



Theoretical studies on kinetics, mechanism and thermochemistry of gas-phase reactions of HFE-449mec-f with OH radicals and Cl atom



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ABSTRACT

A theoretical study on the mechanism and kinetics of the gas phase reactions of $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ (HFE-449mec-f) with the OH radicals and Cl atom have been performed using meta-hybrid modern density functional M06-2X using 6-31+G(d,p) basis set. Two conformers have been identified for $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ and the most stable one is considered for detailed study. Reaction profiles for OH-initiated hydrogen abstraction are modeled including the formation of pre-reactive and post-reactive complexes at entrance and exit channels. Our calculations reveal that hydrogen abstraction from the $-\text{CH}_2$ group is thermodynamically and kinetically more facile than that from the $-\text{CHF}$ group. Using group-balanced isodesmic reactions, the standard enthalpies of formation for HFE-449mecf and radicals generated by hydrogen abstraction, are also reported. The calculated bond dissociation energies for C–H bonds are in good agreement with experimental results. The rate constants of the two reactions are determined for the first time in a wide temperature range of 250–450 K. The calculated rate constant values are found to be 9.10×10^{-15} and $4.77 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reactions with OH radicals and Cl atom, respectively. At 298 K, the total calculated rate coefficient for reactions with OH radical is in good agreement with the experimental results. The atmospheric life time of HFE-449mec-f is estimated to be 0.287 years.

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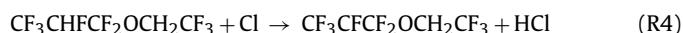
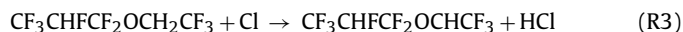
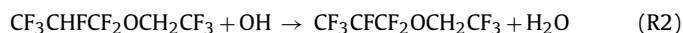
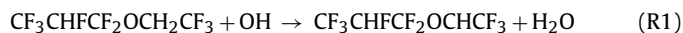
1. Introduction

In order to reduce the adverse effect of chlorofluorocarbons (CFCs) toward Earth's stratospheric ozone layer their commercial production is banned as per the Montreal protocol and an international effort has gone into finding environmentally more acceptable alternatives to replace chlorofluorocarbons [1,2]. In this context, a number of CFCs replaceable compound such as hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) have been developed for short-term use because of their non-reliability toward protection of ozone layer. Volatile organic compounds like hydrofluoroethers (HFEs) are designed and widely recommended as a third generation replacement for CFCs, HFCs and HCFCs in applications such as cleaning of electronic equipments, heat transfer fluid in refrigerators, lubricant deposition and foam blowing agents [3,4]. Hydrofluoroethers do not contain chlorine and bromine atoms that cause the ozone depletion [5]. In addition the rate constant for the reaction of HFEs with OH radical suggest that their atmospheric lifetime should be relatively short

and thus HFEs appear to have less impact for the global warming [6]. Like most volatile organic compounds, HFEs containing C–H bonds are removed from the troposphere by reactions with atmospheric oxidants, OH radicals being the most dominant oxidant. Although the reaction with OH radicals constitutes the main tropospheric sink for degradation of halogenated ethers, the chlorine atom also plays an important role in the atmospheric chemistry [7]. In fact, chlorine atoms have been monitored in concentrations in the order of $10^4 \text{ molecule cm}^{-3}$ over the marine boundary layer [8]. The tropospheric oxidation of HFEs is known to produce corresponding hydrofluorinated esters (FESs) [9]. The degradation of FESs produce environmentally burdened product like trifluoroacetic acid (TFA) and COF_2 . It has been reported that TFA as detected in surface waters has no known sink apart from rainwater and this species may impact on agricultural and aquatic systems [10]. Hence it is important to study the kinetics and mechanistic degradation pathways of HFEs in troposphere for complete assessment of its atmospheric chemistry as well as its impact on global warming and climate change. Therefore, much attention has been paid recently on studying the reactivity of HFEs with OH radicals and Cl atom [11–22]. HFE-449mec-f ($\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$), a C-5 HFE, which is alternative cleaning solvent having dissolving capability of fluoro oils. It is synthesized by Natalia et al.

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[23] by trifluoroethoxylation of hexafluoropropene with 2,2,2-trifluoroethanol (TFE) using an alkali metal fluoride catalyst. Later, Kim et al. [24] also obtained $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$ in high yield and selectivity from the hydroalkoxylation reaction of hexafluoropropylene and 2,2,2-trifluoroethanol conducted in the presence of an imidazolium-based ionic liquid catalyst. In present work, we have studied the mechanism and kinetics of H-abstraction reaction from $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$ with OH radicals and Cl atom using DFT methods. Our calculation suggests that one reaction channel from $-\text{CH}_2$ and one reaction channel from $-\text{CHF}$ groups are feasible for the $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3 + \text{OH}/\text{Cl}$ reactions as given below.



