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A MOLECULAR ORBITAL STUDY ON THE OXIDATIVE
DECOMPOSITION OF HFC-32

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A Molecular Orbital Study on the Oxidative
Decomposition of HFC-32

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A series of *ab initio* molecular orbital calculations, in which Hartree-Fock, second-order Møller-Plesset perturbation, density functional (B3LYP and BHandHLYP) levels of theory were used, was performed on the elementary reactions related to the oxidative decomposition of HFC-32 (CH_2F_2) by hydroxyl (OH) radicals in a supercritical water condition (so-called SCWO). The whole process is written as $\text{CH}_2\text{F}_2 + 4\text{OH} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{HF}$ and consists of (1) H abstraction by OH to form H_2O , (2) OH coupling to C-center, and (3) HF leaving to form C=O bond. Molecular geometries were optimized at each level of theory. The HF leaving was found to be the rate-determining step, but its barrier height was lowered by the reactive solvation with an extra H_2O . Calculations implied that the SCWO of HFC-32 can proceed efficiently.

Keywords: Ab Initio Molecular Orbital Calculation, Hydrofluorocarbon, Oxidative Decomposition, Supercritical Water, Reactive Solvation

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代替フロン HFC-32 に酸化的分解過程
に関する分子軌道計算

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代替フロンは、塩素原子を含まないためにオゾン破壊を招くフロンに比して「問題が(少)ない」とされ、現在、HFC-32 (2 弗化メタン)、HFC-134a (4 弗化エタン) を主に大量に生産・消費されている。しかし、代替フロンは温室効果がフロン以上に大きく、また大気中での分解により有害な弗素化合物が環境に散逸することから、決して自由に放散が許される物質ではなく、回収・分解の閉鎖系での処理が望まれる。近年、フロン類も含め有機系廃棄物一般に対して高い分解能を持つ超臨界水処理に注目が集まっているが、その分解機構に関しては未知の部分が多い。この報告では、大過剰の OH による酸化的分解を想定し、代替フロンとして HFC-32 を選んで、非経験的分子軌道計算により分解反応の素過程群を詳細に検討した結果をまとめる。HFC-32 は最終的には、炭酸ガス、水、それと弗化水素にまで大きく発熱的に分解される。弗化水素の離脱では、超臨界水条件下で隣接する水分子が触媒として作用することが示唆された。計算近似的には、密度汎関数法についての問題性も明らかになった。

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1 Introduction

Manifestly, environmental science researches are getting more and more importance. Since many environmental problems are caused by the chemical compounds like halogenated organics and waste plastics containing heavy metals, the counter-measure and remediation based on the knowledge of chemistry are being of special interest, where the methods of decomposition and conversion from hazardous to safe forms should play a key role. In such a field of environmental engineering chemistry, the supercritical water (SCW) technology has been one of the most promising ways to attack the problems¹⁻³). SCW has the pronounced differences from the normal phase water⁴⁻⁹). The notable characteristics are (1) diminution of networks kept by hydrogen bondings, (2) large density fluctuation, (3) low dielectric constant, and (4) good solvent rather for organics and gases. These properties of SCW could correlate with a high ability of hydrolysis for organic wastes and pollutants, and alkali additives enhance the activity. For example, chlorofluorocarbon (CFC) compounds, are efficiently decomposed in a closed system by using SCW¹⁰). Needless to add, CFC's had been quite massively used as coolants and solvents but have been notoriously known not only as the depleter of stratospheric ozone layer through photochemical releasing the Cl atoms but also as the greenhouse effector¹⁰). When O₂ or hydrogen peroxide (H₂O₂) are introduced, the SCW system shows a power of oxidative decomposition¹²⁻²⁰). This has been known as the so-called SCW oxidation (SCWO) treatment, and investigations on the mechanisms and a variety of applications have been extensively carried out. Hydroxyl (OH) and hydroperoxyl (HO₂) radicals have been considered as the primary oxidants in SCWO, although the details of elementary reactions have not been understood. As an alternative method to the experimental study, *ab initio* molecular orbital (MO) calculation could provide the

detailed information associated with SCWO, involving the energetics and nature of transition state (TS). Understanding based on MO calculations could contribute to designing optimal processes and/or plants of SCWO.

This brief report presents a series of MO calculations, in which Hartree-Fock (HF), second-order Møller-Plesset perturbation (MP2), and hybrid density functional (B3LYP and BHandHLYP) theories²¹⁾ are used, on the elementary reactions of SCWO decomposition of the HFC-32, or CH₂F₂ molecule. The main purpose is to investigate how reactions proceed. HFC-32 is the smallest hydrofluorocarbon (HFC) compound of C1-type. HFC's have been being produced and consumed in a massive fashion, as the *promised alternatives to CFC's* because of no Cl atoms¹¹⁾. However, HFC is still problematic as is CFC since it has also the greenhouse-effect and F-containing pollutants are released during the decompositions in atmosphere. Greenhouse-effect ability of not only CFC's but also HFC's is much larger than CO₂ by more than thousand times. Thus, the recycle and/or decomposition in a closed loop are inherently desirable for HFC compounds. This is a reason why HFC-32 is taken as a model case of the SCWO decomposition, in the present investigation. OH radical is being assumed to be the oxidant and to exist much more than do HFC-32 molecules in reaction system. The total process is written as $\text{CH}_2\text{F}_2 + 4\text{OH} \rightarrow \text{CO}_2 + 2\text{HF} + 2\text{H}_2\text{O}$ and consists of (1) H abstraction by OH to form H₂O, (2) OH addition to C-radical center, and (3) HF leaving to form C=O bond (rate-determining step). The calculations will suggest that the total process is highly exothermic and HFC-32 can be completely decomposed via SCWO. Importance of reactive solvation in the HF leaving will be illustrated.

