

## Quantum Chemical Study of Hydroxylation of Alkanes by Hypofluorous Acid\*

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The experimentally observed hydroxylation of alkanes by hypofluorous acid (one of Rozen's oxidation reactions) was investigated using the methods of quantum chemistry. It was shown that the high efficiency of the reaction may be explained by self-catalysis. The oxidizing HOF molecule transfers the oxygen atom to a substrate, which is accompanied by the HF formation, while the second hypofluorous acid molecule stabilizes the oxidizing HOF molecule by a hydrogen bond. The hydroxylation barriers were found to decrease with increased coordination of the oxidized carbon atom by methyl groups, in agreement with the experiment. In the gas phase, the calculated DFT/B3LYP reaction barriers amount to 22.5, 14.5, 9.0, and 6.4 kcal/mol for oxidation of methane, ethane, central carbon atoms of propane, and 2-methylpropane, respectively; for a terminal C–H propane bond, a barrier was enumerated to 13.9 kcal/mol. It was also found that the reaction can be catalyzed by the product molecule, hydrogen fluoride (as first suggested for ethylene in Sertchook R., Boese A.D., Martin J.M.L., *J. Phys. Chem. A*, **110**, 8275 (2006)), and common features of the H-bond assisted catalysis were investigated. The analogous but very much less favorable hydroxylation by hypochlorous acid molecule was also briefly discussed.

**Key words:** alkane hydroxylation, Rozen's reaction, hypofluorous acid, catalysis

Due to the great role of oxidation reactions in the chemical and pharmaceutical industries, an efficient and selective hydroxylation or oxygenation of saturated hydrocarbons remains a challenging task. The main cause of difficulties in such reactions is related to high chemical inertness of alkanes associated with high activation barriers of those oxidations.

Metal-oxo reagents such as chromates and permanganate can be applied in reactions of this type but they are nonselective and must be used under rather severe conditions. Systems like bare  $\text{FeO}^+$  are capable of activating rather resistant substrates such as methane under mild conditions [1–2], but by this time with propane as a substrate, the discrimination between primary ( $\text{RH}_2\text{C-H}$ ) and secondary ( $\text{R}_2\text{HC-H}$ ) C–H

\* Dedicated to Prof. Zbigniew R. Grabowski on the occasion of his 80th birthday.

bonds is rather poor. A brief review of mechanistic features of gas-phase metal-oxo reagent is provided in ref. [1].

Nature has found several ingenious ways to overcome these problems (inertness, nonselectivity, *etc.*) by means of metalloprotein catalysts, enzymes, such as cytochrome P450 with active ferryl unit or monooxygenase containing a binuclear iron center [3–5]. The role of iron-containing enzymes in activation and transfer of molecular oxygen onto substrates was first demonstrated by Hayaishi *et al.* as early as the 1950s [6].

The extraordinary efficiency of a van der Waals reagent,  $\text{CH}_3\text{CN}\cdot\text{HOF}$ , in oxidation of several types of substrates (such as amines, azides, ketones, aldehydes or alkenes) was discovered and thoroughly investigated by Rozen and is described in a recent microreview [7]. The advantages of this powerful reagent seem to be at least three: (i) relatively easy preparation, (ii) high reaction yields, and (iii) partial or full selectivity. The suggested reaction mechanism of these oxidations (oxygenation, hydroxylation) involves catalysis by both reactant and product molecules (HOF and HF, respectively) [8–9]. On the basis of this knowledge, we feel that hypofluorous acid is worth studying as a promising oxidant of alkanes. Moreover, experimental work has revealed high selectivity with respect to carbon coordination; tertiary carbons are oxidized preferentially [10].

In this paper, we focus our attention on the electronic and steric nature of the neighborhood of the attacked C–H bond (passing from methane to a system with a tertiary C–H bond) and on the energetics of the oxidation process with respect to the efficiency and selectivity of the proposed reaction mechanism.