Two experimental studies were reported for reactions (R1) and (R2) by Chen et al. [11] and Wilson et al. [12]. Chen et al. [11] first studied the hydrogen abstraction channel of these reactions using a relative rate method in the temperature range of 268–308 K and the experimental rate constants were reported as $(9.0 \pm 0.02) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Based on the their SAR results, it has been reported that hydrogen abstraction from $-\text{OCH}_2$ (R1) is more reactive than the same from the $-\text{CHF}$ group (R2) [11]. Subsequently, Wilson et al. [12] performed another experimental study by using relative rate methods and they also reported a rate constants value as $k(\text{OH} + \text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3) = 9.17 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. However, both these experimentally measured values are in reasonable agreement with that was estimated empirically by Urata et al. ($1.54 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) on the basis of bond dissociation enthalpies (BDE's) of the C–H bond by using the artificial neural network (ANN) technique [13]. To the best of our knowledge, no experimental study has been reported for hydrogen abstraction by Cl atom with $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$. Thus, the question arises: which is the major channel for the $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3 + \text{Cl}$ reactions? Are the reaction mechanisms similar to those of the $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3 + \text{OH}$ reactions? In addition, no experimental information is available on the branching ratios of the title reactions. Moreover, experimental studies provided only the total rate constant and it is difficult to predict the detailed mechanism and thermo chemistry. Thus, for better understanding of mechanistic pathways, kinetics and thermochemistry we must rely on quantum chemical methods. This work provides the first kinetic data for the reactions of $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$ with Cl atom at 298 K. The data obtained in this work were used to estimate the effective lifetime in the troposphere of the studied compound. To the best of our knowledge, this is the first detailed theoretical study on gas-phase reactions with OH radicals and Cl atom of hydrofluoroether containing five carbon atoms. Bond dissociation energies (BDEs) of the breaking C–H bonds are known to be strongly correlated with the observed reactivity trend for the hydrogen abstraction reaction, and the ether linkage ($-\text{O}-$) is important for the reactivity of the hydrofluoroethers. Thus, we present BDE of the two types of C–H bonds in $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$. In addition, the knowledge of accurate enthalpy of formation ($\Delta_f H^\circ_{298}$) for $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$, $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCHCF}_3$ and $\text{CF}_3\text{CFCF}_2\text{OCH}_2\text{CF}_3$ radicals is of vital importance for determining the thermodynamic properties and atmospheric modeling. However, no theoretical or experimental study on standard enthalpy of formation has been reported so far for these species. Here, we predict the enthalpies of formation using isodesmic reactions at M06-2X/6-31+G(d,p) level. The tropospheric atmospheric lifetime of this compound is also report.

Table 1

Reaction enthalpies and free energies of reactions calculated at M06-2X/6-31+G(d,p) and M06-2X/6-311++G(d,p) (with in parenthesis) level of theories. All values are in kcal mol⁻¹.

Reaction channels	$\Delta_r H^\circ_{298}$	$\Delta_r G^\circ_{298}$
Reaction (R1)	–15.65 (–15.83)	–17.19 (–17.38)
Reaction (R2)	–13.71 (–13.89)	–15.60 (–15.78)
Reaction (R3)	0.67 (–0.22)	–2.10 (–3.00)
Reaction (R4)	2.61 (1.71)	–0.50 (–1.40)

2. Computational methods

Geometry optimization of the species were made at the M06-2X [25] level of theory using 6-31+G(d,p) basis set. The 6-31+G(d,p) basis set was used because the same basis set was used for developing the model functional. Previous works have shown that the M06-2X hybrid density functional provides reliable results for thermo chemistry and kinetics [26–29]. The M06-2X is a hybrid meta-DFT method with a high percentage of HF exchange, and it has broadest applicability with average mean absolute errors of about 1.3, 1.2, and 0.5 kcal mol⁻¹ for thermochemical, barrier height and noncovalent interaction calculations [30], respectively. Since the formation of pre- and post-reaction complex modifies the shape of potential energy surface for the hydrogen abstraction reactions by OH radicals and hence affects the tunneling factor [19,22]. As a result the rate constant for hydrogen abstraction also changes. Thus we also validated pre- and post-reactive complexes along the entry and exit of the reaction path. In order to determine the nature of different stationary points on the potential energy surface, vibrational frequencies calculations were performed using the same level of theory at which the optimization was made. Further, to ascertain that the identified transition states connect reactant and products smoothly, intrinsic reaction coordinate (IRC) calculations [31] were also performed at the M06-2X/6-31+G(d,p) level. Single point energy calculations were performed at M06-2X using 6-311++G(d,p) basis set. The 6-311++G(d,p) is a valence triple- ζ quality basis set with single polarization and double diffuse functions on all atoms. All calculations were performed with the Gaussian 09 suite of program [32].

3. Results and discussion

Geometry optimization of $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$ molecule predicts two possible conformers (SC1 and SC2) and their structures are shown in Fig. 1. The two conformers differ mainly in the orientation of C3–H2 bond relative to the C–C–O–C backbone. The C3–C1–O1–C2 dihedral angle is 172.90° in the SC1 conformer; whereas the same is 82.35° in the SC2 conformer. Quantum mechanical analysis on the energies of these two conformers shows that SC1 conformer is the most stable conformation of the $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$ molecule. Hence the most stable conformer SC1 is considered for detailed study and thus the transition states are located from SC1 conformer. The calculated enthalpy of reactions ($\Delta_r H^\circ_{298}$) and reaction free energies ($\Delta_r G^\circ_{298}$) at 298 K for the reactions of $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$ with OH radicals and Cl atom are recorded in Table 1. Thermal corrections to the energy at 298 K were included in the determination of these thermodynamic functions. The $\Delta_r G^\circ_{298}$ values for $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3 + \text{OH}$ reactions are much more negative than that for the $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3 + \text{Cl}$ reactions indicating the former reaction is thermodynamically more favorable than the latter. The enthalpy of reaction, ($\Delta_r H^\circ_{298}$) values given in Table 1 for (R1) and (R2) shows that both the reactions are significantly exothermic in nature and hydrogen abstraction from the $-\text{CH}_2$ group is more exothermic than that from the $-\text{CHF}$ group. There are two potential hydrogen abstraction sites of $\text{CF}_3\text{CHF}(\text{CF}_2)\text{OCH}_2\text{CF}_3$, namely the $-\text{CH}_2$ and $-\text{CHF}$ group. It can be