2 Calculation scheme

The scheme of calculation was based on the geometry optimization for each molecule appearing in the SCWO process, at each level of theory. Gaussian94 suite of MO programs²¹⁻²³⁾ was used in all the calculations. The basis sets were Gaussian's 6-31G(d',p') and 6-31+G(d',p'), where the set of diffuse sp-functions were augmented on C, F, and O atoms in the latter set. Exponents of polarization d-functions were optimized values: d-exponents for C and F are 0.626 and 1.75, respectively. Note that the "standard 6-31G(d,p)" has an uniform d-exponent of 0.8 and this is potentially problematic²¹⁾ if the system contains the highly polar bond such as the present case of $C^{\delta+}-F^{\delta-}$. Note that p-exponent for H is also an optimized value. An s-contaminant of cartesian d-functions was removed to reduce errors the in energetic evaluations.

For radical or spin-doublet species, unrestricted types of wavefunctions were used since the analytic second-derivatives were available, where the spin expectation value, S^2 was always less than 0.8 (exact value: 0.75) even for the single HF determinant and it seemed to be acceptable. No frozen-core approximation was applied in MP2 calculations. Recently, B3LYP has been the most popular choice of hybrid density functionals^{21,23-24)}. B3LYP calculations actually provide highly quantitative results for most cases, but can be less reliable for weakly interacting systems such as reaction intermediates and/or dispersion-driven complexes. For example, Mohr et al. calculated the solvation reaction between $C_2H_4^+$ cation-radical and H_2O and found a problematic behavior of B3LYP in predicting the TS structure²⁵⁾. They also showed BHandHLYP, in which the exact HF exchange portion is larger than B3LYP (0.5 versus 0.2 in parameter setting²³⁾), is rather favorable in comparison with the results obtained by calculations of quadratic configuration interaction with singles

and doubles (QCISD). Note that QCISD takes higher than double excitations into account and is formally superior to MP2. Thus, both of B3LYP and BHandHLYP functionals were used in this investigation on this SCWO of HFC-32. To make a reference, QCISD calculations with 6-31G(d',p') basis were also carried out for some of reactions.

So-called reaction-field type calculations for the polarizable solvent effect were not done, since SCW has a variable and rather small dielectric constant depending on the pressure and temperature. Similarly, thermochemical corrections were also not considered. The SCW condition, in which reactant and environmental-water molecules can contact closely each other, was modelled through the reactive solvation by an H₂O. In fact, calculations will show that this special solvation can lower the barrier height of HF leaving step by which C=O double bond is formed.

3 Results and discussion

3.1 Main path

Preliminary calculations indicated that the main path of SCWO decomposition consists of six elementary reactions, labeled with (a)-(f). C—C coupling and/or C—H recoupling among intermediate radicals have been excluded since the interest is being focused not on an accurate modelling of whole process but on a reaction sequence toward the complete decomposition. Table I shows the energetic results calculated by each level of theory for these (a)-(f) reactions, where ΔE and E_a correspond to the reaction energy (minus sign indicates the exothermicity) and barrier height of TS in Kcal/mol, respectively. Symbol "+" in the table means 6-31+G(d',p') basis derived by the addition of diffuse functions onto 6-31G(d',p').

The SCWO decomposition is initiated by the H abstraction of (a), CH₂F₂ +

$\text{OH} \rightarrow \text{CHF}_2 + \text{H}_2\text{O}$, being similar to the usual cases of combustion²⁶). Note also that the first step of atmospheric decompositions of HFC has been well known to be just the H abstraction by OH radical which originates from water molecules in air^{11,27-29}). Some MO studies on H abstraction for C2-type HFC's have been published³⁰⁻³³). From Table I (a), one can see the poor energetics by the HF level calculation. Such a situation is unfortunately common in the other entries of Table I and later. Namely, the necessity of correlated calculations is indicated. However, it must be pointed out that B3LYP functional provides negative E_a for reaction (a). In contrast, BHandHLYP results are comparable to MP2 or QCISD values. Note that "standard 6-31G(d,p)" provides -1.7 Kcal/mol as E_a for B3LYP. When the basis set is enlarged to 6-311+G(2d,2p), it still presents an erratic E_a of -0.1 Kcal/mol for B3LYP. The 6-311+G(2d,2p) values for BHandHLYP and MP2 are +8.8 Kcal/mol and +9.4 Kcal/mol, respectively. Larger 6-311++G(2d,2p) basis (diffuse s-function is furthermore added on H) gives 0.0 Kcal/mol for B3LYP and +8.8 Kcal/mol for BHandHLYP as E_a . Unfortunately, no notable improvement due to basis is observed for B3LYP.

It would be useful to show the TS structure of reaction (a). Table II shows the key values obtained with 6-31G(d',p') basis set. The B3LYP value of $R(\text{C}-\text{H})$ is slightly short and $R(\text{H}-\text{O})$ is considerably long relative to the other correlated methods. Furthermore, the imaginary frequency by B3LYP is pathologically small. These values indicate that the energy surface modelled by B3LYP is too broad, providing a seemingly early TS for reaction (a). BHandHLYP results look better in correspondence to QCISD and MP2 values. This is a similar situation to the case reported by Mohr et al²⁵). Skokov and Wheeler examined the reliability of several density functionals for a variety of H abstraction reactions³⁴). They reported that

$R(\text{C}-\text{H})$ and $R(\text{H}-\text{O})$ at the TS of $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ are 1.274 Å and 1.239 Å, respectively, by B3LYP/6-31G(d). Corresponding results by MP2 were 1.181 Å and 1.330 Å, where the other functionals of BLYP, B3P86, and BP86 provided worse results than B3LYP. The direction of their structural deviations between B3LYP and MP2 is in reverse from the present case of CH_2F_2 in which C-center could be more positive due to more polar C-F bonds. Note that Skokov and Wheeler did not encounter a negative E_a for B3LYP on CH_4/OH reaction although they observed the basis dependency³⁴). As a whole, besides B3LYP, a multi-usage of the other functionals such as BHandHLYP is recommended for safe, if possible.

