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A theoretical investigation of decomposition and reactivity of the atmospheric C₃F₇OCH₂O radical

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KEYWORDS

Decomposition; HFE-7000; IRC; Canonical transition state theory; Density function theory; Reaction mechanism **Abstract** The present theoretical investigation involves the ab initio quantum mechanical study of the decomposition and reactivity mechanism of the $C_3F_7OCH_2O$ radical that is formed from HFE-7000. Geometry of reactants, products and transition states were optimized at B3LYP and B3PW91 levels of theory with 6-311G(d,p) basis set. Five important pathways for decomposition and reactivity of $C_3F_7OCH_2O$ were investigated: reaction with atmospheric O_2 , reaction with atmospheric OH radical, C–O bond cleavage, H elimination and the migration of hydrogen from carbon to oxygen and then C–O bond cleavage with energy barriers of 4.3, 12.6, 17.1, 20.0 and 32.4 kcal mol⁻¹, respectively. Rate constants were calculated by utilizing the canonical transition state theory (CTST) in the range of 200–400 K and the Arrhenius diagrams have been plotted. From the obtained results, it was concluded that reaction with atmospheric O_2 is a dominant pathway for the consumption of the $C_3F_7OCH_2O$ radical in the atmosphere. Intrinsic reaction coordinate (IRC) calculation was performed to confirm the existence of transition state on the corresponding potential energy surface.

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1. Introduction

The ability of chlorofluorocarbons (CFCs) to deplete stratospheric ozone led to the use of hydrofluorocarbons (HFCs) as working fluids. There is no chlorine atom in HFC, therefore its ozone depletion potential is zero but unfortunately, it has

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greenhouse effect. Today, global warming is important, so reduction of HFCs as refrigerant is essential to air conditioners, heat pumps, and refrigeration devices. These devices cause the global warming both by the release of the refrigerant and by the emission of carbon dioxide and other greenhouse gases (Calm and Didion, 1997). Some HFCs have fairly significant global warming potential (Ali and Rajakumar, 2010; IPCC, 1996; Pinnock et al., 1995). Third-generation CFC alternative is the fluorinated ether series that was identified as hydrofluoroethers (HFEs). These species will be formed with the addition of an ether linkage to HFCs. For using as working fluids, the U.S. Environmental Protection Agency published a list of 37 compounds, 13 of which were fluorinated ethers. Identifying the unfavorable effect of CFC release into the atmosphere has led to an international effort to replace CFCs

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with environmentally acceptable suggestions (Farman et al., 1985; Molina and Rowland, 1974). HFEs are a kind of compounds which have been improved to replace CFCs in applications such as the carrier fluids for lubricant deposition, heat transfer agents for semiconductor and electronic manufacture and cleaning of electronic devices.

In the recent years, for the HFE effect on the environmental destruction, several experimental and theoretical studies have been conducted (Jia-yan et al., 2004; Newsted et al., 2002; Ninomiya and Kawasaki, 2000; Singh and Mishra, 2010, 2011; Singh et al., 2010). C₃F₇OCH₃ is a volatile liquid (bp 34 °C) with a vapor pressure of 523 torr at 25 °C and will probably be released into the atmosphere during its use (Christensen et al., 1998; Wallington et al., 1997). Before a large scale industrial use, an evaluation of the atmospheric chemistry and hence environmental impact of n-C₃F₇OCH₃ is needed. The atmospheric oxidation of C₃F₇OCH₃ will be initiated. A general tropospheric degradation mechanism of HFE-7000 is shown in Scheme 1. Like most HFEs, the atmospheric oxidation of C₃F₇OCH₃ will be initiated by reaction with OH radicals and then it reacts with O₂ rapidly to give a peroxy radical (C₃F₇OCH₂O₂) (Ninomiya and Kawasaki, 2000). Then, it can react with NO_X (X = 1, 2) or with tropospheric HO₂, finally leading to the formation of haloalkoxy radicals $(C_3F_7OCH_2O')$. The formed haloalkoxy radicals play an important role in the depletion of the most of the organic compounds in the atmosphere (Atkinson, 1990). We considered depletion of this haloalkoxy radical via five different pathways. It may participate in the unimolecular decomposition or react with O₂ or OH as shown following:

 $C_3F_7OCH_2O + O_2 \rightarrow C_3F_7OCHO + HO_2$ (1)

