

## ***Ab initio* study of formic acid monomer, dimer and trimer**

LESZEK ZIEMCZONEK<sup>1</sup>, TOMASZ WRÓBLEWSKI<sup>1</sup>, GRZEGORZ P. KARWASZ<sup>1,2</sup>

<sup>1</sup>Institute of Physics, Pedagogical University of Słupsk, Arciszewskiego 22 B,  
76-200 Słupsk, Poland

<sup>2</sup>Institut für Chemie – Physikalische und Theoretische Chemie, Freie Universität Berlin,  
14195 Berlin, Germany

Configurations of the formic acid monomer, dimer and trimer are presented. The total energies for these structures have been calculated while the negatively charged clusters were considered and the possible pathways of interaction of low energy electrons with monomers and clusters were discussed. Calculations have been executed using 6-311G\*\* and 6-311++G\*\* basis sets. The electron affinities of monomer and clusters are presented. Influence of choice of the molecular basis set is also discussed. Only such systematic studies allow to explain values observed experimentally, for example, in electron attachment experiments on formic acid (MARTIN I. *et al.*, Phys. Chem. Chem. Phys. 7(10), 2005, p. 2212).

Keywords: formic acid, clusters, electron affinity.

### **1. Introduction**

Formic acid (HCOOH) is the simplest organic acid that can be regarded as an important key compound in the formation of molecules such as acetic acid (CH<sub>3</sub>COOH) or glycine (NH<sub>2</sub>CH<sub>2</sub>COOH) in the interstellar medium [1]. The formic acid dimer is one of the most stable neutral complexes with the estimated formation energy about 15 kcal/mol [2]. It seems that both monomer and dimer could be considered as key compounds in the coming into being of small biomolecules as the building blocks of larger molecular structures of biological interest in the early Universe. Also interaction of dimers and higher clusters (trimers) with slow electrons is very important because of destruction role of electrons.

### **2. Structure of monomer, dimer and trimer**

Structures of neutral formic acid monomer, dimers and trimers are presented in Fig. 1. Geometries has been optimized using *ab initio* method with 6-311G\*\* and after

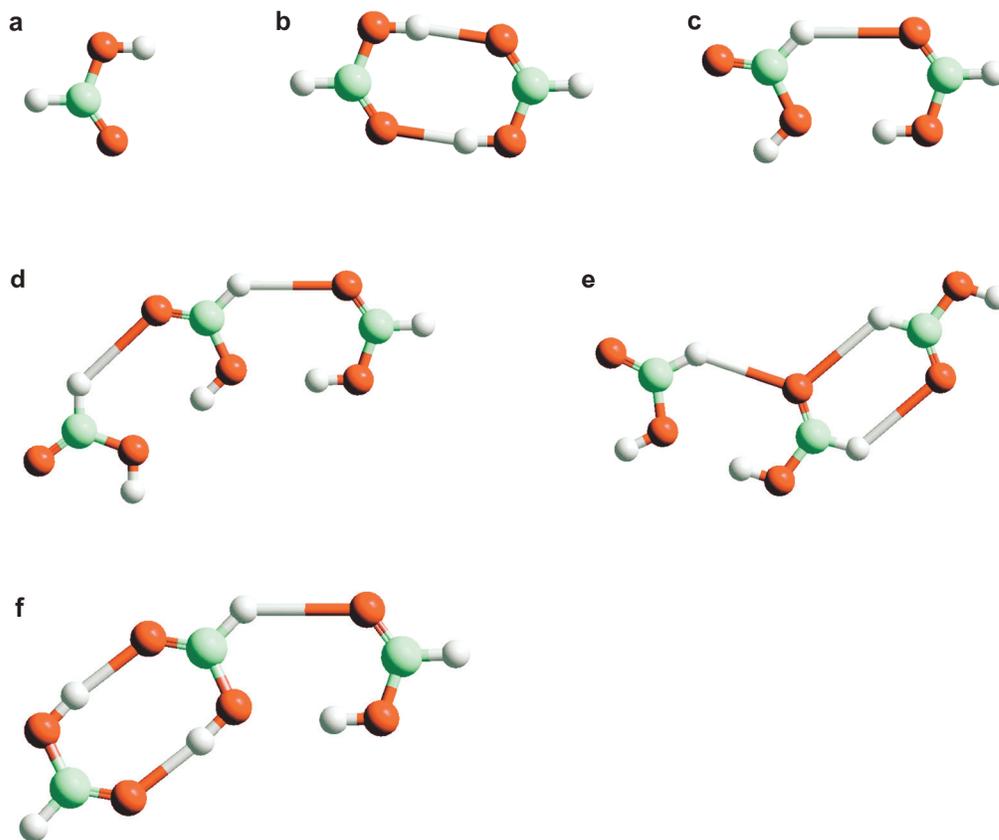


Fig. 1. Formic acid: monomer  $M$  (a), dimer  $D$  (b), dimer  $D_{\text{chain}}$  (c), trimer  $T_{\text{chain}}$  (d), trimer  $T_{\text{prim}}$  (e), trimer  $T_{\text{bis}}$  (f).



Fig. 2. Structure of cluster  $\text{HCOO}^-\text{H}_2\text{O}$ : closed (a), opened (b).