## METHODS

The density functional theory (DFT) was chosen as a both cheap and reliable method. In particular, the hybrid exchange-correlation B3LYP functional was used because inclusion of the Hartree-Fock exchange part is believed to partially cancel a tendency of pure generalized gradient approximation (GGA) functionals to underestimate reaction barriers [12]. The coincidence between results for a selected transition state obtained from restricted and unrestricted Kohn-Sham approximations agrees with the assumption that the studied systems are reliably described with a one-determinant approach of the wave function. The singlet-triplet state splitting is too high and thus only singlet states are considered. The B1B95 functional [13] and the MP2 approach were also used in some cases as benchmark methods. The augmented correlation consistent polarized valenced double-zeta (aug-cc-pVDZ) [14] basis set was chosen. Compared to the alternative Pople's 6-311++G\*\* [15] and Dunning's aug-cc-pVTZ basis sets, it gives results in reasonable agreement with these larger basis sets, with a difference lower than 2 kcal/mol for the reaction path of the methane hydroxylation discussed below.

The effect of the dispersion energy on the association of van der Waals (vdW) complexes was included using the DFT/B3LYP+D approach [16], as implemented in Turbomole 5.8 [17]. The comparison of DFT/B3LYP+D and DFT/B3LYP results suggests a very small contribution of the dispersion energy and structures of the complexes are essentially determined by electrostatic interactions. Moreover, dispersion has only a subtle effect, as was demonstrated for the  $(\text{HOF})_2$  and  $\text{HOF}\cdot\text{HF}$  complexes [9]. The calculated energies were corrected by zero-point energies. The counterpoise correction [18] to the basis set superposition error (BSSE) was included in all calculations. The transition states (Eyring activation complexes) were found by the synchronous transit-guided Newton-Raphson (QST) procedure implemented

in the Gaussian 03 program package [19]. The Gibbs energies,  $\Delta G$ , were determined by summing the rotational-vibrational enthalpic and entropic contributions as obtained from the frequency analysis:  $\Delta E + \Delta H_{\text{nonelect}} - T\Delta S_{\text{nonelect}}$ , where the  $\Delta E$  term stands for the electronic energy difference, the  $\Delta H_{\text{nonelect}}$  and  $T\Delta S_{\text{nonelect}}$  terms are nonelectronic enthalpic and entropic contributions, respectively. The acetonitrile-like solvent (with permittivity of  $\epsilon = 36.65$ ) was introduced by the polarized continuum model COSMO [20]. Atomic charges were obtained from a natural bond orbital (NBO) analysis [21].

We are aware of the fact that intermolecular complexes usually have flat potential-energy surfaces (PES) with many shallow local minima with various structural conformations and therefore the conformational entropy would contribute to the total free energy. However, for each reaction model, we optimized only one of the several conformations, which is believed to be the most appropriate starting point on PES for the oxidation process. Due to this computational simplification, the Gibbs activation barriers may be underestimated.

## RESULTS AND DISCUSSION

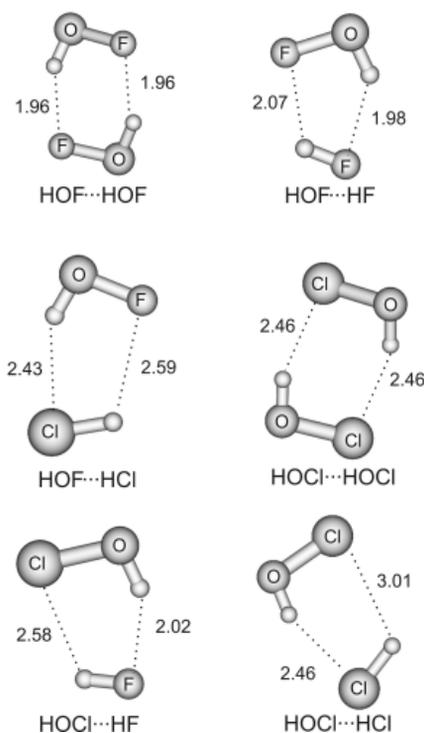
**Energetics of various van der Waals complexes.** In the present work, the study of energetics of various vdW complexes is important for two reasons. First, the oxidation itself follows the formation of the vdW complex of the substrate and the HOF molecule. Second, the oxidation is catalyzed by hydrogen bonding with an additional HOF molecule. More detailed reaction mechanism will be described below. However, for the above-mentioned reasons, the study of the participating vdW molecules seems to be a plausible starting point.