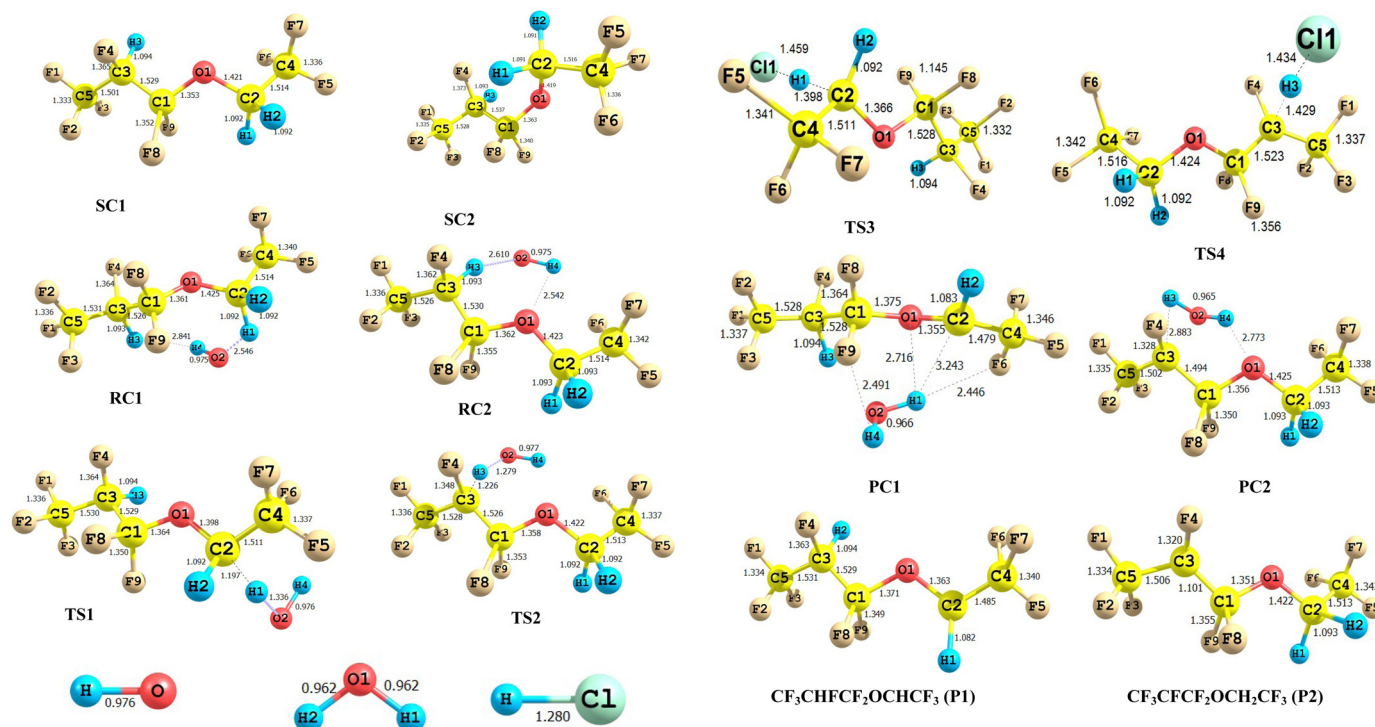


Fig. 1. Optimized geometries of reactants, reactant complexes, transition states, product complexes and products involved in the H atom abstraction reactions of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ by OH radicals and Cl atom at M06-2X/6-31+G(d,p) level. Bond lengths are in Angstroms.

seen from the geometrical parameters and stereographical orientation the hydrogen atoms in the $-\text{CH}_2$ group are equivalent. Two transition states (TS) are therefore located for each of the two reactions $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3 + \text{OH}$ and $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3 + \text{Cl}$; one TS for H-abstraction from the $-\text{CH}_2$ group (TS1 for reaction with OH and TS3 for reaction with Cl atom) and one TS for the same from the $-\text{CHF}$ group (TS2 for reaction with OH and TS4 for reaction with Cl).

In the entrance channel for reactions of hydrogen abstraction by OH radicals (R1 and R2), pre-reactive complexes (RC1 and RC2) have been located in the present work. In the exit channels, there are also product complexes occurring before the release of the final products, which are labeled as PC1 and PC2. In pre-reactive complexes RC1 and RC2, hydrogen bonds are formed between the oxygen atom of hydroxyl radical with the hydrogen atom in $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ with bond distances of 2.546 and 2.610 Å, respectively while the other bond lengths are very close to those in equilibrium structures. At the same time, the post-reaction hydrogen bonded complexes (PC1 and PC2) with energy less than the corresponding products are located at the exits of the reaction channels (R1 and R2) for reactions with OH radicals which can be identified with relatively strong C–H...O and O–H...F bonds, as shown in Fig. 1. So it is clear that the reaction channels (R1 and R2) may proceed via indirect mechanisms. The search was made along the minimum energy path on a relaxed potential energy surface. Optimized geometries of reactant, reactant complexes, transition states, product complexes and products obtained at the M06-2X/6-31+G(d,p) level are shown in Fig. 1. During the formation of transition states, the important structural parameters have to be observed are one of the C–H bond of the leaving hydrogen and the newly formed bond between H and O atoms in the OH radical. Visualization of the optimized structure of TS1 and TS2 further reveals that the breaking C–H bond is found to be longer in a range of 9.61–12.06% than the observed C–H bond length in isolated $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$; whereas the forming O...H bond length

is longer by 33.25 to 38.87% than the O–H bond length in H_2O . The fact that the elongation of forming bond is larger than that of the breaking bond indicates that the barrier of the reactions (R1 and R2) is near the corresponding reactants. This means the reaction will precede via early transition state structure which is in consonance with Hammond's postulate [33] applied to an exothermic hydrogen abstraction reaction. Similarly, for transition states TS3 and TS4 for reactions (R3 and R4), the length of the breaking C–H bond is found to be longer in a range of 28.02–30.62% than the observed C–H bond length in isolated $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$; whereas the forming H...Cl bond length is longer by 13.98–12.03% than the H–Cl bond length in isolated HCl molecule. This implies that the barrier of the reactions (R3 and R4) is closer to the products, and that the reactions with Cl atom proceed via a late transition state.