 $C_3F_7OCH_2O + OH \rightarrow C_3F_7OCHO + H_2O$ (2)

 $C_3F_7OCH_2O \rightarrow C_3F_7O + CH_2O \tag{3}$

 $C_3F_7OCH_2O \to C_3F_7OCHO + H \tag{4}$

$$C_3F_7OCH_2O \rightarrow CF_3OCHOH$$
 (5a)

The haloalkoxy radicals formed from HFEs play the significant role in the decomposition of a variety of organic compounds that are released into the atmosphere. Studying the fate of the $C_3F_7OCH_2O$ radical formed from HFE-7000 is needed from the viewpoint of understanding its role in atmospheric chemistry.

 $C_3F_7OCHOH \rightarrow C_3F_7 + OCHOH$

In the present study, only five pathways for the composition and decomposition mechanism of the $C_3F_7OCH_2O$ radical will be discussed. Rate constants for the five considered channels are calculated by using CTST. Relation of the rate constants to temperature is determined. Transition states on the corresponding potential energy surfaces and energy barriers are determined. Smooth transition from the reactant to the product on the corresponding potential energy surface is ascertained by doing IRC calculation.

2. Calculation methods

Geometry optimization of the reactants, products and transition states have been obtained using the B3LYP/6-311G(d,p) method (Becke, 1993; Lee et al., 1988). Potential energy surface of C₃F₇OCH₂O was scanned around the C₁-O₂ bond (presented in Fig. 1) to ensure that the obtained optimized structure is the most stable structure. Therefore, the nature of different stationary points on the potential energy in 72 points was scanned. Fig. 1 shows that the concern state has the minimum potential energy level. Optimized structures were displayed using GaussView (Roy et al., 2007). The vibrational frequencies were attained in the same level of theory for the optimized reactants, products and transition states. No virtual frequencies of all stationary points were identified (NI-MAG = 0). Transition states were defined by the presence of only one virtual frequency (NIMAG = 1). To ascertain that the identified transition states connect reactants and products smoothly, IRC calculations were done at B3LYP/6-311G(d,p) level (Gonzalez and Schlegel, 1990; Raghavachari et al., 1989). We used the B3PW91/6-311G(d,p) method to evaluate the accuracy of B3LYP/6-311G(d,p). To obtain more reliable energies of reactants and transition states, we didsingle



Scheme 1 Tropospheric degradation of HFE-7000.



Figure 1 Scan chart of $C_3F_7OCH_2O$ potential energy surface around the C_1-O_2 bond.

point calculations at QCISD(T)/6-31G(d,p) level of theory to refine energies of the reactants and transition states. All calculations were performed with the Gaussian 03 program (Frisch et al., 2004).

3. Results and discussion

3.1. Reactivity and decomposition of the $C_3F_7OCH_2O$ radical

This study is focused on the mechanism of reactivity and decomposition of HFE-7000. We considered five possible pathways for reactivity and decomposition. Transition states which were studied on the potential energy surface of reactions (1)-(4), (5a), and (5b) were labeled as TS1, TS2, TS3, TS4, TS5(a) and TS5(b), respectively. The optimized geometries of reactants, transition states and products using the density functional theory (Parr and Yang, 1989) at the B3LYP/6-311G(d,p) level of theory are shown in Fig. 2. The C-H bond length of TS1, TS2, TS4 and TS5(a) will change from 1.103 to 1.227 Å (approx. 11%), 1.103 to 1.241 Å (approx. 13%), 1.103 to 1.742 Å (approx. 58%) and 1.103 to 1.283 Å (approx. 16%), respectively. The C-O bond length which was gained by the optimization structure of other transition states indicated that C-O bond in TS3 and TS5(b) increases from 1.458 to 1.981 Å (approx. 36%) and 1.348 to 1.769 Å (approx. 31%), respectively.