The complexes included in this study are shown in Figure 1. In Table 1, data on their association energies are presented. Apparently, all these vdW molecules exhibit similar stability, ranging from the most stable (HOF)<sub>2</sub> and HOF·HF complexes (2.9 and 2.6 kcal/mol, respectively) to the least stable HOCl···HCl dimer (1.2 kcal/mol). The stabilization energies in acetonitrile-like solvent exhibit the same trend. Open (*i.e.*, non-cyclic) geometries are however preferred, in contrast to the closed ones in the gas phase.

Regarding the effect of acetonitrile on the reaction (either the implicit-solvent effect or direct stabilization of HOF by forming a H-bonded complex), a study of the properties of the CH<sub>3</sub>CN···HOF complex was also made. Its association energy and Gibbs association energy amount to  $-6.6$  kcal/mol and  $2.2$  kcal/mol, respectively. The high stability of the complex and the inert character of acetonitrile are probable reasons for its importance as the reaction solvent.

An equilibrium between the CH<sub>3</sub>CN···HOF and (FOH)<sub>x</sub>···substrate complexes is considered as a basic assumption of the suggested oxidation mechanism. The association of two molecules of hypofluorous acid to the substrate molecule is assumed. In particular, we expect an essential role of the equilibrium equations (1) and (2) in reference to methane.





**Figure 1.** Gas phase geometries of various vdW complexes included in Table 1. Distances are given in Å.

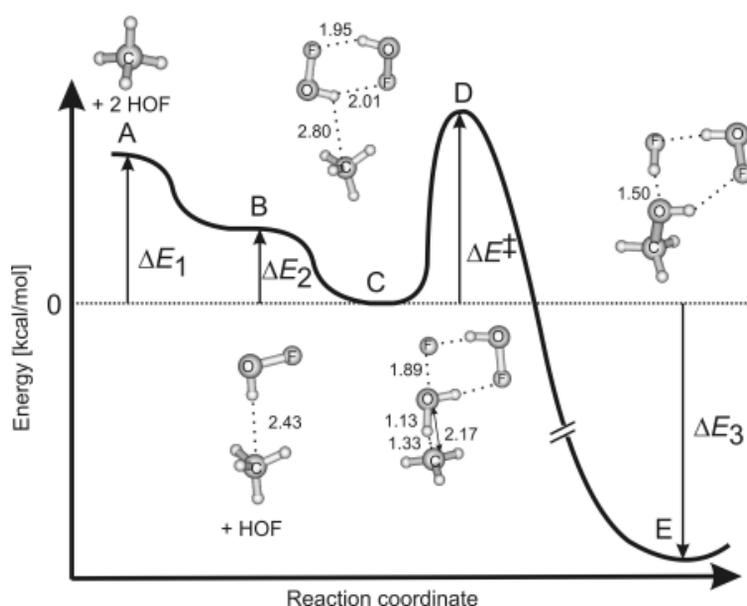
**Table 1.** Association energies (in kcal/mol) of various vdW complexes in the gas phase ( $\Delta E_{GS}$ ) and acetonitrile-like solvent ( $\Delta E_{AS}$ ). In third column, gas phase Gibbs association energies relative to the Gibbs energy of the  $\text{CH}_3\text{CN}\cdots\text{HOF}$  complex are given ( $\Delta\Delta G_{GS}$ ).

