $d = 120.325\ pm$(Figure 4) which expressed in Compton wavelengths of the electron equals $d = 49,592\ \lambda_e$.The associated orbit is π- times longer yielding$s_{OH} = 155.797\ \lambda_e$. Its doubled value of $2s_{OH} = 311,594\ \lambda_e$ is close to the geometrically unstable orbit length$s(311.5\ \lambda_e) = 311,516\ \lambda_e$. Thus, the bonding orbit (red circle in Figure 1) in comparison with the anti-bonding orbits (blue circle and green circle in Figure 1) is energetically more stable (3) but geometrically unfavourable. The subtle bonding between the oxygen atom and hydrogen atom in the formic acid cyclic dimer at saddle point is thus very short-lived.

6.2 The Subtle Anti-Bonding of Dimer at Saddle Point

The length of anti-bonding orbits s_{OH} between oxygen O and hydrogen$H$ is according to the previous section 6.1 approximately the next:

$$s(n) = s_{OH} = s_O + s_H = 155.797\ \lambda_e. \tag{13a}$$

The length of oxygen anti-bonding orbit $s_1 = s_O$ is according to (11b) the next:

$$s(n_1) = s_O = 0.39\ s_{OH} = 60,761\ \lambda_e\ (blue\ circle\ in\ Figure\ 1). \tag{13b}$$

And the length of hydrogen anti-bonding orbit $s_2 = s_H$ is according to (11c) the next:

$$s(n_2) = s_H = 0.61\ s_{OH} = 95,036\ \lambda_e\ (green\ circle\ in\ Figure\ 1). \tag{13c}$$

The length of hydrogen anti-bonding orbit $s_H = 95,036\ \lambda_e$is close to the geometrically stable orbit length $s(95\ \lambda_e) = 95.052\ \lambda_e$. But the doubled length of oxygen anti-bonding orbit $2s_O = 121.522\ \lambda_e$ is close to thegeometrically unstable orbit length $s(121.5\ \lambda_e) = 121.541\ \lambda_e$. The hydrogen anti-bonding orbit at the saddle point of the formic acid cyclic dimer is geometrically preferable what reduces the proton's ability to react with the oxygen of an adjacent molecule. The concerned saddle point is thus unstable from energetic as well as geometric point of view.

7. CONCLUSION

Due to the double surface characteristics the covalent OH distance of formic acid cyclic dimer $H_4C_2O_4$ with valueof $103.30\ pm$ is more favourable than that oneat saddle point with the value of$120.325\ pm$ as wellthan that one of formic acid monomer with value of $97.20\ pm$.

DEDICATION

To the impressionist painter Ivan Grohar for his painting The Sower which should be viewed from the right distance
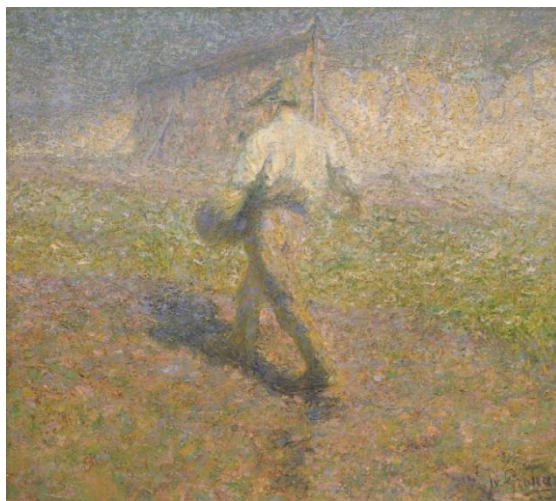
Figure6. *The Sower by Ivan Grohar[7]*

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