The vibrational frequency values at the level of B3LYP/6-311G(d,p) for all optimized structures are collected in Table 1. These results reveal that the reactants and products in a stable minimum potential energy surface were marked with only positive vibrational frequencies. Transition states of TS1, TS2, TS3, TS4, TS5(a) and TS5(b) were characterized by only a negative frequency which were 1023, 1461, 376, 957, 2033 and 602 cm⁻¹, respectively. The IRC calculations at the B3LYP/ 6-311G(d,p) level were used to confirm the connection between the designated transition states and the reactants and products. The minimum energy path was determined by IRC calculation using Gonzalez–Schlegel steepest descent path (Gonzalez and Schlegel, 1990; Raghavachari et al., 1989) in the mass-weighted Cartesian coordinates with a step-size of 0.03 ($amu^{1/2}$ -bohr) for each channel of decomposition. The IRC plots for all transition states are shown in Figs. 3 and 4 that clearly showed a smooth transition from reactants to products on the potential energy surface. Zero-point energy was obtained by the B3LYP/6-311G(d,p) method and corrected with scale factor of 0.962 (Uvdal and Andersson, 2005).

Total corrected zero-point energies using the standard method B3LYP/6-311G(d,p) for the different species are recorded in Table 2. The results of the energy barrier in Table 3 show that depending on the level of theory, the energy barrier for C_1 – O_2 bond cleavage in reactions (3) and (5b) is in the range of 17.1–19.2 and 11.9–12.4 kcal mol⁻¹, respectively and for C–H bond scission in reactions (1), (2), (4), and (5a) is 4.3–4.7, 12.6–13.3, 20.0–20.0 and 30.8–32.4 kcal mol⁻¹, respectively. The B3LYP/6-11G(d,p) method yields energy barriers 17.1 and 11.9 kcal mol⁻¹ for C–O bond cleavage in reactions (3) and (5b), respectively and bond scission for C–H in reactions (1), (2), (4), and (5a) is 4.3, 12.6, 20.0 and 32.4 kcal mol⁻¹, respectively.

It is obvious from Fig. 5 that the reaction (2) is dominant in comparison with other pathways for consumption of the $C_3F_7OCH_2O$ radical. Also, for open shell systems unrestricted calculations were performed and spin contamination was found to be negligible.

3.2. Rate constants

The rate constants of decomposition and reactivity of the $C_3F_7OCH_2O$ radical were calculated using CTST and given by the following (Truhlar et al., 1996):

$$k = \Gamma(T) \frac{k_{\rm B}T}{h} \frac{Q_{\rm TS}^{\neq}}{Q_{\rm R}} \exp \frac{-\Delta E}{RT}$$
(6)

where, $k_{\rm B}$ is the Boltzmann constant and *h* is Plank's constant. *T* is the temperature in Kelvin, $Q_{\rm TS}^{\neq}$ and $Q_{\rm R}$ are partition functions of the transition states and the reactants, respectively. ΔE



Figure 2 Optimized geometries of reactants, products, and transition states involved in the decomposition pathways of the $C_3F_7OCH_2O$ radical obtained at B3LYP/6-311G(d,p) level.

is the barrier height (including zero-point energy), and *R* is the universal gas constant. The value of $\Gamma(T)$ was calculated by using Wigner's method and given by the following (Wigner, 1932):

$$\Gamma(T) = 1 + \frac{1}{24} \left(\frac{hv^{\neq}}{k_B T} \right) \tag{7}$$

in which v^{\neq} is the imaginary frequency associated with the transition state. Wigner's tunneling formula only has one variable, the imaginary frequency v^{\neq} . For high temperature or small v^{\neq} , the quantum tunneling effect is a small deviation from classical behavior, so the tunneling correction factor can be obtained by Eq. (7).