	$\Delta E_{GS}$	$\Delta E_{AS}$	$\Delta\Delta G_{GS}$
$\text{HOF}_2$	-2.9	-0.9	4.4
$\text{HOF}\cdots\text{HF}$	-2.6	-1.2	3.8
$\text{HOF}\cdots\text{HCl}$	-1.5	-0.7	3.5
$(\text{HOCl})_2$	-1.6	-0.4	5.7
$\text{HOCl}\cdots\text{HF}$	-2.2	-0.6	3.7
$\text{HOCl}\cdots\text{HCl}$	-1.2	-0.3	3.7
$\text{CH}_3\text{CN}\cdots\text{HOF}$	-6.6	-7.7	0.0

**Oxidation of alkanes by the hypofluorous acid dimer.** The following series of alkanes was chosen as the representative for an estimation of the effect of the alkane side-chains for the oxidation feasibility: methane, ethane, propane, and 2-methylpropane. For propane and 2-methylpropane, hydrogen of the central carbon was chosen

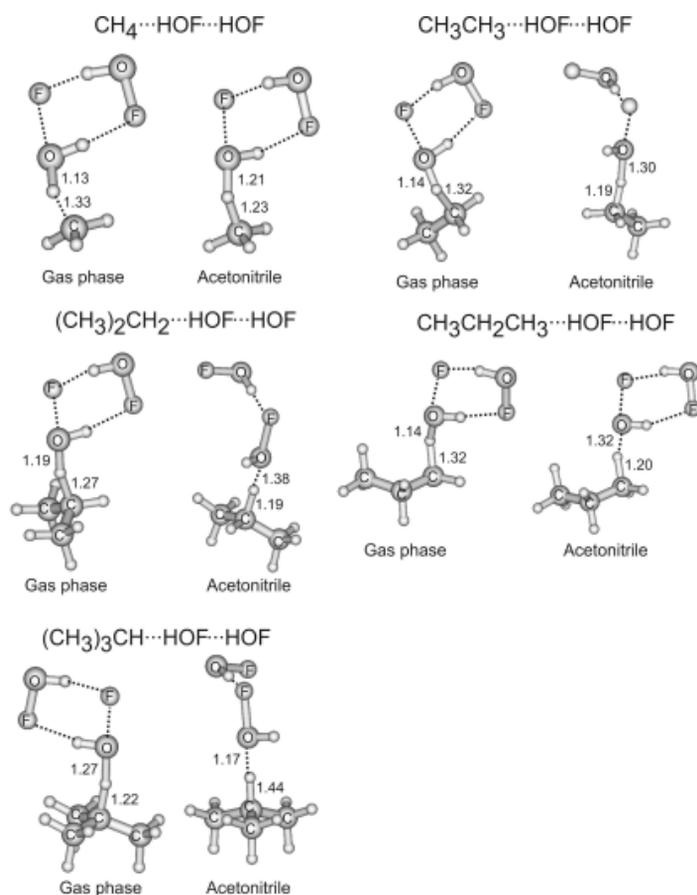
to be oxidized; the oxidized carbon is therefore substituted by zero, one, two and three methyl groups, respectively.

The common gas-phase mechanism of the alkane oxidation by hypofluorous acid is demonstrated in Figure 2 for methane, transition states of other reactions are depicted in Figure 3, the respective energies are collected in Table 2. Initially, the  $\text{CH}_4 \cdots \text{HOF}$  complex is created with association energy  $\Delta E_1$  of 0.4 kcal/mol (structure **B**). Then, the second HOF molecule is attached to form the  $\text{CH}_4 \cdots (\text{HOF})_2$  complex (structure **C**,  $\Delta E_2 = 2.7$  kcal/mol of energy), with a cyclic structure of the HOF molecules. From this point, the oxidation of methane to methanol occurs through transition state **D** to form the  $\text{CH}_3\text{OH} \cdots \text{HF} \cdots \text{HOF}$  complex (structure **E**). The activation energy  $\Delta E^\ddagger$  equals to 22.5 kcal/mol, while the energy gain  $\Delta E_3$  is 84.0 kcal/mol. Finally, HOF and HF can dissociate from complex **E** with energy costs of 8.0 and 7.6 kcal/mol, respectively (not shown in Figure 2).



**Figure 2.** Qualitative reaction profile of hydroxylation of methane by HOF; the respective energies are presented in Table 2. Distances are given in Å.

