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A DFT study on kinetics of the gas phase reactions of $CH_3CH_2OCF_3$ with OH radicals and Cl atoms

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ABSTRACT

A theoretical study on the mechanism and kinetics of the gas phase reactions of $CH_3CH_2OCF_3$ (HFE-263) with the OH radicals and Cl atoms have been performed using meta-hybrid density functional MPWB1K method and 6-31+G(d,p) basis set. Energetics are further refined by calculating the energy of the species with a high level G2(MP2) method. Reaction profiles are modeled including the formation of pre-reactive and post-reactive complexes at entrance and exit channels. The hydrogen abstraction from $-CH_2$ group is found to be the dominant reaction channel for reaction with OH radicals, whereas hydrogen abstraction from CH_3 group is the dominant channel for Cl atoms, especially at higher temperature. Using group-balanced isodesmic reactions, the standard enthalpies of formation for $CH_3CH_2OCF_3$ and radicals generated by hydrogen abstraction, CH_3CHOCF_3 and $CH_2CH_2OCF_3$ are reported for the first time. 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 250–1000 K. The G2(MP2) calculated rate constant values are 0.52×10^{-13} and 0.77×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively for reactions with OH radicals and Cl atoms at 298 K.

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. Recently, volatile organic compound especially hydrofluoroethers (HFEs) is 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 [3–6]. Also HFEs are believed to be more reactive in the troposphere due to the presence of –O– ether linkage [7]. Although HFEs do not contain Cl atom and have zero ozone depletion potential, they are potential greenhouse gases because of their strong absorption in the range of 1000–3000 cm^{-1} [8,9]. Reactions of HFEs with OH radicals constitute the main degradation channel of HFEs in the troposphere [10]. The major degradation pathways of HFEs in atmosphere may be initiated by photolytic degradation with OH radicals. Although the reaction with OH radicals constitutes the main tropospheric sink for degradation of halogenated ethers, the chlorine atom plays an important role in the atmospheric chemistry [11]. In fact, chlorine atoms have been monitored in concentrations in the order of 10^4 molecule cm^{-3} over the marine boundary layer [12]. Thus, it is important to study the kinetics and mechanistic degradation pathways of HFEs for complete assessment of atmospheric chemistry as well as to explore the impact of HFEs on the environment. Therefore, considerable attention has been paid in recent years to perform experimental and theoretical studies on the decomposition kinetics of HFEs [13–30]. In the present work, we have investigated the hydrogen abstraction reactions between $CH_3CH_2OCF_3$ (HFE-263) and OH radicals and Cl atoms by using quantum chemical methods. To the best of our knowledge, very little attention has been paid to this reaction and this is the first detail theoretical study for this important reaction. Recently, this reaction has been studied experimentally by Oyaro et al. [31] by the relative rate method at 298 K using gas chromatography–mass spectroscopy (GC–MS) detection and reported a rate constants as

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$k(OH + CH_3CH_2OCF_3) = 1.55 \times 10^{-13}$ and $k(Cl + CH_3CH_2OCF_3) = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. Our calculation indicates that one reaction channel from $-CH_2$ and two reaction channels from $-CH_3$ groups are feasible for the $CH_3CH_2OCF_3$ + OH/Cl reactions as given below:

$$CH_3CH_2OCF_3 + OH \rightarrow CH_3CHOCF_3 + H_2O \qquad (R1)$$

$$CH_3CH_2OCF_3 + OH \rightarrow CH_2CH_2OCF_3 + H_2O \qquad (R2)$$

$$CH_3CH_2OCF_3 + Cl \rightarrow CH_3CHOCF_3 + HCl \qquad (R3)$$

$$CH_3CH_2OCF_3 + Cl \rightarrow CH_2CH_2OCF_3 + HCl \qquad (R4)$$

It has been reported from experimental findings that $-CH_2$ is more reactive than the hydrogen atoms at the $-CH_3$ group [31]. However, 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. The aim of the present paper is to have a more accurate thermo chemical data using G2(MP2) method. Canonical Transition State Theory (CTST) is also utilized to predict the rate constant of the title reactions on the basis of *ab initio* data obtained during the present investigation. To the best of our knowledge this is the first detailed theoretical study of the above mentioned H-abstraction reactions of HFE-263 with OH radicals and Cl 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 (–O–) is important for the reactivity of the haloethers. Thus, we present BDE of the two types of C–H and C–O bonds in $CH_3CH_2OCF_3$. In addition, the knowledge of accurate enthalpy of formation ($\Delta_f H_{298}^\circ$) for $CH_3CH_2OCF_3$ and radicals generated CH_3CHOCF_3 and $CH_2CH_2OCF_3$ 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 by performing single-point energy calculation at high level of theory, G2(MP2) with geometry parameters obtained at the MPWB1K/6-31+G(d,p) level. We also report here the rate constant for the reactions ((R1)–(R4)) in a wide temperature range of 250–1000 K.