Table 1 Un	scaled vibrational frequencies of reactant, products, and transition states involved in C ₃ F ₇ OCH ₂ O decomposition calculated at B3LYP/6-311G(d,p) level of theory.
Species	Vibrational frequencies (cm ⁻¹)
TS1	1023i, 23, 38, 45, 77, 87, 124, 162, 188, 209, 223, 232, 234, 291, 331, 350, 374, 458, 501, 511, 532, 561, 598, 608, 656, 663, 748, 775, 909, 1017, 1077, 1117, 1131, 1156, 1180, 1222, 1229, 1237, 1301, 1326, 1342, 1377, 1546, 1694, 2969
TS2	1416i,15, 25, 50, 80, 101, 163, 196, 221, 230,243, 264, 291, 331, 349, 374, 459, 494, 510, 532, 557, 596, 608, 654, 676, 748, 796, 925, 978, 1030, 1122, 1127, 1143, 1172, 1181, 1125, 1129, 1259,1288, 1327, 1341, 1375, 1891, 3015, 3628
TS3	376i, 18, 26, 61, 82, 101, 167, 218, 226, 234, 289, 327, 341, 368, 388, 460, 527, 532, 560, 603, 637, 656, 726, 769, 962, 988, 1057, 1076, 1104, 1175, 1177, 1221, 1227, 1236, 1319, 1348, 1660, 2707, 3006
TS4	957i, 18, 60, 84, 104, 151, 198, 220, 230, 231, 291, 331, 347, 374, 445, 483, 512, 531, 532, 578, 615, 634, 663, 753, 814, 957, 1029, 1070, 1137, 1146, 1160, 1184, 1225, 1233, 1320, 1342, 1367, 1726, 3038
TS(5a)	2033i, 26, 59, 83, 94, 149, 207, 223, 230, 237, 292, 332, 347, 375, 454, 507, 532, 554,579, 607, 646, 671, 748, 807, 941, 987, 1090, 1119, 1143, 1155, 1183, 1210, 1230, 1235, 1324, 1342, 1368, 2368, 3120
TS(5b)	602i, 24, 42, 61, 92, 127, 188, 206, 226, 232, 281, 324, 339, 369, 391, 415, 449, 515, 531, 598, 617, 643, 669, 719, 767, 999, 1091, 1149, 1180, 1202, 1207, 1252, 1275, 1303, 1316, 1349, 1507, 3102, 3822
C ₃ F ₇ OCH ₂ O	17, 45, 65, 94, 127, 209, 218, 227, 279, 290, 330, 342, 373, 442, 517, 534, 536, 591, 629, 659, 728, 759, 831, 883, 1018, 1093, 1118, 1140, 1167, 1182, 1209, 1226, 1242, 1329, 1338, 1349, 1395, 2933, 2967
C ₃ F ₇ OCHOH	18, 52, 67, 99, 132, 210, 221, 231, 271, 291, 331, 344, 373, 439, 445, 515, 535, 537, 589, 628, 658, 733, 770, 883, 936, 1045, 1089, 1137, 1166, 1183, 1201, 1225, 1234, 1318, 1333, 1348, 1413, 3205, 3793
C ₃ F ₇ OCHO	18, 60, 87, 106, 197, 200, 222, 232, 233, 291, 332, 351, 375, 464, 511, 532, 565, 613, 631, 665, 753, 828, 967, 1025, 1069, 1139, 1145, 1170, 1186, 1224, 1235, 1319, 1345, 1400, 1868, 3077
C_3F_7O	22, 77, 158, 215, 225, 266, 301, 320, 328, 364, 440, 523, 540, 551, 600, 615, 655, 753, 901, 985, 1115, 1122, 1187, 1205, 1240, 1246, 1329
C_3F_7	35, 66, 144, 207, 219, 265, 322, 345, 379, 449, 527, 565, 604, 627, 723, 776, 1012, 1091, 1166, 1209, 1215, 1282, 1343, 1362
OCHOH	632, 700, 1058, 1131, 1310, 1411, 1837, 3042, 3737
CH ₂ O	1202, 1270, 1539, 1827, 2868, 2918
O_2H	1164, 1428, 3611
H ₂ O	1638, 3813, 3910
O ₂	1626
OH	3705
Н	-



Figure 3 IRC plots performed for transition states TS1 and TS2 obtained during thermal and oxidative decomposition of C₃F₇OCH₂O.



Figure 4 IRC plots performed for transition states TS3, TS4, TS5(a) and TS5(b) obtained during thermal and oxidative decomposition of $C_3F_7OCH_2O$.

For correcting of the Wigner approximation, Eckart used an analytical potential function fitted by the energies of reactants, products and transition states and the imaginary frequency (Eckart, 1930):

$$V = \frac{Ae^{2\pi x}/L}{1 + e^{2\pi x}/L} + \frac{Be^{2\pi x}/L}{\left(1 + e^{2\pi x}/L\right)^2}$$
(8)

where x is the reaction coordinate, and A, B, and L are parameters calculated from forward and reverse barrier heights and the imaginary frequency. The transmission coefficient is computed by solving the Schrodinger equation to obtain (Zhang and Dibble, 2011):

$$K(E) = \frac{\cosh(a+b) - \cosh(a-b)}{\cosh(a+b) - \cosh(d)}$$
(9)

Equations for parameters a, b, and d in Eq. (9) can be found in the literature (Eckart, 1930). Using K(E) and Boltzmann distribution leading to the temperature dependent tunneling correction factor:

$$\Gamma(T) = \frac{\exp(E_0/k_B T)}{k_B T} \int_0^\infty K(E) \exp(E_0/k_B T) dE$$
(10)

Because of their simplicity, the Wigner and asymmetric Eckart tunneling corrections (one-dimensional tunneling corrections) are often used however they can insert large errors. Multidimensional tunneling corrections require energies, gradients and Hessians along the reaction path.