Results obtained by frequency calculations for species involved in reactions (R1–R4) are recorded in Table 2. These results show that the reactants, reactant complexes, product complexes and products have stable minima on their potential energy surface characterized by the occurrence of only real positive vibrational frequencies. On the other hand, transition states are characterized by the occurrence of only one imaginary frequency obtained at 1335i, 1675i, 960i and 911i cm^{-1} for TS1, TS2, TS3 and TS4, respectively. Visualization of the normal-mode corresponding to the calculated imaginary frequencies shows a well defined transition state geometry connecting reactants and products during transition. The existence of transition state on the potential energy surface is further ascertained by intrinsic reaction coordinate (IRC) calculation [31] performed at the same level of theory. The relative energies (including ZPE) for all the species involved in reaction channels (R1)–(R4) obtained from both the M06-2X/6-31++G(d,p) and M06-2X/6-31+G(d,p) levels are given in Table 3. From Table 3 it can be seen that the calculated barrier heights at both levels are consistent with each other. These results also reveal that energy barriers for H atom abstraction by OH radicals and Cl atom from

Table 2
Harmonic vibrational frequencies of reactants, reaction complexes, transition states, product complexes and products at M06-2X level of theory using 6-31+G(d,p) basis set.

Species	Vibrational frequencies (cm ⁻¹)
SC1	32, 40, 42, 62, 90, 128, 164, 220, 234, 264, 304, 347, 366, 429, 460, 520, 537, 544, 557, 569, 615, 663, 709, 799, 875, 897, 924, 993, 1101, 1166, 1190, 1207, 1226, 1248, 1313, 1340, 1349, 1354, 1423, 1444, 1483, 1502, 3115, 3156, 3184
SC2	27, 38, 50, 69, 98, 138, 159, 225, 236, 259, 298, 318, 350, 378, 393, 462, 513, 528, 534, 556, 598, 635, 668, 688, 750, 872, 876, 9119, 995, 1117, 1181, 1235, 1242, 1245, 1273, 1290, 1306, 1343, 1350, 1372, 1416, 1434, 1471, 1502, 3132, 3158, 3201
OH	3758
RC1	29, 34, 69, 89, 106, 127, 156, 177, 149, 191, 202, 220, 224, 256, 266, 307, 342, 347, 393, 425, 461, 524, 539, 544, 555, 574, 616, 660, 710, 801, 876, 898, 923, 994, 1102, 1168, 1190, 1201, 1226, 1248, 1261, 1295, 1313, 1340, 1348, 1350, 1427, 1442, 1486, 1519, 3113, 3155, 3155, 3184, 3769
RC2	24, 80, 86, 134, 143, 214, 248, 360, 366, 425, 443, 450, 609, 634, 701, 844, 886, 1003, 1135, 1165, 1209, 1250, 1328, 1366, 1370, 1446, 1495, 1524, 1534, 1560, 3134, 3153, 3208, 3223, 3234, 3824
TS1	1335i, 23, 30, 39, 52, 71, 78, 95, 146, 166, 205, 219, 225, 240, 262, 306, 319, 347, 422, 460, 524, 546, 555, 568, 615, 655, 710, 774, 799, 839, 881, 911, 928, 1053, 1123, 1166, 1184, 1198, 1224, 1254, 1261, 1294, 1310, 1316, 1325, 1348, 1424, 1438, 1454, 1493, 3151, 3156, 3768
TS2	1675i, 27, 40, 49, 60, 66, 94, 119, 131, 160, 219, 230, 232, 266, 271, 307, 347, 358, 401, 429, 469, 531, 539, 550, 564, 571, 617, 661, 726, 772, 831, 900, 925, 983, 988, 1123, 1145, 1194, 1216, 1227, 1249, 1257, 1287, 1303, 1339, 1343, 1358, 1387, 1469, 1483, 1503, 3115, 3185, 3745
TS3	960i, 24, 33, 51, 54, 66, 72, 86, 147, 152, 221, 223, 234, 261, 306, 308, 348, 420, 459, 508, 524, 540, 548, 559, 567, 617, 670, 711, 798, 858, 881, 918, 937, 978, 1132, 1137, 1193, 1217, 1227, 1252, 1261, 1273, 1292, 1319, 1331, 1351, 1430, 1440, 1464, 3159, 3186
TS4	911i, 24, 42, 44, 50, 62, 65, 82, 132, 178, 201, 217, 238, 264, 301, 332, 349, 366, 433, 468, 531, 541, 550, 554, 575, 615, 671, 721, 808, 848, 877, 880, 988, 992, 1010, 1133, 1184, 1209, 1245, 1258, 1269, 1286, 1313, 1344, 1365, 1392, 1407, 1469, 1499, 3125, 3194
PC1	14, 29, 33, 57, 64, 86, 101, 125, 146, 156, 207, 223, 225, 230, 261, 305, 308, 345, 359, 427, 432, 458, 502, 525, 547, 614, 633, 673, 714, 6803, 879, 919, 932, 1133, 1182, 1188, 1199, 1223, 1252, 1266, 1285, 1309, 1325, 1350, 1435, 1452, 1508, 1601, 3163, 3267, 3829, 3972
PC2	23, 28, 32, 43, 48, 61, 83, 103, 118, 126, 163, 189, 225, 232, 265, 312, 347, 355, 358, 408, 426, 463, 518, 534, 548, 555, 570, 620, 661, 715, 757, 833, 899, 983, 988, 1121, 1156, 1214, 1221, 1226, 1254, 1276, 1304, 1341, 1344, 1424, 1450, 1480, 1501, 1590, 3118, 3187, 3858, 3999
H ₂ O	1596, 3887, 4012
HCl	3031
P1	27, 34, 45, 65, 81, 132, 147, 215, 221, 235, 262, 306, 345, 351, 428, 458, 496, 524, 545, 558, 571, 613, 628, 671, 711, 802, 879, 922, 929, 1142, 1188, 1192, 1208, 1223, 1246, 1260, 1292, 1320, 1323, 1349, 1427, 1443, 1498, 3151, 3276
P2	29, 36, 41, 49, 72, 118, 147, 166, 219, 231, 269, 311, 349, 363, 422, 462, 503, 537, 547, 556, 566, 619, 653, 688, 739, 827, 897, 984, 1121, 1149, 1216, 1220, 1226, 1247, 1271, 1302, 1345, 1348, 1419, 1466, 1484, 1503, 3111, 3179