The reaction (b) is a C-O bond formation by the coupling between OH and CHF_2 and is highly exothermic as is shown in Table I (b). Correlated treatments are shown to be desirable. The next reaction (c) is the second H abstraction of $\text{CHF}_2(\text{OH}) + \text{OH} \rightarrow \text{CF}_2(\text{OH}) + \text{H}_2\text{O}$. B3LYP again provides poor results for E_a . This step is followed by the second OH coupling (d), and then $\text{CF}_2(\text{OH})_2$ is formed.

The remaining part of SCWO process corresponds to two HF leavings to form C=O double bond: reactions (e) and (f). For the later $\text{CFO}(\text{OH}) \rightarrow \text{CO}_2 + \text{HF}$, (f), the reaction proceeds through a typical four-membered TS, as shown in illustration (a) for reactant and illustration (b) for TS of Fig. 1. The bond breakings of O-H and C-F and bond formings of H-F and C=O (π type) proceed in a concerted manner in the plane, and the dehybridization takes place at the C atom during the reaction. A cyclic charge relation of $-\text{C}^{\delta+}-\text{F}^{\delta-}-\text{H}^{\delta+}-\text{O}^{\delta-}-$ matches the flow of reacting electrons. Table I shows that both of HF leaving reactions have a fairly large E_a relative to that of H abstraction, especially for reaction (e). Thus, the HF leaving is revealed to be just the rate-determining step in SCWO of HFC-32. At each of MP2, B3LYP, and BHandHLYP levels of theory, E_a is not so affected by the

addition of diffuse functions in basis, but ΔE is shifted to the (more) exothermic side. The diffuse functions (represented as "+" in the table) could improve the description of negatively charged O atom in CO_2 and F atom in HF. Note that B3LYP provides no serious difference from MP2 (and QCISD with 6-31G(d',p') basis) for the HF leaving.

When the MP2/6-31+G(d',p') values are taken as the most reliable results in the present investigation, the total exothermicity is as large as -287.7 Kcal/mol. However, two HF leaving reactions exist as the rate-determining step. Their barrier heights are estimated to be +39.6 Kcal/mol for the first (e) and +30.7 Kcal/mol for the second (f). One of reasons why the height is so high may be a structural strain in the four-membered TS (see illustration (b) of Fig. 1). Table III compiles the structure parameters of reactant CFO(OH) and TS calculated at the MP2/6-31+G(d',p') level of theory, where the carbonyl O atom is labeled as $\text{O}_{(\text{C})}$ for convenience. The structural deformation during HF leaving to form CO_2 is found as expected. The value of $\theta(\text{F}-\text{C}-\text{O})$ is as small as 88 degree, corresponding to a representative strain in TS. A certain mechanism should play a role in lowering the height for the totally high efficiency of oxidative decomposition. That is the reactive solvation, as will be demonstrated later.

3.2 Branch path

One of energetically probable branch paths, toward the final CO_2 formation, starts on the HF leaving of $\text{CHF}_2(\text{OH}) \rightarrow \text{COHF} + \text{HF}$. This reaction is followed by two successive reactions of the H abstraction by OH and the OH coupling to C-center. Energetic results are given in Table IV. E_a for the HF leaving (g) is slightly higher than reaction (e) in the main path, where MP2/6-31+G(d',p') provides +46.2

Kcal/mol. B3LYP fails in the H abstraction (h), as was observed for (a) and (c). Again, BHandHLYP is rather preferable. The branching terminates at the formation of CFO(OH) by reaction (i).

3.3 Reactive solvation for HF leaving

As has been noted, the SCW condition could provide a close contact between reactant and environmental-water molecules. Thus, the reactive solvation, in which the extra H₂O plays a catalytic role to lower the barrier height, is considered for the crucial HF leaving step. Prior to showing the present results, a demonstrative example is addressed here. Rice et al. examined kinetically the reactive solvation effect in the so-called water-gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, in SCW³⁵⁾, based on the precedent *ab initio* results by Melius et al.³⁶⁾. Calculations by Melius et al. estimated -26.1 Kcal/mol for the lowering of height catalyzed even by an extra H₂O. Rice et al. actually observed a high negative-volume change in activation step, by which the reactive participation of extra H₂O is experimentally justified. It has been known that the water additions to sulfur trioxide³⁷⁻³⁸⁾ (SO₃) and formaldehyde³⁹⁻⁴⁰⁾ (CH₂O) are similarly catalyzed by the second water molecule although both of these may not directly relate with SCW.

Now, the present cases of HF leaving are discussed. Table V shows how the barrier height is lowered by the reactive solvation with an H₂O. The system first obtains the stabilization since two hydrogen bondings are formed to give an intermediate complex, as illustrated in illustration (a) of Fig. 2 for reaction (k) of [CFO(OH) → CO₂ + HF] / H₂O. MP2/6-31+G(d',p') stabilization energy (or ΔE') is -9.8 Kcal/mol and this seems to be reasonable by comparing with the double of typical hydrogen bonding energy of ~5 Kcal/mol. The form of six-membered ring is

no longer completely planar. For the complex (and TS) of reaction (k), the key structural parameters obtained by MP2/6-31+G(d',p') are given in Table VI. It is notable that C-F and O-H bonds start to be weakened due to hydrogen bondings of F-H_(W) and H-O_(W) in this formation of six-membered ring, where subscript "(W)" identifies the reactive water in Table VI.