Multidimensional tunneling treatments refer to the following two important items: (1) the contribution of vibrational energies from all vibrational modes that changes the shape of the potential for tunneling; (2) the coupling between the reaction coordinate and orthogonal vibrational modes, known

Method	DFT		DFT + ZPE	
	B3LYP/6-311G(d,p)	B3PW91/6-311G(d,p)	B3LYP/6-311G(d,p)	B3PW91/6-311G(d,p)
TS1	-1153.531134	-1153.091521	-1153.460058	-1153.020445
TS2	-1078.910346	-1078.499602	-1078.832061	-1078.421318
TS3	-1003.143603	-1002.761030	-1003.078437	-1002.695863
TS4	-1003.135542	-1002.756254	-1003.073884	-1002.694595
TS(5a)	-1003.118972	-1002.742225	-1003.054165	-1002.677418
TS(5b)	-1003.153986	-1002.773869	-1003.086872	-1002.706755
$C_3F_7OCH_2O + O_2$	-1153.539443	-1153.100385	-1153.466959	-1153.027901
$C_3F_7OCH_2O + OH$	-1078.929180	-1078.519574	-1078.852173	-1078.442567
$C_3F_7OCHO + O_2H$	-1153.592858	-1153.152453	-1153.519145	-1153.078740
$C_3F_7OCHO + H_2O$	-1079.089898	-1078.681101	-1079.009260	-1078.600463
C ₃ F ₇ OCH ₂ O	-1003.174652	-1002.795333	-1003.105766	-1002.726446
C ₃ F ₇ OCHOH	-1003.182851	-1002.804544	-1003.112727	-1002.734420
$C_3F_7OCHO + H$	-1003.144605	-1002.766196	-1003.084482	-1002.706073
$C_3F_7O + CH_2O$	-1003.147087	-1002.745912	-1003.083553	-1002.701472
$C_3F_7 + OCHOH$	-1003.185135	-1002.805275	-1003.117654	-1002.737794

Table 2Zero-point corrected total energy for species involved in C–O bond scission from $C_3F_7OCH_2O$ decomposition. Geometriesare optimized at B3LYP/6-311G(d,p) level (unit: hartree).

Table 3 Calculated energy barriers for reaction (1), (2), (3), (4), (5a), and (5b) in kcal mol⁻¹.

Reaction	DFT		DFT + ZPE	DFT + ZPE	
	B3LYP/6-311G(d,p)	B3PW91/6-311G(d,p)	B3LYP/6-311G(d,p)	B3PW91/6-311G(d,p)	
(1)	5.2	5.6	4.3	4.7	
(2)	11.8	12.5	12.6	13.3	
(3)	19.5	20.5	17.1	19.2	
(4)	24.5	24.5	20.0	20.0	
(5a)	34.9	33.3	32.4	30.8	
(5b)	13.0	13.5	11.9	12.4	

as the corner-cutting effect, which reveals itself by the curvature of the reaction path. This shortens the tunneling path and increases the tunneling (Zhang and Dibble, 2011). The first aspect was included by Skodje and Truhlar in the zero-curvature tunneling (ZCT) approximation (Skodje and Truhlar, 1981) that seriously underestimates tunneling corrections to rate constants. The small- and large-curvature tunneling (SCT and LCT) approximations take into account both item (1) and (2) with respect to small and large curvature, respectively. ZCT, SCT and LCT approximations are beyond the scope of this work.

We prepared a M-file for MATLAB and calculated tunneling correction with the Eckart method, but achieved unusual and sophisticated results. For example, for path (1), tunneling correction of 7 was at 400 K, 1200 at 300 K and 3.5×10^7 at 200 K!, for path (2), tunneling correction of 0.05 was at 400 K, 1.94 at 300 K and 1.8×10^3 at 200 K!. Arnaut et al. confirmed our results (Arnaut et al., 2007). So, we concluded that this method for low temperatures is not correct and the Eckart barrier permeability tends to overestimate the tunneling corrections at lower temperatures for our reactions.