the $-\text{CH}_2$ group of $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ (R1) and (R3) are 2.74 and 4.27 kcal mol⁻¹, respectively at M06-2X/6-311G++(d,p) level of theory. On the other hand, the same from the $-\text{CHF}$ group (R2) and (R4) are found to be 3.13 and 6.45 kcal mol⁻¹, respectively at M06-2X/6-311G++(d,p) level of theory. The barrier height values suggest that hydrogen abstraction by OH radical and Cl atom from the $-\text{CH}_2$ group of $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ is more facile than that from the $-\text{CHF}$ group. This finding is in line with the calculated C–H bond dissociation energy from $-\text{CH}_2$ group (103.03 kcal mol⁻¹) is lower than that for the $-\text{CHF}$ group (104.97 kcal mol⁻¹). The calculations also reveal that H-abstraction by OH radicals is kinetically more favorable than that by Cl atom. A potential energy diagram of the title reaction is constructed and shown in Fig. 2. In the construction of energy diagram, zero-point energy corrected total energy data as recorded in Table 3 are utilized. These energies are plotted with respect to the ground state energy of $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3 + \text{OH/Cl}$ including ZPE arbitrarily taken as zero. The values given in parentheses in Fig. 2 are ZPE corrected values obtained at M06-2X/6-31+G(d,p) level. Moreover, spin contamination is not important for the $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3 + \text{OH/Cl}$ reactions

Table 3
Relative energies (in kcal mol⁻¹) with zero-point energy correction for the reactants, reaction complexes, transition states, product complexes and products.

Species	M06-2X/6-311+G(d,p)	M06-2X/6-31+G(d,p)
SC1 + OH	0.00	0.00
RC1	-0.89	-1.42
RC2	-2.15	-2.61
TS1	2.74	3.04
TS2	3.13	3.43
TS3	4.27	4.52
TS4	6.45	6.70
PC1	-21.41	-21.09
PC2	-15.39	-14.86
P1 + H ₂ O	-16.23	-16.04
P2 + H ₂ O	-14.34	-14.15
P1 + HCl	-1.75	-1.08
P2 + HCl	1.13	2.03

because $\langle S^2 \rangle$ is found to be 0.76 at M06-2X/6-31+G(d, p) before annihilation that is only slightly larger than the expected value of $\langle S^2 \rangle = 0.75$ for doublets.

The standard enthalpy of formation ($\Delta_f H^\circ_{298}$) at 298 K for $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ and the radicals $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ (P1) and $\text{CF}_3\text{CF}_2\text{OCH}_2\text{CF}_3$ (P2) generated from hydrogen abstraction, can be valuable information for understanding the mechanism and thermochemical properties of their reactions and most importantly for atmospheric modeling, but these values are not yet reported. The group-balanced isodesmic reactions, in which the number and types of bonds are conserved, are used as working chemical reactions herein to calculate the $\Delta_f H^\circ_{298}$. Here, two

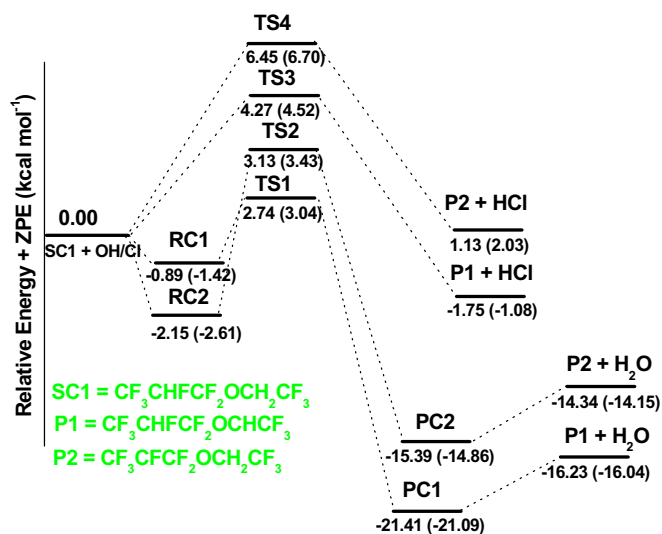
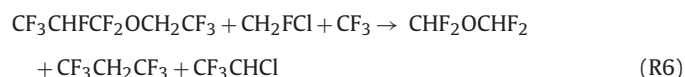
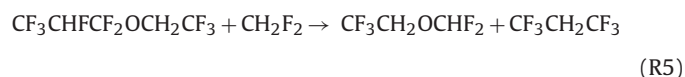


Fig. 2. Schematic potential energy diagram for the $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3 + \text{OH/Cl}$ reactions. Relative energies (in kcal mol⁻¹) with ZPE at M06-2X/6-31+G(d,p) level. The values given in parentheses are calculated at M06-2X/6-31+G(d,p) + ZPE level of theory.