Successively, the system goes to the TS where the HF molecule is being formed not by the direct coupling of H-F but by H_(W)-F and a water molecule is being reproduced and released as H-O_(W)-H_{(W)'} (see illustration (b) of Fig. 2). This may be considered as a variant of "proton transfer phenomena". Mulliken charges calculated by BHandHLYP/6-31+G(d',p') for reactive H and H_(W) atoms are +0.42 and +0.39, respectively, at TS. Through such a mechanism, the barrier height (E_a') is considerably lowered, where the amount reaches up to ~20 Kcal/mol depending on reactions and theories. The lowering calculated at MP2/6-31+G(d',p') level of theory is as large as -12.7 Kcal/mol in comparison between reactions (f) and (k), and the height to pass over for HF leaving turns to be only +18.0 Kcal/mol. Comparison among TS structures in Tables III and VI implies that the strain in TS is lower than the case (f) without an H₂O, especially for angles around the C atom. These facts could correlate with the lowering of barrier height for HF leaving. E_a' of the first HF leaving (j) is now +23.2 Kcal/mol by MP2/6-31+G(d',p') calculations. B3LYP and BHandHLYP functionals give the comparable values. The height for branching initiated by reaction (l) is also lowered. If a sort of D₂O-based experiments is performed, the presently proposed scheme of reactive solvation may be verified. As a conclusion of the present investigation, the SCWO process of HFC-32, $\text{CH}_2\text{F}_2 + 4\text{OH} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{HF}$, is expected to easily proceed, with a crucial help of reactive solvation for the HF leaving of rate-determining step. Such a nature of

special solvation may be general in high activities of SCWO for organic wastes¹²⁻²⁰).

4 Summary

A series of MO calculations was performed on the elemental reactions for SCWO of HFC-32 (CH_2F_2), where the oxidant was assumed to be hydroxyl (OH) radical. Calculations showed that the total process is highly exothermic toward the final CO_2 formation and the barrier height of HF leaving, by which $\text{C}=\text{O}$ double bond is formed, is lowered by the reactive solvation with an H_2O . This reactive solvation seemed to correlate with the high decomposition power of SCWO. The pathological behavior of B3LYP was found for the H abstraction by OH, and BHandHLYP looked rather favorable. Multi-usage of density functionals is recommended for a cross checking.

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References

- 1) K. P. Johnston and C. Haynes: *AIChE J.* **33** (1987) 2017.
- 2) J. S. Seewald: *Nature* **370** (1994) 285.
- 3) C. A. Eckert, B. L. Fknutson and P. G. Debenedetti: *Nature* **383** (1996) 313.
- 4) S. Kim and K. P. Johnston in: ACS Symp. Ser. 329, *Critical Fluids, Chemical and Engineering Principles and Applications*, ed. T. G. Squires and M. E. Paulatis (American Chemical Society, Washington DC, 1987).
- 5) J. M. Seminario, M. C. Concha, J. S. Murray and P. Politzer: *Chem. Phys. Lett.* **222** (1994) 25.
- 6) A. K. Soper, F. Bruni and M. A. Ricci: *J. Chem. Phys.* **106** (1997) 247.
- 7) N. Matsubayashi, C. Wakai and M. Nakahara: *J. Chem. Phys.* **107** (1997) 9133.
- 8) M. Kalinichev, J. D. Bass: *J. Phys. Chem. A* **101** (1997) 9720.
- 9) R. Biswas and B. Bagchi: *Chem. Phys. Lett.* **290** (1998) 223.
- 10) T. Sugeta, T. Sako, N. Nakazawa, K. Otake and M. Sato in: *Development and Evaluation of Countermeasure Technologies for Stratospheric Ozone Depletion* (National Institute of Materials and Chemical Research Agency of Industrial Science and Technology, Japanese Ministry of International Trade and Industry, Tsukuba, 1996).
- 11) N. Ototake: *Daitaifuron no Tansaku* (Kogyo-chousa-kai, Tokyo, 1989) [in Japanese], as an useful monograph.
- 12) M. Modell in: *Standard handbook of hazardous waste treatment and disposal* (McGraw-Hill, New-York, 1989).
- 13) R. W. Shaw, T. R. Brill, A. A. Clifford, C. A. Eckert, and E. U. Franck: *Chem. Eng. News* **69** (1991) 26.

- 14) L. Li, P. Chen, and E. F. Gloyna in: ACS Symp. Ser. 514, *Supercritical fluids engineering science* (American Chemical Society, Washington DC, 1993).
- 15) G. E. Bennett and K. P. Johnston: *J. Phys. Chem.* **98** (1994) 441.
- 16) P. B. Balbuena, K. P. Johnston and P. J. Rossky: *J. Am. Chem. Soc.* **116** (1994) 2689.
- 17) T. Xiang and K. P. Johnston: *J. Phys. Chem.* **98** (1994) 7915.
- 18) E. F. Gloyna and L. Li: *Environ. Prog.* **14** (1995) 182.
- 19) Internet address of <http://scwo.mit.edu/> contains a number of hyperlinks about SCWO.
- 20) US EPA (Environmental Protection Agency) is promoting the project "EnviroSenSe" in which SCW technology is of a special interest, and the corresponding internet address of <http://es.epa.gov/> is informative.
- 21) J. B. Foresman and A. Frisch: *Exploring Chemistry with Electronic Structure Methods* 2nd ed. (Gaussian Inc., Pittsburgh, 1996).
- 22) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. A. Ayala, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople: *Gaussian94* (Gaussian, Inc., Pittsburgh, 1995).
- 23) M. J. Frisch, A. Frisch and J. B. Foresman: *Gaussian94 User's Reference* (Gaussian, Inc., Pittsburgh, 1995).
- 24) *Recent Advances in Density Functional Methods, Part II* ed. D. P. Chong (World Scientific, Singapore, 1997).