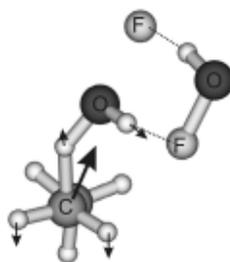
The most interesting issue has to do with the geometry of transition state **D**. It turns out that a stabilization of the acting HOF molecule is provided by an additional catalyzing HOF molecules. The involved methane C–H bond is prolonged to 1.335 Å (from 1.097 Å), which allows exposing the carbon atom to the oxygen atom of the oxidizing HOF molecule. Following the minimum energy path, the hydrogen atom originated from methane stays on methanol, while the hydrogen atom from the HOF molecule is deposited in hydrogen fluoride, coordinated to methanol in the structure **E**. The characteristic reaction mode is common for all transition states studied and is illustrated for ethane in Figure 4.



**Figure 3.** The transition states of several hydroxylations of alkanes in the gas phase and in the acetonitrile-like solvent. Energy characteristics of the respective reactions are summarized in Table 2. Distances are given in Å.

**Table 2.** Energies (in kcal/mol) along the reaction path of hydroxylation of various alkanes in the gas phase and acetonitrile-like solvent. With propane and isobutane, central carbons are oxidized. The meaning of symbols and respective geometries are shown in Figures 2 and 4.

		$\Delta E_1$	$\Delta E_2$	$\Delta E^\ddagger$	$\Delta G^\ddagger$	$\Delta E_3$	$\Delta G_3$
Methane	gas phase	3.1	2.7	22.5	24.7	-84.0	-76.5
	acetonitrile	1.5	1.2	19.9	21.8	-84.7	-78.8
Ethane	gas phase	3.0	2.7	14.5	15.3	-89.7	-84.1
	acetonitrile	2.1	1.7	10.9	12.5	-91.1	-85.6
Propane	gas phase	3.3	2.7	9.0	11.2	-93.4	-87.7
	acetonitrile	1.8	1.5	9.8	10.5	-92.6	-90.0
Isobutane	gas phase	3.2	2.7	6.4	7.6	-95.6	-90.1
	acetonitrile	2.1	1.9	6.5	7.0	-96.0	-90.7



**Figure 4.** The reaction mode in the transition state of ethane hydroxylation as a representative example. The length of arrows corresponds approximately to the amplitude of the motion.

Based on the NBO population analysis, it was found that the charge transfer from the methane molecule to the oxidizing HOF occurs in the transition state. The total charge on the  $\text{CH}_4$  part is  $0.56 |e|$ , the total charge on the oxidizing HOF subsystem is  $-0.51 |e|$ . The whole process can therefore be considered as the electron transfer from the C–H  $\sigma$  orbital to the  $\sigma^*$  orbital of the O–F bond of HOF. The high charge on fluorine is then stabilized by the second HOF molecule, which is otherwise almost unaffected and does not take part in the bond breaking/making. These features are common for the transition states of all the reactions studied both for the gas phase and implicit solvent calculations.

Also, the applicability of other theoretical methods was studied concerning methane hydroxylation. The hydroxylation barriers for the *meta*-GGA DFT functional B1B95 and MP2 approach were calculated as 25.3 and 30.5 kcal/mol, respectively. It can be concluded that in this particular case the DFT method tends to underestimate the reaction barrier compared to the MP2 approach.

Turning to larger alkanes (from the primary to the tertiary carbon atom), there is an apparent reduction of the activation barrier of the hydroxylation. While the hydroxylation barrier of ethane to ethanol amounts to 14.5 kcal/mol, the analogous conversion of propane to 2-propanol has a barrier of 9.0 kcal/mol and finally only 6.4 kcal/mol was found for the *tert*-butylalcohol formation. Comparing the activation energies of the gas-phase processes with that in the acetonitrile solvent, it is seen that the same trend of the decreasing barrier appears when passing to higher coordinated carbon. The very low barrier for the hydroxylation of 2-methylpropane matches with the experimentally observed facile oxidations of the tertiary  $\text{sp}^3$  CH centers [10].