The reactant always has more internal rotors than the saddle point, so correction coefficient related to hindered rotation does not exceed unity and decreases the computed rate constant. The hindered rotor effect is most important at low temperatures (Zhang and Dibble, 2011). At high temperature correction coefficient is closer to unity for the reaction with internal rotation in the transition state than the other reactions with the absence of internal rotation in the transition state. Accurate rate constants require proper treatment of partition functions for transition states and reactants. Because, internal rotations are very anharmonic, for rate constants calculation that deal with them as harmonic vibrations may lead to large errors. The hindered rotor partition function for each torsional mode requires solving the Schrodinger equation. The hindrance potential must be computed by a relaxed scan at the same levels of theory for which calculations have been done. Rate constants must be computed using the HO approximation and were corrected for hindered rotor effects. Correction coefficient related to hindered rotation is beyond the scope of the present work and we neglected this correction. For a comprehensive discussion see Ayala and Schlegel, 1998; Zhang and Dibble, 2011.

The rate coefficients were obtained in the temperature range of 200–400 K with an interval of 20 K. These calculations were done for all eleven transition states. The partition functions for the respective transition states and reactants were obtained from the vibrational frequency calculation performed at B3LYP/6-311G(d,p) level. The rate constant for C–O bond cleavage in TS3 of $C_3F_7OCH_2O$ decomposition was about 3.73×10^{-6} at 298 K and 1 atm. Similar calculation was performed for H-elimination that occurred via reaction (1), (2), (4), and (5a) involving TS1, TS2, TS4, TS5(a) as the transition states yield rate constants 9.17 × 10⁻³, 2.56, 1.11 × 10³ and 2.21 × 10⁻⁹ s⁻¹ at 298 K and 1 atm, respectively.



Figure 5 Relative energy diagram in kcalmol⁻¹ for the thermal and oxidative decomposition of C₃F₇OCH₂O at B3LYP/6-311G(d,p) level. The values in parentheses are for QCISD(T)/6-31G(d,p) level of theory.

Moreover, the rate constants in the temperature range of 200–400 K were also calculated and the results are depicted in Fig. 6. It shows that decomposition and reactivity rate increase with increasing temperature for the $C_3F_7OCH_2O$ radical. Also, for 200–225 K, path (2) has the highest rate constant and for 225–400 K path (4) is a dominant reaction. Therefore, dominant reaction for the degradation of the $C_3F_7OCH_2O$ radical in the atmosphere depends on atmospheric temperature. An extensive literature survey reveals no experimental or theoretical data to compare the calculated val-



Figure 6 Arrhenius plot of all considered paths over the temperature range of 200–400 K.

ues with them. As a conclusion it should be said that the present study may provide useful information for the future investigation in this research area.

4. Conclusions

Geometry of reactants, products and transition states was optimized at B3LYP and B3PW91 levels of theory with 6-311G(d,p) basis set. Zero point energy calculation at B3LYP/6-311G(d,p) level was performed. Single point calculations at QCISD(T)/6-31G(d,p) level of theory were done to refine energies of the reactants and transition states. Five important channels of reactivity and decomposition of the C₃F₇OCH₂O radical were considered in detail. The energy barriers for the channels (1), (2), (3), (4), (5a), and (5b) obtained were 11.1, 7.2, 28.3, 18.1, 32.4 and 19.9 kcal mol⁻¹, respectively. Rate constants for the above five considered pathways were calculated by utilizing CTST tunneling corrections by Wigner and asymmetric Eckart methods at 298 K and 1 atm and found to be 9.17×10^{-3} , 2.56, 3.73×10^{-6} , 1.11×10^{3} and 2.21×10^{-9} , respectively. The rate constants in the range of 200-400 K were also obtained. The results showed that decomposition and reactivity rate increase with increasing temperature. Also, for 200-225 K, path (2) has the highest rate constant but for 225-400 K path (4) is a dominant reaction. Therefore, dominant reaction for degradation of the C₃F₇O-CH₂O radical in the atmosphere depends on atmospheric temperature.

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