- 25) M. Mohr, H. Zipse, D. Marx and M. Parrinello: *J. Phys. Chem. A* **101** (1997) 8942.
- 26) *Combustion Chemistry* ed. J. W. C. Gardiner (Springer, Berlin, 1984).
- 27) D. D. Nelson, Jr., M. S. Zahniser and C. E. Kolb: *Geophys. Res. Lett.* **20** (1993) 197.
- 28) V. L. Orkin and V. G. Khamaganov: *J. Atmos. Chem.* **16** (1993) 157.
- 29) A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen and A. R. Ravishankara: *J. Phys. Chem.* **97** (1993) 8976.
- 30) A. Suga, Y. Mochizuki, N. Nagasaki, Y. Gotoh, H. Ito, S. Yamashita, T. Uchimaru, M. Sugie, A. Sekiya, S. Kondo and M. Aoyagi: *Chem. Lett.* **19** (1994) 2365.
- 31) J. M. Martell and R. J. Boyd: *J. Phys. Chem.* **99** (1995) 13402.
- 32) J. M. Martell, J. B. Tee and R. J. Boyd: *Can. J. Chem.* **74** (1996) 786.
- 33) F. Louis, A. Talhaoui, J.-P. Sawerysyn, M.-T. Rayez and J.-C. Rayez: *J. Phys. Chem. A* **101** (1997) 8503.
- 34) S. Skokov and R. A. Wheeler: *Chem. Phys. Lett.* **271** (1997) 251.
- 35) S. F. Rice, R. R. Steeper and J. D. Aiken: *J. Phys. Chem. A* **102** (1998) 2673.
- 36) C. F. Melius, N. E. Bergan and J. E. Shepherd in: *Proceedings of the Twenty-Third symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1990).
- 37) K. Morokuma and C. Muguruma: *J. Am. Chem. Soc.* **116** (1994) 10316.
- 38) E. J. Meijer and M. Sprik: *J. Phys. Chem. A* **102** (1998) 2893.
- 39) I. H. Williams, D. Spangler, D. A. Femec, G. M. Maggiora and R. L. Schowen: *J. Am. Chem. Soc.* **105** (1983) 31.

- 40) O. N. Ventura, E. L. Coitino, A. Lledos and J. Bertran: J. Comp. Chem.
13 (1992) 1037.

Table I. Calculated energetics for the main path of $\text{CH}_2\text{F}_2 + 4\text{OH} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{HF}$. The process consists of six elementary reactions (a)-(f). Energetics are evaluated at each level of theory: HF, MP2, B3LYP, BHandHLYP, and QCISD. For clearance, symbol "+" indicates 6-31+G(d',p') basis. ΔE and E_a are the reaction energy and activation energy (or barrier height) of TS in Kcal/mol, respectively. Minus sign indicates the exothermicity.

		HF	MP2	B3LYP	BHandHLYP	QCISD
(a)	$\text{CH}_2\text{F}_2 + \text{OH} \rightarrow \text{CHF}_2 + \text{H}_2\text{O}$					
ΔE	6-31G(d',p')	+7.8	-16.5	-14.7	-11.1	-12.2
	+	-2.1	-17.9	-15.5	-10.7	
E_a	6-31G(d',p')	+28.1	+9.9	-1.8	+6.2	+9.1
	+	+28.6	+10.2	-0.1	+8.8	
(b)	$\text{CHF}_2 + \text{OH} \rightarrow \text{CHF}_2(\text{OH})$					
ΔE	6-31G(d',p')	-90.2	-118.1	-112.7	-110.0	-109.7
	+	-78.9	-116.6	-109.2	-105.8	
(c)	$\text{CHF}_2(\text{OH}) + \text{OH} \rightarrow \text{CF}_2(\text{OH}) + \text{H}_2\text{O}$					
ΔE	6-31G(d',p')	+3.5	-13.0	-11.6	-7.7	
	+	+1.0	-14.9	-13.1	-7.9	
E_a	6-31G(d',p')	+31.8	+12.6	+1.4	+9.8	
	+	+32.3	+9.4	+3.3	+12.3	
(d)	$\text{CF}_2(\text{OH}) + \text{OH} \rightarrow \text{CF}_2(\text{OH})_2$					
ΔE	6-31G(d',p')	-83.6	-118.9	-112.6	-110.8	
	6-31+G(d',p')	-79.3	-116.3	-107.5	-105.2	
(e)	$\text{CF}_2(\text{OH})_2 \rightarrow \text{CFO}(\text{OH}) + \text{HF}$					
ΔE	6-31G(d',p')	+8.4	+4.5	+9.8	+13.3	
	+	+3.3	-1.5	+1.0	+6.0	
E_a	6-31G(d',p')	+53.3	+40.6	+37.2	+45.1	
	+	+51.6	+39.6	+36.3	+44.1	
(f)	$\text{CFO}(\text{OH}) \rightarrow \text{CO}_2 + \text{HF}$					
ΔE	6-31G(d',p')	-10.0	-14.6	-4.0	-2.7	-11.3
	+	-15.5	-20.5	-12.9	-10.3	
E_a	6-31G(d',p')	+49.8	+32.7	+32.9	+40.7	+37.7
	+	+47.7	+30.7	+31.5	+39.2	

Table II. Characteristics of the transition state structure of the first H abstraction reaction: $\text{CH}_2\text{F}_2 + \text{OH} \rightarrow \text{CHF}_2 + \text{H}_2\text{O}$. The values shown here are obtained by using 6-31G(d',p') basis.

	HF	MP2	B3LYP	BHandHLYP	QCISD
R(C-H) (ang.)	1.30	1.20	1.17	1.24	1.23
R(H-O) (ang.)	1.20	1.34	1.43	1.25	1.27
θ (C-H-O) (deg.)	175	171	174	173	173
Imaginary ω (cm^{-1})	3253	2101	273	1865	1834

Table III. Key structural parameters of the CFO(OH) reactant and transition state toward HF leaving (see text and Fig. 1). The values are calculated at MP2/6-31+G(d',p') level of theory. Both structures are essentially of planar form. Length and angles are in angstrom and degree, respectively. Subscript "(C)" for O atom identifies the carbonyl type.

	CFO(OH)	transition state
R(C-O _(C))	1.19	1.16
R(C-O)	1.33	1.26
R(C-F)	1.37	1.80
R(O-H)	0.97	1.12
R(F-H)	2.14	1.30
θ (O _(C) -C-O)	127	153
θ (F-C-O)	110	88
θ (C-O-H)	109	86

Table IV. Calculated energetics for the branch path consisting of three elementary reactions (g)-(i). Entries in this table are similar to those in Table I, except for the absence of QCISD.

