Theoretical studies on the mechanism and kinetics of the hydrogen abstraction reactions from $C_4F_9OC_2H_5$ (HFE-7200) by OH and Cl radicals

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A B S T R A C T

The potential energy surfaces for the hydrogen abstraction reactions from $C_4F_9OC_2H_5$ by OH (reaction R_A) and Cl (reaction R_B) radicals are investigated theoretically by density functional theory methods. The stationary points including reactants, saddle-points and products of the title reactions are optimized by using M06-2X density functional method along with the standard 6-31 + G(d,p) basis set. The vibrational frequencies are computed at the same level of theory. More accurate energies are estimated by single-point calculations at the M05-2X/MG3S, M06-2X/MG3S, MPWB1K/MG3S, BB1K/MG3S and KMLYP/6-311 + + G(2d,2p) levels of theory. The computed barrier heights are slightly sensitive to the DFT method. Conventional transition state theory employing the tunneling for Eckart potential barrier is used to compute the thermal rate coefficients in the temperature range from 200 to 2000 K. The rate coefficients computed by using M05-2X/MG3S and MPWB1K/MG3S are in more agreement with the available experimental data. On the basis of the present computed rate coefficients, the atmospheric lifetime of the $C_4F_9OC_2H_5$ is estimated to be about 0.5 year.

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1. Introduction

Ozone layer depletion and global warming have been two major environmental problems over the past four decades due to the emission of a diversity of halogen-containing compounds by different industries from earth surface and their accumulation in the atmosphere [1]. A worldwide effort have been made to replace the stable chlorofluorocarbons (CFC's) with the more reactive hydrogen-containing halocarbons such as hydrochlorofluorocarbons (HCFC's), hydrofluorocarbons (HCFC's) and hydrofluoroethers (HFE's). The latter halocarbons have shorter atmospheric lifetimes because they undergo hydrogen-abstraction reactions with reactive atmospheric species especially OH radicals, known as atmospheric detergents.

$C_4F_9OC_2H_5$ (HFE-7200) is a volatile liquid which is used in industry for the cleaning of electronic equipments, heat transfer agents in refrigeration systems and carrier fluids for lubricant deposition [2]. The atmospheric oxidation process of $C_4F_9OC_2H_5$ is initiated by it hydrogen-abstraction reaction with OH and Cl radicals. As a consequence, some groups have attempted to measure the rate coefficients for the reactions $C_4F_9OC_2H_5 + OH$ (the

reaction R_A) and $C_4F_9OC_2H_5 + Cl$ (the reaction R_B). Christensen et al. [2] have measured the rate constant for the HFE-7200 + OH reaction by relative rate techniques and obtained value of $6.4 \times 10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 295 K. Bravo et al. [3] have employed a discharge flow technique coupled with mass-spectrometric detection to determine the Arrhenius parameters of the $C_4F_9OC_2H_5 + OH$ reaction over the temperature range 288–368 K and reported the rate expression $6.9 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \exp(-2030/T)$. To the best of our knowledge, there are two experimental data for the reaction of Cl atoms with $C_4F_9OC_2H_5$. Christensen et al. [2] have reported the value of $2.7 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 295 K for $C_4F_9OC_2H_5 + Cl$ reaction. Aranda et al. [4] have measured the rate constants for $C_4F_9OC_2H_5 + Cl$ reaction by using a discharge flow mass spectrometric technique in the temperature range 234–333 K and obtained the rate expression as $3.7 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \exp(-852/T)$.

Due to its significance in atmospheric studies, we are inspired to do an ab initio study on the title reactions. Here, it is attempted to employ well-tested density functional theory (DFT) methods to investigate the potential energy surfaces (PES's) of the title reactions. Next, Conventional transition state theory (CTST) employing the tunneling for Eckart potential barrier is used to compute the thermal rate coefficients of the reactions R_A and R_B and to estimate the lifetime of $C_4F_9OC_2H_5$.

2. Computational details

2.1. Electronic-Structure calculations

In the present work, the PES's for the reactions of OH and Cl radicals with $C_4F_9OC_2H_5$ are explored by M06-2X hybrid meta density functional theory (HMDFT) method [5] along with the standard 6-31+G(d,p) basis set and the structures for all of the stationary points, i.e., minimum energy structures and saddle points are optimized. The harmonic vibrational frequencies of the optimized geometries are calculated at same level of theory. Other HMDFT methods such as M05-2X [6], MPWB1K [7] and BB1K [8] along with the larger MG3S basis [9] set are used to obtain more accurate energies. M05-2X, M06-2X, MPWB1K and BB1K methods have been developed by Truhlar and coworkers and optimized against various databases containing energetic data, bond lengths, vibrational frequencies and vibrational zero point energies and they are recommended for applications in kinetics and non-covalent interactions. The KMLYP method [10] developed by Kang and Musgrave is also employed to compute the molecular energies. In the latter DFT method, the exchange functional is obtained by mixing Slater exchange and exact exchange and the correlation functional is mix of Vosko, Wilk, Nusair (VWN) [11] and that of Lee, Yang, and Parr (LYP) [12] correlation functionals. The predicted reaction barrier heights by KMLYP method is proved to have the same accuracy as CBS-APNO, and transition state barriers and reaction enthalpies have smaller errors in comparison with B3LYP, BHandHLYP, and G2. All of the quantum chemical calculations are carried out by Gaussian 09 package of programs [13].