Oxidation of the terminal carbon atom of propane was also considered in order to investigate the influence of carbon coordination on a hydroxylation barrier. In that case, the activation barrier was found to amount to 13.9 kcal/mol for  $\Delta E^\ddagger$  in the gas phase, contrary to 9.0 kcal/mol to oxidize the central carbon of the propane and 14.5 kcal/mol for ethane. This supports forementioned high selectivity of carbon hydroxylation with respect to its substitution and also shows a substantially smaller effect of the size of the attached alkyl group.

It is worth mentioning an alternative mechanism of the C–H bond breaking occurring in nature as discussed by Neese *et al.* for iron-containing metalloenzyme, bleomycin [22]. In many respects, the concept of activated bleomycin can be considered similar to the transition state of the substrate with a HOF molecule. As for the bleomycin, the protonation of peroxide greatly lowers the energy of its antibonding  $\sigma^*$  orbital and therefore increases the electrophilicity of the peroxides. This activates the peroxide for an electrophilic attack on the C–H bond. A charge transfer from the C–H  $\sigma$ -bonding orbital into the  $O_2^{2-}$   $\sigma^*$  orbital leads to a weakening of both the C–H and the O–O bonds. This prompts the H-atom transfer to form water.

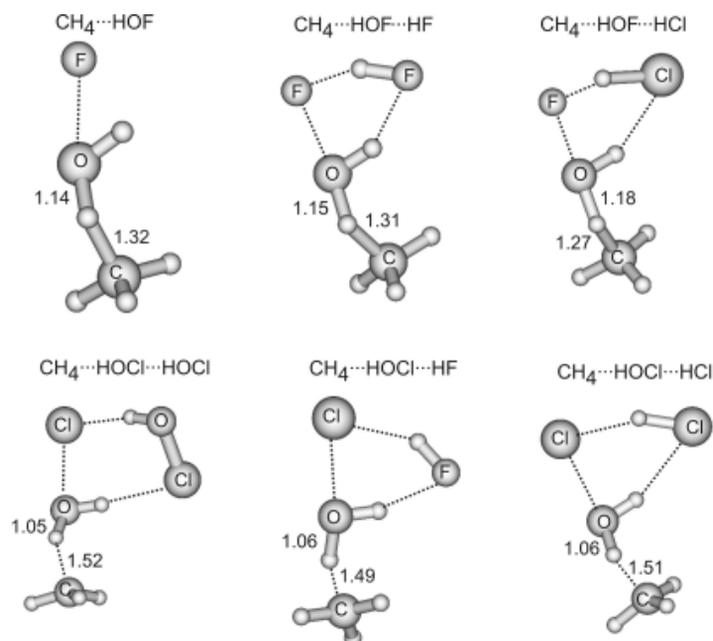
Finally, the role of the acetonitrile molecule as a part of the  $FOH \cdots NCCH_3$  complex should be addressed. According to [9], the polar hydrogen-containing substrates may form a hydrogen bond with HOF. For example, the  $(CH_3)_3N \cdots HOF$  complex is connected with an association energy of  $-9.7$  kcal/mol, which is comparable to  $-6.6$  kcal/mol for the formation of the  $FOH \cdots NCCH_3$  complex. However, as alkanes are significantly nonpolar, the association energies of the substrates with the HOF molecule are substantially lower. Here, the polarization and dispersion terms can be considered as the main contributions of the nonbonding interactions. The possible role of the  $FOH \cdots NCCH_3$  complex with relatively high association energy can be therefore assumed. However, as was shown in [8], the barrier of the ethylene epoxidation by the  $FOH \cdots NCCH_3$  complex comparing to epoxidation by the simple HOF molecule is not reduced substantially, in fact it is changed from 13.7 to 11.1 kcal/mol at the B3LYP/aug-pc2 level, respectively. The leading importance of the stabilization of the fluorine atom of the reacting HOF should therefore be emphasized.

Also, the same general mechanism of hydroxylation can be assumed for the oxidation of ethers to ketones with the intermediate where the oxidized carbon shares alkoxy and OH groups [7]. In this case, the formation of the H-bond to the ether oxygen can be presumed during the first HOF association.