		HF	MP2	B3LYP	BHandHLYP
(g)	$\text{CHF}_2(\text{OH}) \rightarrow \text{CFOH} + \text{HF}$				
ΔE	6-31G(d',p')	+11.9	+7.2	+14.0	+17.0
	+	+7.3	+1.8	+6.1	+10.3
E_a	6-31G(d',p')	+60.6	+46.6	+43.3	+51.2
	+	+59.2	+46.2	+43.3	+51.0
(h)	$\text{CFOH} + \text{OH} \rightarrow \text{CFO} + \text{H}_2\text{O}$				
ΔE	6-31G(d',p')	+0.7	-17.2	-14.4	-10.4
	+	+0.5	-19.1	-15.9	-10.5
E_a	6-31G(d',p')	+30.2	+11.1	-1.7	+7.1
	+	+30.8	+11.4	-0.1	+9.6
(i)	$\text{CFO} + \text{OH} \rightarrow \text{CFO}(\text{OH})$				
ΔE	6-31G(d',p')	-84.2	-117.5	-114.0	-111.7
	+	-81.8	-115.5	-109.7	-107.0

Table V. Calculated energetics for the HF leaving with the reactive solvation by an extra H₂O, (j)-(l). $\Delta E'$ and E_a' are the stabilization energy by complex formation and activation energy from the complex, respectively (see text). $\Delta(E_a - E_a')$ is the lowering due to reactive solvation. Unit is in Kcal/mol.

		HF	MP2	B3LYP	BHandHLYP
(j)	[CF ₂ (OH) ₂ →CFO(OH)+HF]/H ₂ O				
$\Delta E'$	6-31G(d',p')	-8.9	-11.9	-12.7	-12.3
	+	-9.7	-9.8	-9.0	-9.5
E_a'	6-31G(d',p')	+38.0	+23.5	+19.3	+26.5
	+	+37.9	+23.2	+19.2	+26.4
$\Delta(E_a - E_a')$	6-31G(d',p')	-15.3	-17.1	-17.9	-18.6
	+	-13.7	-16.4	-17.1	-17.7
(k)	[CFO(OH)→CO ₂ +HF]/H ₂ O				
$\Delta E'$	6-31G(d',p')	-10.9	-13.0	-14.1	-13.9
	+	-9.6	-9.8	-9.0	-9.5
E_a'	6-31G(d',p')	+33.8	+18.2	+16.1	+22.7
	+	+33.8	+18.0	+16.5	+23.0
$\Delta(E_a - E_a')$	6-31G(d',p')	-16.0	-14.5	-16.8	-18.0
	+	-13.9	-12.7	-15.0	-16.2
(l)	[CHF ₂ (OH)→CFOH+HF]/H ₂ O				
$\Delta E'$	6-31G(d',p')	-9.2	-12.5	-13.2	-12.7
	+	-7.4	-9.4	-8.8	-9.2
E_a'	6-31G(d',p')	+42.0	+27.4	+23.2	+30.5
	+	+41.6	+26.7	+23.1	+30.0
$\Delta(E_a - E_a')$	6-31G(d',p')	-18.0	-19.2	-20.1	-20.7
	+	-17.6	-19.5	-20.2	-21.0

Table VI. Key structural parameters of the CFO(OH)/H₂O complex and transition state toward HF leaving (see text and Fig. 2). Length and angles (θ and φ) are in angström and degree, respectively. The values are calculated at MP2/6-31+G(d',p') level of theory, as is in Table III. Subscript "(W)" identifies the extra water molecule.

	complex	transition state
R(C-O _(C))	1.19	1.18
R(C-O)	1.32	1.24
R(C-F)	1.38	1.72
R(O-H)	0.98	1.27
R(F-H)	2.16	2.23
R(H-O _(w))	1.72	1.13
R(F-H _(w))	2.78	1.43
R(H _(w) -O _(w))	0.96	1.03
R(H' _(w) -O _(w))	0.96	0.96
θ (O _(C) -C-O)	129	146
θ (F-C-O)	110	105
θ (C-O-H)	110	113
θ (H-O _(w) -H _(w)'))	126	112
θ (H _(w) -O _(w) -H _(w)'))	106	109
φ (F-C-O-H)	0	-1
φ (F-H _(w) -O _(w) -H)	6	-3
φ (C-F-H _(w) -O _(w))	-8	1
φ (F-H _(w) -O _(w) -H _(w)'))	150	-116

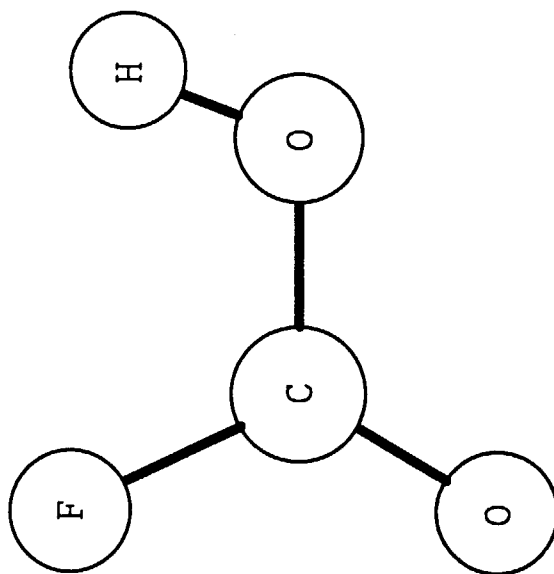
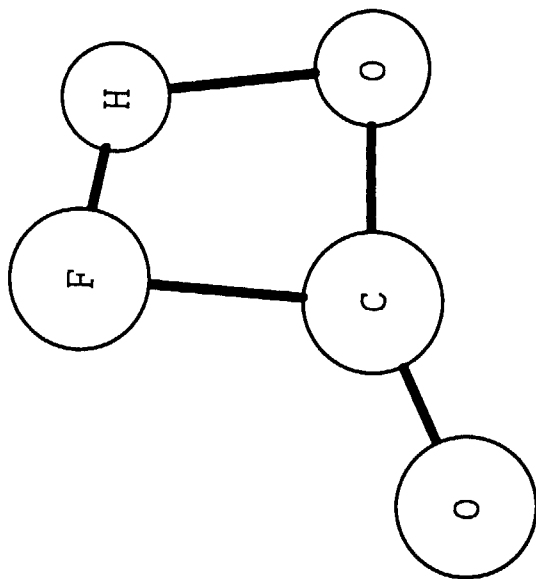


Figure 1 (b). Illustration for the transition state of $\text{CFO(OH)} \rightarrow \text{CO}_2 + \text{HF}$ reaction.