6-311++ $G^{**}$  molecular basis sets. The second base with diffuse functions ( $s$  and  $p$  for hydrogen, and  $s$ ,  $p$  and  $d$  for carbon and oxygen) is useful for finding negative structures of monomer and clusters. Table 1 shows an obvious result that the energies calculated using first base are higher than the energies calculated using second one. The global minimum structure for the neutral and also negative formic acid dimer  $D$

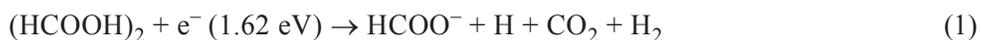
is in good agreement with other authors [1]. For example hydrogen bonds in dimer are practically linear. The angle O–H–O is about  $172^\circ$  as compared to  $178^\circ$  reported in [1] where calculations were performed at the density-functional level of the theory (DFT).

### 3. Total energies and electron affinities

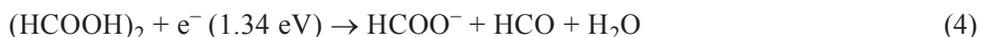
It appears that the clusterization energy for the formic acid is negative:  $D = 2M - 10.87$  kcal/mol,  $D_{\text{chain}} = 2M - 3.95$  kcal/mol,  $T_{\text{chain}} = 3M - 8.19$  kcal/mol,  $T_{\text{prim}} = 3M - 6.71$  kcal/mol,  $T_{\text{bis}} = 3M - 15.56$  kcal/mol. Thus the neutral clusters of the formic acid are stable. The total energies of calculated structures are presented in Tab. 2. Also zero point vibrational corrections are given. We see that the negative structures are less stable than the neutral ones (near 0 K). Their energies are higher than those for neutral structures except for the case of the trimers  $T_{\text{bis}}$  and  $T_{\text{chain}}$ . Also electron affinities are positive. The adiabatic electron affinity is much more. Maybe at standard conditions (298 K, 1 atm) and in terms of Gibbs free energy the electron affinity (EA) becomes lower. For the dimer  $D$  under standard conditions it has been shown in [1] that EA equals 0.9 kcal/mol.

### 4. Conclusions – comparison with some experimental results

From our calculations we can, for example, predict following channels of reactions of the formic acid clusters with slow electrons:



for dimer  $D$ ;



for dimer  $D_{\text{chain}}$ ;



for trimer  $T_{\text{prim}}$ .

Reactions (1) and (4) may be possible if we compare Fig. 1 from [3]. In experimental beam closed dimers  $D$  are produced in the first case and opened dimers  $D_{\text{chain}}$  in the second. Reactions (2) and (3) correspond to cleavage of dimer. In

Table 1. Total energies calculated for two molecular basis sets: 6-311G\*\* and 6-311++G\*\*.

Structure	Total energy [kcal/mol]		
	6-311G**	Neutral	6-311G**
<i>M</i>	Neutral	Negative	Negative
	-118486.93	-118432.21	-118460.94
<i>D</i>	-236988.26	-236967.26	-236966.43
<i>D</i> <sub>chain</sub>	-236979.82	-236931.52	-236962.69
<i>T</i> <sub>chain</sub>	-355472.92	-355437.08	-355462.21
<i>T</i> <sub>prim</sub>	-355470.98	-355431.13	-355456.76
<i>T</i> <sub>bis</sub>	-355481.73	-355434.93	-355487.12

Table 2. Total energies with zero point vibrations correction (ZPVE) and electron affinities for formic acid monomer, dimers and trimers.

Structure	Total energy [kcal/mol]			Electron affinity (EA) [kcal/mol]
	Neutral	After electron attachment before optimization	Adiabatic electron affinity (EA <sub>a</sub> ) [kcal/mol]	
<i>M</i>	-118490.20	-118431.50	-118490.94	29.26
ZPVE=	23.00		21.71	27.97
<i>D</i>	-236993.26	-236936.15	-236966.43	26.83
ZPVE=	47.99		48.26	27.10
<i>D</i> <sub>chain</sub>	-236985.46	-236926.65	-236962.69	22.77
ZPVE=	47.11		37.12	12.78
<i>T</i> <sub>chain</sub>	-355480.99	-355421.58	-355462.21	18.78
ZPVE=	71.20		42.95	-9.47
<i>T</i> <sub>prim</sub>	-355479.14	-355454.45	-355456.76	22.38
ZPVE=	70.83		69.89	21.44
<i>T</i> <sub>bis</sub>	-355489.20	-355487.11	-355487.12	2.08
ZPVE=	72.04		69.78	-0.18

reaction (2) closed cluster of  $\text{HCOO}^- \text{H}_2\text{O}$  (Fig. 2a) and in reaction (3) opened one (Fig. 2b) are respectively produced. Discussion given in [3] suggests that the reaction (2) is more likely. Also from the mass spectra (see Figs. 3 and 4 in [3]) we can conclude, that reaction (5) is possible.

## References

- [1] BACHORZ R.A., HARAŃCZYK M., DĄBKOWSKA I., RAK J., GUTOWSKI M., *Anion of the formic acid dimer as a model for intermolecular proton transfer induced by a  $\text{H}^*$  excess electron*, Journal of Chemical Physics **122**, 2005, p. 204304.
- [2] GIANTURCO F.A., LUCCHESI R.R., LANGER J., MARTIN I., STANO M., KARWASZ G., ILLENBERGER E., *Modelling electron-induced processes in "condensed" formic acid. Resonant states of  $(\text{HCOOH})_2^-$  at low energies*, The European Physical Journal D **35**, 2005, pp. 417–28.
- [3] MARTIN I., SKALICKY T., LANGER J., ABDOUL-CARIME H., KARWASZ G., ILLENBERGER E., STANO M., MATEJCIK S., *Low energy electron driven reactions in single formic acid molecules (HCOOH) and their homogeneous clusters*, Physical Chemistry Chemical Physics **7**(10), 2005, pp. 2212–6.

Received January 30, 2006