isodesmic reactions are used to estimate the enthalpies of formation of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$. The used isodesmic reactions are as follows:



All geometrical parameters of the species involved in the isodesmic reactions (R5) and (R6) were first optimized at the M06-2X/6-31+G(d,p) level and then energies of the species were further refined at M06-2X/6-311++G(d,p) level of theory. At first we have calculated the reaction enthalpies ($\Delta_f H^\circ_{298}$) of the isodesmic reactions (R5) and (R6) as mentioned above using total energies of the species obtained at M06-2X/6-311++G(d,p) level including thermal correction to enthalpy estimated at M06-2X/6-31+G(d,p) level. Since, the ($\Delta_f H^\circ_{298}$) value corresponds to the difference of the enthalpy of formation ($\Delta_f H^\circ_{298}$) values between the products and the reactants, the ($\Delta_f H^\circ_{298}$) values of the reactant and product species are easily evaluated by combining them with the known enthalpies of formation of the reference compounds involved in our isodesmic reaction schemes. The experimental $\Delta_f H^\circ_{298}$ values for CH_2F_2 : $-107.77 \text{ kcal mol}^{-1}$ [34], $\text{CF}_3\text{CH}_2\text{OCHF}_2$: $-319.38 \text{ kcal mol}^{-1}$ [35] $\text{CF}_3\text{CH}_2\text{CF}_3$: $-336.5 \text{ kcal mol}^{-1}$ [36] CH_2FCl : $-63.13 \text{ kcal mol}^{-1}$ [37], CF_3 : $-111.9 \text{ kcal mol}^{-1}$ [38], $\text{CHF}_2\text{OCHF}_2$: $-259.1 \text{ kcal mol}^{-1}$ [39] and CF_3CHCl : $-131.93 \text{ kcal mol}^{-1}$ [40], to evaluate the required enthalpies of formation. The calculated values of enthalpies of formation are listed in Table 4. As can be seen from Table 4, the values of $\Delta_f H^\circ_{298}$ for the species obtained by the two working chemical reactions at both levels are consistent with each other. The average $\Delta_f H^\circ_{298}$ for $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ calculated from M06-2X/6-311++G(d,p) and M06-2X/6-31+G(d,p) results are -526.59 and $-525.68 \text{ kcal mol}^{-1}$, respectively. It is seen that the calculated $\Delta_f H^\circ_{298}$ for $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ at M06-2X method is found to be in consistent with a theoretical value of $-528.68 \text{ kcal mol}^{-1}$ reported by Kondo et al. [35] using the both bond additivity corrected MP2 method (BAC-MP2/6-31G**) and atom additivity corrected MP2 method (AAC-MP2/6-31G**). The $\Delta_f H^\circ_{298}$ values for $\text{CF}_3\text{CHFCF}_2\text{OCHCF}_3$ (P1) and $\text{CF}_3\text{CFCF}_2\text{OCH}_2\text{CF}_3$ (P2) radicals can also be easily calculated from the reported $\Delta_f H^\circ_{298}$ values for reactions (R1) and (R2) in Table 1, the calculated $\Delta_f H^\circ_{298}$ value for $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ and the experimental $\Delta_f H^\circ_{298}$ values for H_2O ($-57.8 \text{ kcal mol}^{-1}$) and OH ($8.93 \text{ kcal mol}^{-1}$) radical [35]. The $\Delta_f H^\circ_{298}$ values for P1 and P2 radicals calculated from the M06-2X/6-311++G(d,p) results are -475.70 and $-473.76 \text{ kcal mol}^{-1}$; whereas the same from M06-2X/6-31+G(d,p) results are found to be -474.61 and $-472.67 \text{ kcal mol}^{-1}$, respectively. These data are not available in the literature and can therefore be useful for further thermochemical and kinetic modeling of reaction involving these species.

The calculated bond-dissociation energies, BDE (D°_{298}) of the C–H bonds of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ molecule along with literature value are recorded in Table 5. The D°_{298} value obtained from the M06-2X/6-311++G(d,p) results for C–H bonds in the $-\text{CH}_2$ and $-\text{CHF}$ sites of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ amount to be 103.03 and $104.97 \text{ kcal mol}^{-1}$, respectively. On the other hand the same from M06-2X/6-31+G(d,p) results are found to be 103.21 and $105.15 \text{ kcal mol}^{-1}$, respectively. Moreover, our calculated BDE values for the C–H bonds is found to be in good agreement with the theoretical value of 101.96 and $100.70 \text{ kcal mol}^{-1}$, respectively for $-\text{CH}_2$ and $-\text{CHF}$ sites of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ reported

by Urata et al. [13] using ANN technique. The lower C–H bond dissociation energy for $-\text{CH}_2$ group shows that hydrogen abstraction from the $-\text{CH}_2$ group is more facile than that from the $-\text{CHF}$ group. This is also reflected in the calculated barrier height for hydrogen abstraction from $-\text{CH}_2$ and $-\text{CHF}$ sites. However this finding contradicts with the observation made by Urata et al. [13] but is consistent with the experimental observation of Oyaro et al. [15] for a similar species, $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CH}_3$ that hydrogen abstraction from the $-\text{CH}_2$ group is more facile. The reported BDE for $-\text{CH}_2$ and $-\text{CHF}$ sites of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CH}_3$ molecule is 97.27 and $100.86 \text{ kcal mol}^{-1}$, respectively. Our calculated BDE for $-\text{CH}_2$ and $-\text{CHF}$ sites are found to be somewhat higher than the corresponding values for $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CH}_3$ molecule. This is in line of the fact that fluorine atom substitution for hydrogen atom on carbon atom reduces the reactivity of the C–H bond toward hydrogen abstraction [16].