Figure 1 (a). Illustration for the reactant of $\text{CFO(OH)} \rightarrow \text{CO}_2 + \text{HF}$ reaction.

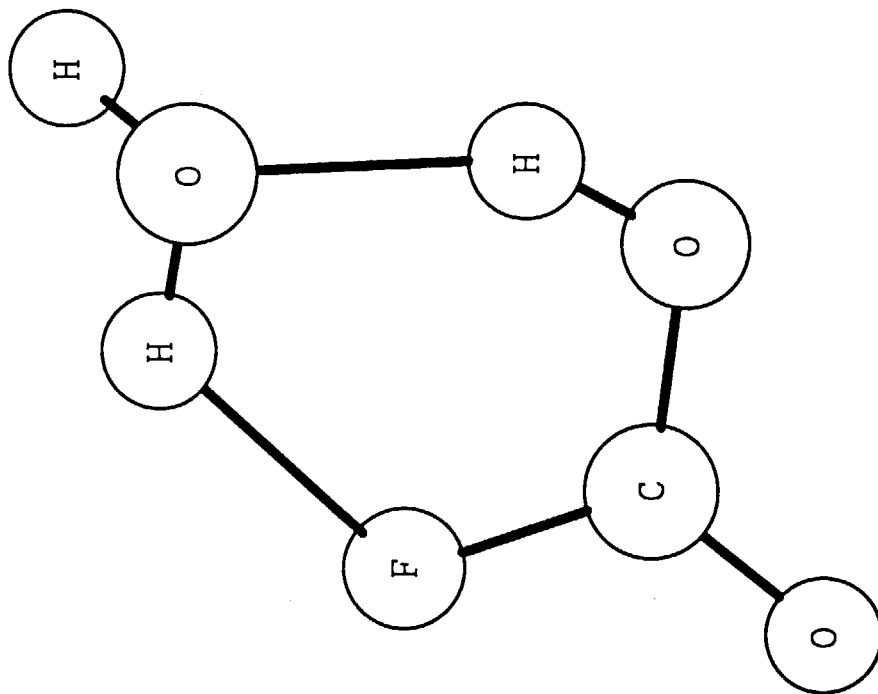


Figure 2 (b). Illustration for the transition state of $\text{CFO(OH)} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{HF}$ reaction through the reactive solvation by an H_2O .

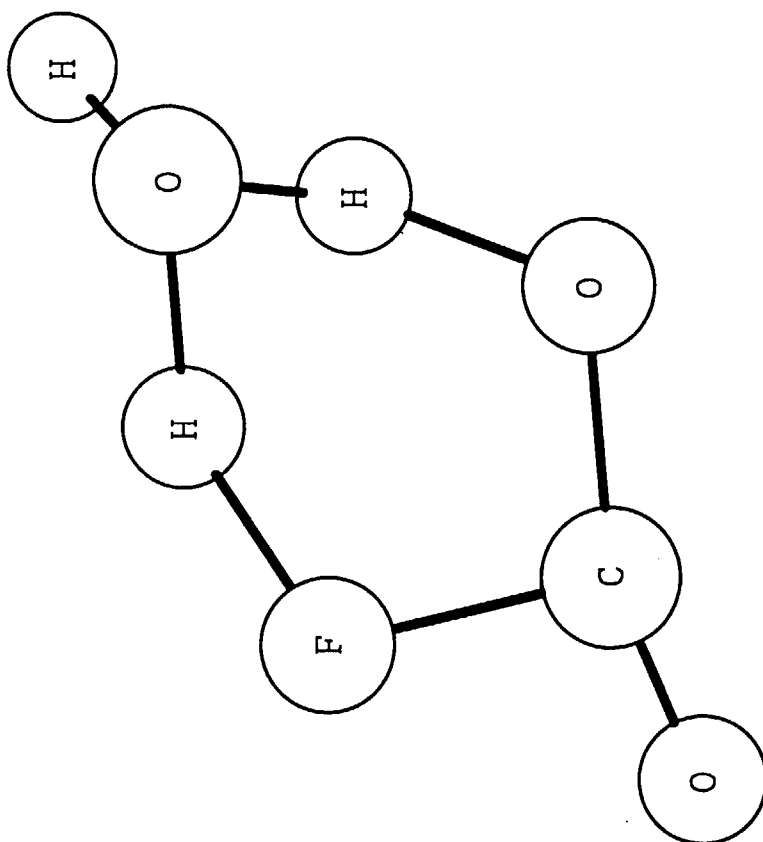


Figure 2 (a). Illustration for the $\text{CFO(OH)}/\text{H}_2\text{O}$ stable complex of $\text{CFO(OH)} + \text{CO}_2 + \text{HF}$ reaction through the reactive solvation by an H_2O . The six-membered ring does not have a planarity.