#### **Oxidation of alkanes by hypofluorous acid molecule with various catalysts.**

The mechanism described in the previous section can be generalized as follows: the hydroxylation by means of hypofluorous acid, which is catalyzed by the H-bond interaction with a third molecule which need not to be HOF. To illustrate this point, the methane oxidation pathways were calculated also with other small polar hydrogen-containing molecules, in particular HF and HCl. The results are shown in Table 3 and the respective transition states are depicted in Figure 5. Furthermore, oxidation by only one HOF molecule was also considered.

As to the hydroxylation by a single HOF molecule, the reaction seems to be much less effective than that with the  $(HOF)_2$  dimer. Although the corresponding transition state possesses a very similar geometry as does the structure **D** in Figure 2, the related activation barrier is about 11 kcal/mol higher. Comparing various small polar molecules as a catalyst, the HF molecule is proven to be of comparable power to that of HOF, with a barrier about 1 kcal/mol lower. The barrier of reaction with HCl as a catalyst is larger by about 1 kcal/mol. It can be seen that while HOF as a catalyst interacts electrostatically with both hydrogen and fluorine of the hydroxylating HOF, HF and



**Figure 5.** The transition states of several hydroxylations of methane in the gas phase. Energy characteristics of the respective reactions are summarized in Table 3. Distances are given in Å.

HCl as the catalysts stabilize only the fluorine atom (see Figure 5). To summarize the results above, the stabilization of the fluoride atom of the oxidizing HOF seems to be the main factor which facilitates the oxidation.

**Table 3.** Energies (in kcal/mol) along the reaction path of hydroxylation of methane with various oxidizing species in the gas phase. Meaning of the symbols is shown in Figure 2. The respective transition states are shown in Figure 5.

Oxidizing species	$\Delta E_1$	$\Delta E_2$	$\Delta E^\ddagger$	$\Delta G^\ddagger$	$\Delta E_3$	$\Delta G_3$
HOF	–	0.4	33.7	33.0	–79.0	–74.4
HOF·HF	2.7	2.3	21.4	23.6	–84.2	–77.3
HOF·HCl	1.8	1.3	23.3	26.2	–80.6	–72.8
HOCl <sub>2</sub>	1.7	1.4	37.3	41.9	–42.9	–36.3
HOCl·HF	2.4	2.1	35.5	38.3	–43.6	–38.6
HOCl·HCl	1.4	1.0	38.4	40.5	–41.2	–38.4

**Oxidation of alkanes by hypochlorous acid.** To investigate the suggested mechanism further, the oxidation by hypochlorous acid, HOCl, was also considered. Data for the methane-to-methanol conversion by HOCl, catalyzed by various small hydrogen-containing molecules HOCl, HF and HCl, are summarized in Table 3.

Transition states of the reactions are shown in Figure 5. The barriers of the oxidation are substantially higher than those in the catalyzed HOF oxidation but, on the other hand, comparable to the oxidation by one HOF molecule. Therefore, with larger alkanes, we may assume that the energy barrier could be surpassed at the elevated temperature. Note also that the exothermicity of the reaction is lower than in the case of the HOF oxidation. This can be explained by the formation of cyclic structures after the oxidation is finished.

## CONCLUSIONS

In the present study, the hydroxylation of the representatives of the alkane series by hypofluorous acid was investigated using methods of quantum chemistry. The association energies and geometries of various vdW complexes were calculated and the cyclic (HOF)<sub>2</sub> dimer was found to be the most stable molecule in the gas phase compared to the other complexes studied, with the association energy of 2.9 kcal/mol. However, the stabilization energy of the FOH...NCCH<sub>3</sub> complex was calculated to be 6.4 kcal/mol and the complex with acetonitrile may also play a role in the oxidation reaction; on the other hand, this role seems to be of a minor importance compared to the H-bond catalysis [8].