The rate constant for title reactions are calculated by using Canonical Transition State Theory [41] given by the following expression:

$$k = \sigma \Gamma(T) \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_A \cdot Q_B} \exp \frac{-\Delta E^\ddagger}{RT} \quad (1)$$

where, σ is the reaction path degeneracy, $\Gamma(T)$ is the tunneling correction factor at temperature T , Q_{TS} , Q_A and Q_B are the total partition functions (per unit volume) for the transition states and reactants, respectively. ΔE^\ddagger is the barrier height including zero point energy correction, k_B is the Boltzmann constant, h is the Planck's constant and R represents the universal gas constant. The tunneling correction was estimated by using the Eckart's unsymmetrical barrier method [42,43]. The tunneling correction factor at 298 K is found to be 4.47 , 6.77 , 2.54 and 2.42 for TS1, TS2, TS3 and TS4, respectively. All vibrational modes, except for the lowest vibrational mode, were treated quantum mechanically as separable harmonic oscillators, whereas for the lowest-frequency mode, the partition function was evaluated by the hindered-rotor approximation by Truhlar and Chuang [44] method. Using Truhlar's procedure [45] the $q^{\text{HIN}}/q^{\text{HO}}$ ratio was found to be close to unity. In the calculation of reactant electronic partition function, the excited state of the OH radicals is included, with a 140 cm^{-1} splitting; the $^2P_{3/2}$ and $^2P_{1/2}$ electronic states of Cl atom are also included with 881 cm^{-1} splitting due to spin-orbit coupling. As discussed before, the H-abstraction by OH radicals from the $-\text{CH}_2$ and $-\text{CHF}$ groups proceeds via two-step mechanism. The first step involves a fast pre-equilibrium (K_{eq}) between the reactants and the hydrogen bonded reaction complex (RC) and the second step is the hydrogen abstraction with the rate constant k_2^\ddagger (Table 6). The overall rate constant including equilibrium constant (K_{eq}) and rate constant (k_2^\ddagger) are given by,

$$K_{\text{eq}} = \frac{Q_{\text{RC}}}{Q_A \cdot Q_B} e^{(E_R - E_{\text{RC}})/RT} \quad (2)$$

and k_2^\ddagger can be obtained from TST in the from

$$k_2^\ddagger = \sigma \Gamma(T) \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_{\text{RC}}} e^{-(E_{\text{TS}} - E_{\text{RC}})/RT} \quad (3)$$

The rate constant for H-abstraction from $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ via reactions (R1) and (R2) is then obtained by the following expression,

$$k = K_{\text{eq}} \times k_2^\ddagger = \sigma \Gamma(T) \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_A \cdot Q_B} e^{-(E_{\text{TS}} - E_R)/RT} \quad (4)$$

where Q_A , Q_B , Q_{RC} and Q_{TS} represents the total partition functions (per unit volume) of the reactants, reaction complex and transition states, respectively. E_{TS} , E_{RC} and E_R are the total energies (ZPE corrected) of transition state, reaction complex and reactants, respectively. Thus, it seems that the final expression (Eq. (4)) for estimating rate constant and barrier height turns out

Table 4Enthalpies of formation ($\Delta_f H^\circ_{298}$) for the species at 298 K from the isodesmic reactions along with literature values. All values are in kcal mol⁻¹.

Species	Reaction schemes	M06-2X/6-311++G(d,p)	M06-2X/6-31+G(d,p)	Literature value ^a
CF ₃ CHFCF ₂ OCH ₂ CF ₃	(R5)	−527.14	−526.68	−528.68
	(R6)	−526.04	−525.68	
	Average	−526.59	−525.68	
CF ₃ CHFCF ₂ OCHCF ₃		−475.70	−474.61	
CF ₃ CFCF ₂ OCH ₂ CF ₃		−473.76	−472.67	

^a Kondo et al. [35].**Table 5**Calculated bond dissociation energy (D^0_{298}) (kcal mol⁻¹) for species at 298 K at various levels of theory along with literature values.

Bond dissociation type	M06-2X/6-311++G(d,p)	M06-2X/6-31+G(d,p)	Literature value ^a
C–H bond			
CF ₃ CHFCF ₂ OCH ₂ CF ₃ → CF ₃ CHFCF ₂ OCHCF ₃ + H	103.03	103.21	101.96
CF ₃ CHFCF ₂ OCH ₂ CF ₃ → CF ₃ CFCF ₂ OCH ₂ CF ₃ + H	104.97	105.15	100.70

^a Urata et al. [13].**Table 6**Rate constant values (in cm³ molecule⁻¹ s⁻¹) for hydrogen abstraction reactions of CF₃CHFCF₂OCH₂CF₃ with OH radicals and Cl atom as calculated from M06-2X/6-311++G(d,p) results.

T (K)	k_{TS1}	k_{TS2}	k_{OH}	k_{TS3}	k_{TS4}	k_{Cl}
250	5.16E−15	2.40E−15	7.56E−15	3.03E−17	1.49E−18	3.18E−17
298	5.92E−15	3.18E−15	9.10E−15	4.54E−17	2.34E−18	4.77E−17
300	6.10E−15	3.22E−15	9.32E−15	4.64E−17	2.45E−18	4.89E−17
350	7.71E−15	4.29E−15	1.20E−14	5.22E−17	5.61E−18	5.78E−17
400	9.70E−15	5.60E−15	1.53E−14	7.91E−17	7.71E−18	8.68E−17
450	1.19E−14	7.19E−15	1.9E−14	1.01E−16	8.41E−18	1.09E−16

