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Theoretical studies on kinetics, mechanism and thermochemistry of gas-phase reactions of $CF_3CHFCF_2OCF_3$ with OH radicals and Cl atoms and fate of alkoxy radical at 298 K

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ABSTRACT

Detailed theoretical investigation has been performed on the mechanism, kinetics and thermochemistry of the gas phase reactions of $CF_3CHFCF_2OCF_3$ with OH radicals and Cl atoms using M06-2X/6-31+G(d,p) level of theory. The energetic calculations were refined by using aug-cc-pVTZ basis set. Our calculations reveal that OH-initiated hydrogen abstraction is thermodynamically and kinetically more facile than that from the Cl-initiated hydrogen abstraction. Using group-balanced isodesmic reactions, the standard enthalpies of formation (ΔH_f°) for species and bond dissociation energies for C–H bond are also reported. The ΔH_f° for $CF_3CHFCF_2OCF_3$ and $\bullet CF(CF_3)CF_2OCF_3$ species calculated from M06-2X/6-31+G(d,p) results are −523.15 and −471.65 kcal mol^{-1}, respectively. The rate constants evaluated by canonical transition state theory (CTST) are found to be 1.22×10^{-15} and 3.40×10^{-17} cm^3 molecule^{-1} s^{-1} which are in a reasonable agreement with the available experimental data of $(1.43 \pm 0.28) \times 10^{-15}$ and $(4.09 \pm 0.42) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, respectively, for OH and Cl-initiated hydrogen abstraction reactions. The atmospheric life time of $CF_3CHFCF_2OCF_3$ is estimated to be 38.5 years. The atmospheric fate of the alkoxy radical, $CF_3CF(O\bullet)CF_2OCF_3$ is also investigated for the first time using same level of theory.

1. Introduction

Recently, volatile organic compounds like hydrofluoroethers (HFEs) are designed and widely recommended as a third generation replacement for chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) in applications such as cleaning of electronic equipment, heat transfer fluids in refrigerators, lubricant deposition and foam blowing agents [1–4]. Hydrofluoroethers do not contain chlorine and bromine atoms that cause ozone depletion [5]. In addition the rate constant for the reaction of HFEs with OH radicals suggest that their atmospheric lifetime should be relatively short and thus HFEs appear to have less impact for 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 [7]. Although global atmospheric abundance of OH radicals is around 2 orders of magnitude greater than that of chlorine atoms, Cl reactions are generally faster than OH reactions, so their contribution to the degradation of VOCs may not be negligible compared to the role of OH radicals [8]. This contribution of Cl could be significant in areas where the concentration of Cl precursor species has been reported to be high, such as the coastal boundary layer [9]. Thus, chlorine atom also plays an important role in atmospheric chemistry [10]. The tropospheric oxidation of HFEs (containing $-CH_2$ group in alpha position) is known to produce the corresponding fluorinated esters (FESs) [11,12]. The degradation of FESs produces trifluoroacetic acid (TFA) which is classified as detrimental to aquatic life [13]. Hence it is important to study the kinetics and mechanistic degradation pathways of HFEs in the troposphere for complete assessment of its atmospheric chemistry as well as its impact on global warming and climate change. Considerable attention has been paid in recent years to performing experimental and theoretical studies on the reactivity of HFEs with OH radicals and Cl atoms [14–26]. $CF_3CHFCF_2OCF_3$ has been used as a fire extinguishing agent and thus may be released into the atmosphere during its use. Prior to its industrial use, appraisal of the environmental impact of $CF_3CHFCF_2OCF_3$ is needed. This motivated us to perform a

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comprehensive study on sound theoretical basis. In the present work, we have studied the mechanism and kinetics of OH and Cl-initiated H-abstraction reactions from $CF_3CHFCF_2OCF_3$ using DFT methods. Our calculation suggests that a reaction channel is feasible for the $CF_3CHFCF_2OCF_3$ + OH/Cl reactions as given below.

$$CF_3CHFCF_2OCF_3 + \bullet OH \rightarrow \bullet CF(CF_3)CF_2OCF_3 + H_2O \qquad (R1)$$

$$CF_3CHFCF_2OCF_3 + \bullet Cl \rightarrow \bullet CF(CF_3)CF_2OCF_3 + HCl \qquad (R2)$$

Two experimental studies were reported for reactions (R1) and (R2) by Wallington et al. [14] and Wilson et al. [15]. Wallington et al. [14] first studied the hydrogen abstraction channel of these reactions using Fourier transform infrared (FTIR) smog chamber techniques in 700 Torr of N_2/O_2 diluent at 296 K and the experimental rate constant were reported as $k_{OH} = (1.43 \pm 0.28) \times 10^{-15}$ and $k_{Cl} = (4.09 \pm 0.42) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. Subsequently, Wilson et al. [15] performed another experimental study by using relative rate methods and they also reported a rate constants value as $k(OH + CF_3CHFCF_2OCF_3) = 1.84 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Moreover, experimental study provides only the total rate constant and it is difficult to predict the detailed mechanism and thermochemistry. Thus, for better understanding of mechanistic pathways, kinetics and thermochemistry we must rely on quantum chemical methods. To the best of our knowledge, this is the first detailed theoretical study on gas-phase reactions with OH radicals and Cl atoms of this hydrofluoroethers. 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 reactions from hydrofluoroethers. Thus, we also estimated BDE of C–H bond in $CF_3CHFCF_2OCF_3$. 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. In order to have reliable thermochemical properties and the barrier heights for reaction channels (R1) and (R2), single point energy calculations were also performed at the M06-2X/aug-cc-pVTZ level.