2. Results and discussion

The calculated enthalpy of reactions ($\Delta_r H^\circ$) and reaction free energies ($\Delta_r G^\circ$) at 298 K for the reaction of $CH_3CH_2OCF_3$ with OH radicals and Cl atoms are recorded in Table 1. Thermal corrections to the energy at 298 K were included in the determination of these thermodynamic functions. The free energy values show that all reaction channels are exergonic ($\Delta G < 0$) and therefore should be spontaneous in nature. The $\Delta_r G^\circ$ values for $CH_3CH_2OCF_3$ + OH reaction is much more negative than that for the $CH_3CH_2OCF_3$ + Cl reaction indicating the former reaction is thermodynamically more favorable than the latter. The enthalpy of reaction ($\Delta_r H_{298}^\circ$) values given in Table 1 for (R1) and (R2) shows that both the reactions are significantly exothermic in nature.

Table 1
Thermochemical data for the H abstraction reaction channels of $CH_3CH_2OCF_3$ calculated at G2(MP2) and MPWB1K/6-31+G(d,p) (within parenthesis) level of theories. All values are in kcal mol^{-1}.

Reaction channels	$\Delta_r H^\circ$	$\Delta_r G^\circ$
Reaction (R1)	−19.39 (−17.05)	−20.80 (−18.45)
Reaction (R2)	−16.34 (−11.80)	−18.09 (−13.55)
Reaction (R3)	−4.01 (−2.89)	−6.65 (−5.53)
Reaction (R4)	−0.97 (2.35)	−3.94 (−0.62)

There are two potential hydrogen abstraction sites of $CH_3CH_2OCF_3$, namely the $-CH_2$ and $-CH_3$ group. However, as can be seen from the geometrical parameters and stereographical orientation, the hydrogen atoms in the $-CH_3$ group are not equivalent. One H-atom is different from the other two in the $-CH_3$ group. Three transition states (TS) are therefore located for each of the two reactions $CH_3CH_2OCF_3$ + OH and $CH_3CH_2OCF_3$ + Cl; one TS for H-abstraction from the $-CH_2$ group (TS_1 for reaction with OH and TS_3 for reaction with Cl atom) and two TSs for the same from the $-CH_3$ group (TS_{2a} and TS_{2b} for reaction with OH and TS_{4a} and TS_{4b} for reaction with Cl). Therefore three H-abstraction reaction channels exist for both the reactions studied here. In the entrance channel for reaction (R1) and one of the channels for (R2) (through TS_{2b} and defined as R_{2b}), pre-reactive complexes ((R1) and (R2)) have been found 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 (R1) and (R2), hydrogen bonds are formed between the oxygen atom of hydroxyl radical with the hydrogen atom in $CH_3CH_2OCF_3$ with bond distances of 2.71 and 2.79 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.

The optimized geometries of reactants, reactive complex, transition states, product complexes and products obtained at MPWB1K/6-31+G(d,p) level with available limited experimental values for OH, H_2O and HCl are shown in Fig. 1. Our calculated values are in very good agreement with the corresponding experimental values (given in parentheses) in Fig. 1 [32]. 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. It can be observed from Fig. 1 that the length of the breaking C–H bond (C3-H5) increases from 1.087 to 1.186 Å (almost 9% increase) in the optimized structure of TS_1, whereas the length of the newly formed H–O bond (H5-O2: 1.349 Å) is longer by about 40% from the normal O–H bond length (0.953 Å) in H_2O. Similarly, for transition states TS_{2a} and TS_{2b} for reactions (R2), the length of the breaking C–H bond increases by almost 12% whereas the newly formed H–O bonds are longer by almost 33% from 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 is near the corresponding reactants. This means that the reactions (R1) and (R2) will proceed via early transition state. In the optimized structures of TS_3, TS_{4a} and TS_{4b}, the reactive C–H bonds that will be broken, increases by 24%, 35% and 34%, respectively compared to the C–H equilibrium bond length in $CH_3CH_2OCF_3$, and the forming H–Cl bonds are about 16%, 9% and 10%, respectively longer than the regular bond length of the isolated HCl. This implies that the barrier of the reactions (R3) and (R4) is closer to the products, and that the reactions with Cl atoms proceed via a late transition state.