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国際単位系 (SI) と換算表

表1 SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質質量	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表3 固有の名称をもつSI組立単位

量	名称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	s ⁻¹
力	ニュートン	N	m·kg/s ²
圧力、応力	パスカル	Pa	N/m ²
エネルギー、仕事、熱量	ジュール	J	N·m
工率、放射束	ワット	W	J/s
電気量、電荷	クーロン	C	A·s
電位、電圧、起電力	ボルト	V	W/A
静電容量	ファラド	F	C/V
電気抵抗	オーム	Ω	V/A
コンダクタンス	ジーメンズ	S	A/V
磁束	ウェーバ	Wb	V·s
磁束密度	テスラ	T	Wb/m ²
インダクタンス	ヘンリー	H	Wb/A
セルシウス温度	セルシウス度	°C	
光度	ルーメン	lm	cd·sr
照射度	ルクス	lx	lm/m ²
放射能	ベクレル	Bq	s ⁻¹
吸収線量	グレイ	Gy	J/kg
線量当量	シーベルト	Sv	J/kg

表2 SIと併用される単位

名称	記号
分、時、日	min, h, d
度、分、秒	°, ', "
リットル	l, L
トン	t
電子ボルト	eV
原子質量単位	u

1 eV = 1.60218 × 10⁻¹⁹ J

1 u = 1.66054 × 10⁻²⁷ kg

表4 SIと共に暫定的に維持される単位

名称	記号
オングストローム	Å
バ	b
バ	bar
ガ	Gal
キュリー	Ci
レントゲン	R
ラ	rad
レ	rem

1 Å = 0.1 nm = 10⁻¹⁰ m

1 b = 100 fm² = 10⁻²⁸ m²

1 bar = 0.1 MPa = 10⁵ Pa

1 Gal = 1 cm/s² = 10⁻² m/s²

1 Ci = 3.7 × 10¹⁰ Bq

1 R = 2.58 × 10⁻⁴ C/kg

1 rad = 1 cGy = 10⁻² Gy

1 rem = 1 cSv = 10⁻² Sv

表5 SI接頭語

倍数	接頭語	記号
10 ¹⁸	エクサ	E
10 ¹⁵	ペタ	P
10 ¹²	テラ	T
10 ⁹	ギガ	G
10 ⁶	メガ	M
10 ³	キロ	k
10 ²	ヘクト	h
10 ¹	デカ	da
10 ⁻¹	デシ	d
10 ⁻²	センチ	c
10 ⁻³	ミリ	m
10 ⁻⁶	マイクロ	μ
10 ⁻⁹	ナノ	n
10 ⁻¹²	ピコ	p
10 ⁻¹⁵	フェムト	f
10 ⁻¹⁸	アト	a

(注)

- 表1-5は「国際単位系」第5版、国際度量衡局 1985年刊行による。ただし、1 eV および 1 uの値はCODATAの1986年推奨値によった。
- 表4には海里、ノット、アール、ヘクタールも含まれているが日常の単位なのでここでは省略した。
- barは、JISでは流体の圧力を表わす場合に限り表2のカテゴリーに分類されている。
- EC閣僚理事会指令ではbar, barnおよび「血圧の単位」mmHgを表2のカテゴリーに入れていない。

換算表

力	N (=10 ⁵ dyn)	kgf	lbf
	1	0.101972	0.224809
	9.80665	1	2.20462
	4.44822	0.453592	1

粘度 1 Pa·s (=N·s/m²) = 10 P (ポアズ) (g/(cm·s))

動粘度 1 m²/s = 10⁴ St (ストークス) (cm²/s)

圧	MPa (=10 bar)	kgf/cm ²	atm	mmHg (Torr)	lbf/in ² (psi)
	1	10.1972	9.86923	7.50062 × 10 ³	145.038
力	0.0980665	1	0.967841	735.559	14.2233
	0.101325	1.03323	1	760	14.6959
	1.33322 × 10 ⁻⁴	1.35951 × 10 ⁻³	1.31579 × 10 ⁻³	1	1.93368 × 10 ⁻²
	6.89476 × 10 ⁻³	7.03070 × 10 ⁻²	6.80460 × 10 ⁻²	51.7149	1

エネルギー・仕事・熱量	J (=10 ⁷ erg)	kgf·m	kW·h	cal (計量法)	Btu	ft·lbf	eV
	1	0.101972	2.77778 × 10 ⁻⁷	0.238889	9.47813 × 10 ⁻⁴	0.737562	6.24150 × 10 ¹⁶
	9.80665	1	2.72407 × 10 ⁻⁶	2.34270	9.29487 × 10 ⁻³	7.23301	6.12082 × 10 ¹⁹
	3.6 × 10 ⁶	3.67098 × 10 ⁵	1	8.59999 × 10 ⁵	3412.13	2.65522 × 10 ⁶	2.24694 × 10 ²⁵
	4.18605	0.426858	1.16279 × 10 ⁻⁶	1	3.96759 × 10 ⁻³	3.08747	2.61272 × 10 ¹⁹
	1055.06	107.586	2.93072 × 10 ⁻⁴	252.042	1	778.172	6.58515 × 10 ²¹
	1.35582	0.138255	3.76616 × 10 ⁻⁷	0.323890	1.28506 × 10 ⁻³	1	8.46233 × 10 ¹⁶
	1.60218 × 10 ⁻¹⁹	1.63377 × 10 ⁻²⁰	4.45050 × 10 ⁻²⁶	3.82743 × 10 ⁻²⁰	1.51857 × 10 ⁻²²	1.18171 × 10 ⁻¹⁹	1

- 1 cal = 4.18605 J (計量法)
 = 4.184 J (熱化学)
 = 4.1855 J (15 °C)
 = 4.1868 J (国際蒸気表)
- 仕事率 1 PS (仏馬力)
 = 75 kgf·m/s
 = 735.499 W

放射能	Bq	Ci
	1	2.70270 × 10 ⁻¹¹
	3.7 × 10 ¹⁰	1

吸収線量	Gy	rad
	1	100
	0.01	1

照射線量	C/kg	R
	1	3876
	2.58 × 10 ⁻⁴	1

線量当量	Sv	rem
	1	100
	0.01	1