2. Results and discussion

2.1. Structure and energetics

The calculated enthalpy of reaction (ΔH_r°) and free energy of reaction (ΔG_r°) at 298 K for the reactions of $CF_3CHFCF_2OCF_3$ with OH radicals and Cl atoms are recorded in Table 1. The enthalpy of reaction, (ΔH_r°) values given in Table 1 shows that reaction (R1) is significantly exothermic and thus thermodynamically more facile. One transition state (TS) is located for each of the two reactions $CF_3CHFCF_2OCF_3$ + •OH and $CF_3CHFCF_2OCF_3$ + •Cl.

In the entrance channel for reaction (R1), pre- reactive complex (COMR1) has been located in the present work. In the exit channel, there is also product complex occurring before the release of the final products, which are labeled as COMP1. In pre-reactive complex (COMR1), OH radical interacts with $CF_3CHFCF_2OCF_3$ compound. The interatomic distances between the H-atom of OH radical and the O-atom of the $CF_3CHFCF_2OCF_3$ are found to be 2.315 and 2.704 Å, respectively, while the other bond lengths are very close to those in equilibrium structures. At the same time, the post-reaction complex (COMP1) with energy less than the corresponding products are located at the exits of the reaction channel (R1) for reactions with OH radicals as shown in Fig. 1. So it is clear that the reaction channel (R1) may proceed via indirect mechanisms. The indirect mechanism means reaction channel precede through reactants ≥ reactant complex ≥ TS ≥ product complex ≥ products. The search of stationary points was made along the minimum energy path on a relaxed potential energy surface. Optimized geometries of reactants, reactant complex, transition states, product complex and products obtained at the M06-2X/6-31+G(d,p) level are shown in Fig. 1.

Table 1
Reaction enthalpies, free energies of reactions, free energies of activation and bond dissociation energy calculated at M06-2X/6-31+G(d,p) and M06-2X/aug-cc-pVTZ levels of theory. All values are in kcal mol^{-1}.

	M06-2X/6-31+G(d,p)	M06-2X/aug-cc-pVTZ
ΔH_r°		
Reaction (R1)	−15.23	−13.58
Reaction (R2)	−0.03	2.75
Reaction (R6)	3.05	−1.06
Reaction (R7)	5.48	2.65
ΔG_r°		
Reaction (R1)	−16.37	−14.69
Reaction (R2)	−2.37	0.41
Reaction (R6)	−11.41	−14.54
Reaction (R7)	−8.54	−11.37
$\Delta G^\#$		
Reaction (R1)	12.48	12.26
Reaction (R2)	14.93	14.13
Reaction (R6)	10.24	9.86
Reaction (R7)	13.61	13.10
D°		
$CF_3C^*HFCF_2OCF_3$	103.64	105.29

During the formation of transition states, important structural parameters that have to be observed are the C–H bond of the leaving hydrogen and the newly formed bond between H and O atom in the OH radical. Visualization of the optimized structure of TS1 further reveals that the breaking C–H (C2–H1) bond is found to be longer by 11.70% than the observed C–H bond length in isolated $CF_3CHFCF_2OCF_3$ molecule whereas the forming O…H bond length is longer by 33.37% 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 reaction (R1) is near the corresponding reactants. This means the reaction (R1) will precede via early transition state structure which is consistent with Hammond's postulate [27] applied to an exothermic hydrogen abstraction reaction. Similarly, for transition state TS2 for reaction (R2), the length of the breaking C–H (C2–H1) bond is found to be longer by 31.44% than the observed C–H bond length in isolated $CF_3CHFCF_2OCF_3$ molecule whereas the forming H···Cl (H1–Cl1) bond length is longer by 11.56% than the H–Cl bond length in isolated HCl molecule. This implies that the barrier of the reaction (R2) is closer to the products, and that the reaction with Cl atoms proceeds via a late transition state.

Results obtained by frequency calculations for species involved in reactions (R1) and (R2) are recorded in Table S1 of Supporting information. These results show that the reactants, reactant complex, product complex 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 1667*i* and 904*i* cm^{-1}, respectively, for TS1 and TS2. Visualization of the normal-mode corresponding to the calculated imaginary frequency 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 [28] performed at the same level of theory. The relative energies (including ZPE) for all the species involved in reaction channels (R1) and (R2) obtained at both M06-2X/6-31+G(d,p) and M06-2X/aug-cc-pVTZ levels are given in Table S2 of Supporting information. From Table S2 of Supporting information it can be seen that the calculated barrier heights at both levels are consistent with each other. These results reveal that energy barriers for H atom abstraction by OH radicals and Cl atoms are 3.81 and 5.61 kcal mol^{-1}, respectively, at M06-2X/6-31+G(d,p) level of theory. On the other hand, the same are found to be 3.60 and 7.18 kcal mol^{-1}, respectively, at M06-2X/aug-cc-pVTZ level of