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ORIGINAL ARTICLE

A theoretical investigation of decomposition and reactivity of the atmospheric $C_3F_7OCH_2O$ radical

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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.

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 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). $C_3F_7OCH_3$ 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-$C_3F_7OCH_3$ is needed. The atmospheric oxidation of $C_3F_7OCH_3$ will be initiated. A general tropospheric degradation mechanism of HFE-7000 is shown in Scheme 1. Like most HFEs, the atmospheric oxidation of $C_3F_7OCH_3$ will be initiated by reaction with OH radicals and then it reacts with O_2 rapidly to give a peroxy radical ($C_3F_7OCH_2O_2^{\cdot}$) (Ninomiya and Kawasaki, 2000). Then, it can react with NO_X ($X = 1, 2$) or with tropospheric HO_2, finally leading to the formation of haloalkoxy radicals ($C_3F_7OCH_2O^{\cdot}$). 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 O_2 or OH as shown following:

$$C_3F_7OCH_2O + O_2 \rightarrow C_3F_7OCHO + HO_2 \tag{1}$$

$$C_3F_7OCH_2O + OH \rightarrow C_3F_7OCHO + H_2O \tag{2}$$

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

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

$$C_3F_7OCH_2O \rightarrow CF_3OCHOH \tag{5a}$$

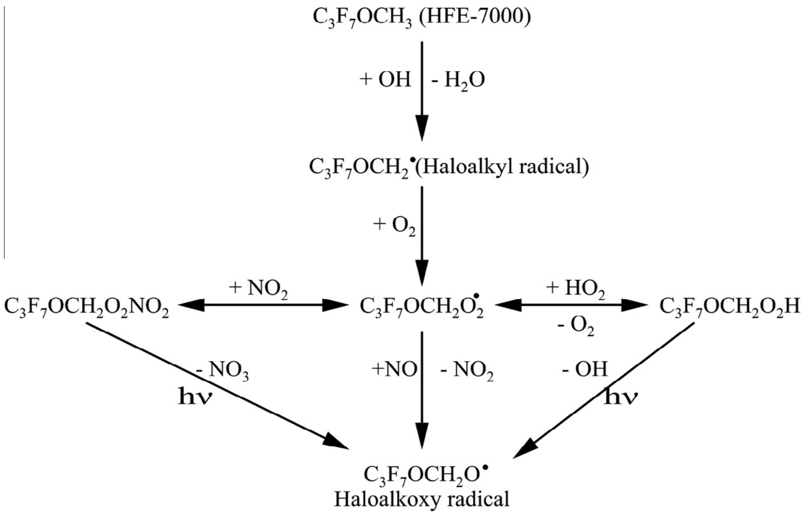
$$C_3F_7OCHOH \rightarrow C_3F_7 + OCHOH \tag{5b}$$

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.

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 $C_3F_7OCH_2O$ was scanned around the C_1–O_2 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 (NIMAG = 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.

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