2.2. Rate constant calculations

Having the molecular parameter for the reactants and transition states, Conventional Transition State Theory (CTST) [14–20] is used to compute the thermal rate constants for the rations R_A and R_B in the temperature range between 250 and 2000 K. In the CTST, canonical rate constant is computed according to the following equation:

$$k(T) = \Gamma \frac{k_B T}{h} \frac{Q_t^\ddagger Q_r^\ddagger}{Q_t Q_r Q_v} \exp(-E_0/k_B T) \quad (1)$$

where h is Planck's constant, k_B is Boltzmann's constant, T is the temperature, Q_t, Q_r and Q_v are the translational, rotational and vibrational partition functions for the reactants, respectively; and the $Q_t^\ddagger$ and $Q_r^\ddagger$ represent corresponding values for transition state. Γ in the above equation is the ratio of quantum-mechanical barrier-crossing rate to classical-mechanical barrier-crossing rate (tunneling effect) which is computed for an Eckart potential barrier according to following equation [21–23]:

$$\Gamma = \exp(V_1/RT) \int_0^\infty \kappa \exp(-E/k_B T)\, dE/k_B T \quad (2)$$

where V_1 is the height of the potential barrier towards the exothermic direction of the reaction, and κ is the transmission probability for tunneling given by

$$\kappa(E) = 1 - \frac{\cosh 2\pi(a-b) + \cosh 2\pi d}{\cosh 2\pi(a+b) + \cosh 2\pi d} \quad (3)$$

The parameters in above equation are given by the following equations

$$a = \frac{[\alpha_1 \xi]^{1/2}}{\pi} \left(\frac{1}{\alpha_1^{1/2}} + \frac{1}{\alpha_2^{1/2}} \right)^{-1} \quad (4)$$

$$b = \frac{[\alpha_1(1+\xi) - \alpha_2]^{1/2}}{\pi} \left(\frac{1}{\alpha_1^{1/2}} + \frac{1}{\alpha_2^{1/2}} \right)^{-1} \quad (5)$$

$$d = \frac{1}{\pi} [\alpha_1 \alpha_2 - 2\pi^2/16]^{1/2} \quad (6)$$

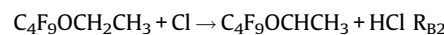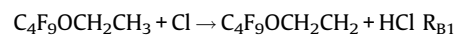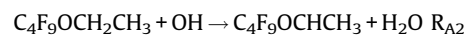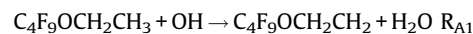$$\alpha_1 = 2\pi V_1/h\nu^* \quad (7)$$

$$\alpha_2 = 2\pi V_2/h\nu^* \quad (8)$$

$$\xi = E/V_1 \quad (9)$$

where ν^* in imaginary frequency of the saddle-point, V1 and V2 are the heights of the potential barrier towards the exothermic direction and its reverse reaction, respectively. In this research work, MULTIWELL program package [24] is used to compute the thermal rate coefficients.

3. Results and discussion

On the basis of the present theoretical study, the following reaction paths can be considered for the hydrogen abstraction reactions from $C_4F_9OC_2H_5$ by OH and Cl radicals:

$C_4F_9OCH_2CH_3 + OH \rightarrow C_4F_9OCH_2CH_2 + H_2O$ R_{A1}

$C_4F_9OCH_2CH_3 + OH \rightarrow C_4F_9OCHCH_3 + H_2O$ R_{A2}

$C_4F_9OCH_2CH_3 + Cl \rightarrow C_4F_9OCH_2CH_2 + HCl$ R_{B1}

$C_4F_9OCH_2CH_3 + Cl \rightarrow C_4F_9OCHCH_3 + HCl$ R_{B2}

According to the computed energies at the MPWB1K/MG3S level of theory, the mechanism of the hydrogen-abstraction reactions from $C_4F_9OC_2H_5$ by OH radical can be described as follows. The reaction proceed through a van der Waals complex, denoted as vdWiA, with an energy of 12.85 kJ mol^{-1} lower that the reactants. This complex is formed via hydrogen bonding between H atom of OH radical and O atom of $C_4F_9OC_2H_5$. Next, hydrogen atoms transfer from $C_4F_9OC_2H_5$ to OH radicals through the transition state structures TS1A and TS2A leading to van der Waals complexes vdWf1A and vdWf2A, respectively. The energies of the transition states TS1A and TS2A relative to reactants are 12.43 and 4.10 kJ mol^{-1}, respectively. In the van der Waals complexes vdWf1A and vdWf2A, water molecules are attached to the produced radicals via hydrogen bonding interactions. The relative energies of the complexes vdWf1A and vdWf2A are −70.41 and −88.24 kJ mol^{-1} and dissociate to give the products $C_4F_9OCH_2CH_2 + H_2O$ (P1A) and $C_4F_9OCHCH_3 + H_2O$ (P2A), respectively. The products P1A and P2A are −55.85 and −78.24 kJ mol^{-1} more stable than the reactants, respectively. The structure of the reactants and transition states of the $C_4F_9OC_2H_5 + OH$ reaction are depicted in Fig. 1. The z-matrices of the reactants, van der Waals complexes and transition states are provided in the Supplemental Information. It is noteworthy to mention that the most stable conformations of the HFE-7200 and transition states are used in the rate constant calculations. It is found that the transition state structures used in the present calculations are relatively more