to be the usual CTST expression (Eq. (1)) used for the determination of rate constant and barrier height of a direct reaction, irrespective of the energy of pre-reactive hydrogen bonded complex (RC). However, the tunneling factor $\Gamma(T)$ will obviously be different due to pre- and post-reaction complex formation and as a result will affect the total rate constant. The contribution from each of two channels is taken into account while calculating the total rate coefficient (k_{OH}) for the CF₃CHFCF₂OCH₂CF₃ + OH reactions. The total rate coefficient (k_{OH}) is therefore obtained from the addition of rate coefficients for the two channels: $k_{OH} = k_{R1} + k_{R2}$. At 298 K, our calculated k_{OH} value using M06-2X/6-311++G(d,p) barrier heights is 9.10×10^{-15} cm³ molecule⁻¹ s⁻¹ which is in very good agreement with the experimental value of $(9.0 \pm 0.02) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ reported by Chen et al. [11] and 9.17×10^{-15} cm³ molecule⁻¹ s⁻¹ by Wilson et al. [12]. However, the rate coefficient obtained from the M06-2X/6-31+G(d,p) results (9.37×10^{-15} cm³ molecule⁻¹ s⁻¹) is also in good agreement with the M06-2X/6-311++G(d,p) and experimental values at 298 K. Similarly, the rate constant for H atom abstraction reactions of CF₃CHFCF₂OCH₂CF₃ by Cl atom as given by reactions (R3) and (R4) are calculated as $k_{Cl} = 4.77 \times 10^{-17}$ and 5.68×10^{-17} cm³ molecule⁻¹ s⁻¹ at 298 K using M06-2X/6-311++G(d,p) and M06-2X/6-31+G(d,p) barrier heights, respectively. Although no comparison between theory and experiment can be made due to the lack of the experimental rate constant for CF₃CHFCF₂OCH₂CF₃ + Cl reactions, the calculated rate constant during present study can be expected to provide good reference information for upcoming laboratory investigations. From our theoretical study it can be concluded that OH-initiated H-abstraction of CF₃CHFCF₂OCH₂CF₃ is more dominate as compare to its Cl-initiated H-abstraction reactions. The branching ratios for the H-abstraction reaction channels, which represent the individual contribution of a reaction channel toward overall reaction rate has been determined by using the following expression,

$$\text{Branching ratio} = \frac{k}{k_{\text{total}}} \times 100 \quad (5)$$

The calculated branching ratio values show that the −CH₂ group has greater contribution (~65%) to the overall rate constant for OH-initiated hydrogen abstraction from CF₃CHFCF₂OCH₂CF₃ whereas the same for CF₃CHFCF₂OCH₂CF₃ + Cl reaction is found to be 95%. Thus, the hydrogen abstraction from −CH₂ group is found to be the dominant reaction channel for both OH and Cl-initiated hydrogen abstraction reactions of CF₃CHFCF₂OCH₂CF₃.

3.1. Atmospheric lifetime

In general, tropospheric lifetime (τ_{eff}) of CF₃CHFCF₂OCH₂CF₃ can be estimated by assuming that its removal from troposphere occurs only through the reactions with OH radicals and Cl atom. Then (τ_{eff}) can be expressed as [46],

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} \quad (6)$$

where, $\tau_{OH} = (k_{OH} \times [OH])^{-1}$ and $\tau_{Cl} = (k_{Cl} \times [Cl])^{-1}$. Using the 298 K value of $k_{OH} = 9.10 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ and $k_{Cl} = 4.77 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ and the global average atmospheric OH concentration of 1.0×10^6 molecule cm⁻³ [47] and Cl concentration of 1.0×10^4 molecule cm⁻³ [48], the estimated atmospheric lifetime of CF₃CHFCF₂OCH₂CF₃ is found to be 0.287 years.

4. Conclusions

The potential energy surface and reaction kinetics of the H atom abstraction reaction of CF₃CHFCF₂OCH₂CF₃ with OH radicals and Cl atom are investigated at M06-2X/6-31+G(d,p) level of theory. The reaction with OH radicals is found to follow an indirect path through the formation of pre- and post-reaction complexes. Two important reaction channels have been identified for each reaction. The barrier height for hydrogen abstraction by OH radicals from −CH₂ and −CHF groups are found to be 2.74 and 3.13 kcal mol⁻¹, respectively; whereas the same for reactions with Cl atom are found

to be 4.27 and 6.45 kcal mol⁻¹, respectively. The thermal rate constant for the H atom abstraction of CF₃CHFCF₂OCH₂CF₃ by OH radicals is found to be 9.10×10^{-15} cm³ molecule⁻¹ s⁻¹ at 298 K using canonical transition state theory which is in very good agreement with experimental data. The thermal rate constant for the H atom abstraction of CF₃CHFCF₂OCH₂CF₃ by Cl atom are calculated for the first time and found to be 4.77×10^{-17} cm³ molecule⁻¹ s⁻¹ at 298 K. From our theoretical study it can be concluded that hydrogen abstraction from —CH₂ group is thermodynamically and kinetically more facile than that from —CHF group. The $\Delta_f H^\circ_{298}$ for CF₃CHFCF₂OCH₂CF₃, CF₃CHFCF₂OCHCF₃ and CF₃CFCF₂OCH₂CF₃ species calculated from M06-2X results are -526.59, -475.70 and -473.76 kcal mol⁻¹, respectively. The D⁰₂₉₈ value obtained for the C—H bonds in the —CH₂ and —CHF sites of CF₃CHFCF₂OCH₂CF₃ amount to 103.03 and 104.97 kcal mol⁻¹, respectively. Atmospheric lifetime of CF₃CHFCF₂OCH₂CF₃ is estimated to be 0.287 years. These data can be useful for further thermo-kinetic modeling of other reactions involving these species. Due to lack of the experimental rate constant for reactions with Cl atom, we hope our results may provide a good estimate for future laboratory investigation.

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