The suggested mechanism was explored in details for the (HOF)<sub>2</sub> dimer as a reacting species in the methane hydroxylation. After the association of two hypofluorous acid molecules, the first HOF molecule was found to transfer the oxygen to the substrate and to form hydrogen fluoride. The second HOF molecule acts as a catalyst stabilizing the charge transfer from the substrate to the  $\sigma^*$  orbital of the O–F bond in the HOF molecule. After the oxidation barrier is surpassed, a substantial portion of energy is released and the products dissociate.

It was learned that the oxidation barrier decreases with the increasing coordination of the oxidized carbon by the methyl groups, in complete agreement with experiment, where smooth oxidation of the tertiary carbons is revealed. The energies computed for the acetonitrile-like solvent exhibit the same trend. Also, the same mechanism is suggested for the oxidation of secondary alcohols to ketones.

The HF and HCl molecules as possible catalysts were compared to the HOF molecule and it was learned that the differences in the activation barrier height are negligible. Also, mechanism can be extended to the oxidation by the hypochlorous acid; however, the barriers of the HOCl oxidations catalyzed by H-bond forming species (HOCl, HF or HCl) were found to be comparable to hydroxylation by a single HOF molecule.

### Dedication

This work is dedicated to Zbigniew Ryszard Grabowski, a brilliant scientist, a brave man and moral authority, and a true democrat.

## REFERENCES

1. Schröder D. and Schwarz H., *Top. Organomet. Chem.*, **22**, 1 (2007).
2. Nachtigallová D., Roeselová M. and Zahradník R., *Chem. Phys. Lett.*, **270**, 357 (1997).
3. Solomon E.I., Brunold T.C., Davis M.I., Kemsley J.N., Lee S.K., Lehnert N., Neese F., Skulan A.J., Yang Y.S. and Zhou J., *Chem. Rev.*, **100**, 235 (2000).
4. Shaik S., Hirao H. and Kumar D., *Nat. Prod. Rep.*, **24**, 533 (2007).
5. Groves J.T., *Proc. Natl. Acad. Sci. USA*, **100**, 3569 (2003).
6. Hayaishi O., Katagiri M. and Rothberg S., *J. Am. Chem. Soc.*, **77**, 5450 (1955).
7. Rozen S., *Eur. J. Org. Chem.*, **12**, 2433 (2005).
8. Sertchook R., Boese A.D. and Martin J.M.L., *J. Phys. Chem. A*, **110**, 8275 (2006).
9. Srnec M., Ončák M. and Zahradník R., *J. Phys. Chem. A*, submitted (2008).
10. Rozen S., Brand M. and Kol M., *J. Am. Chem. Soc.*, **111**, 8325 (1989).
11. Becke A.D., *J. Chem. Phys.*, **98**, 1372 (1993).
12. Cramer C.J., *Essentials of Computational Chemistry: Theories and Models*, John Wiley & Sons., Chichester 2002, 1st edition.
13. Becke A.D., *J. Chem. Phys.*, **104**, 1040 (1996).
14. Dunning T.H., *J. Chem. Phys.*, **90**, 1007 (1989).
15. Krishnan R., Binkley J.S., Seeger R. and Pople J.A., *J. Chem. Phys.*, **72**, 650 (1980).
16. Jurečka P., Šponer J., Černý J. and Hobza P., *Phys. Chem. Chem. Phys.*, **8**, 1985 (2006).
17. Ahlrichs R., Bar M., Haser M., Horn H. and Kolmel C., *Chem. Phys. Lett.*, **162**, 165 (1989).
18. Boys S.F. and Bernardi F., *Mol. Phys.*, **19**, 553 (1970).
19. Gaussian 03, R.C., Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Jr., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C. and Pople J.A., Gaussian, Inc., Wallingford CT, 2004.
20. Klamt A. and Schuurmann G., *J. Chem. Soc., Perkin Trans. 2*, **5**, 799 (1993).
21. Reed A.E., Curtiss L.A. and Weinhold F., *Chem. Rev.*, **88**, 899 (1988).
22. Neese F., Zaleski J.M., Zaleski K.L. and Solomon E.I., *J. Am. Chem. Soc.*, **122**, 11703 (2000).