

Review Article

Cl-Initiated Oxidation Mechanism and Thermochemistry of Trifluoromethyl Methyl Ether CH_3OCF_3 (HFE- 143a): An Insight from DFT Study

Subrata Paul¹, Satyajit Dey Baruah¹, Gargi Goswami², Ritika Borah², Nand Kishor Gour^{1*} and Ramesh Chandra Deka^{1*}

¹Department of Chemical Sciences, Tezpur University Tezpur, Assam, India

²Department of Chemistry, Darrang College Tezpur, Assam, India

*Corresponding author: Nand Kishor G and Ramesh Chandra D, Department of Chemical Sciences, Tezpur University Tezpur, Assam, India

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Abstract

In this work, we have performed theoretical investigations on the oxidation of trifluoromethyl methyl ether (CH_3OCF_3) molecule initiated by Cl atom using the Density Functional Theory (DFT) method. Here we have constructed an energy profile diagram for the three reaction channels viz. $\text{CH}_3\text{OCF}_3 + \text{Cl} \rightarrow \text{C}\cdot\text{H}_2\text{OCF}_3 + \text{HCl}$ (R1), $\text{CH}_3\text{OCF}_3 + \text{Cl} \rightarrow \text{CH}_3\text{O}\cdot + \text{CF}_3\text{Cl}$ (R2) and $\text{CH}_3\text{OCF}_3 + \text{Cl} \rightarrow \text{CF}_3\text{O}\cdot + \text{CH}_3\text{Cl}$ (R3) along with the transition states at M06-2X/6-31+G (d,p) level of theory. Our energy profile result shows that R1 channel is found to be the lowest energy barrier reaction as compared to the other two channels. Thermochemical results also suggest that the product of R1 reaction is more stable than others. In addition to this, we have also determined heats of formation ($\Delta_f H_{298}^\circ$) using isodesmic reactions method and Bond Dissociation Energy (BDE) of CH_3OCF_3 molecule. The value of $\Delta_f H_{298}^\circ$ and BDE of the molecule are found to be in good agreement with the value reported in the literature.

Keywords: HFE; DFT; Isodesmic; Heat of formation; BDE

Introduction

Hydrofluoroethers (HFEs) are a class of non-ozone depleting organic compounds. They serve as an alternative to Chlorofluorocarbons (CFCs), Hydrofluorocarbons (HFCs), and Hydrochlorofluorocarbons (HCFCs) for a wide range of commercial applications such as cleaning of electronic equipment, heat transfer fluid in refrigerators, lubricant deposition and foam blowing agents. Chlorine and bromine atoms are responsible for ozone depletion which remains absent in HFE [1,2]. The C-F bonds of HFEs absorb infrared radiation, thus acting as greenhouse gases [3]. Consequently, HFEs are considered to be the potential candidate for the global warming effect. In general, the HFEs having C-H bond, happens to get oxidized in the atmosphere by highly reactive radical species, such as OH radical and Cl atom. These reactions constitute the initial step of their degradation and thus results in short atmospheric lifetimes and Global Warming Potentials (GWPs) reducing their environmental impact. Also, the presence of an ether (-O-) linkage in HFEs enhances their reactivity in the troposphere, resulting in a shorter atmospheric lifetime which limits their accumulation in the atmosphere and decreases their potential impact as greenhouse gases [4]. Numerous studies on HFEs with OH radical has been explored both theoretically and experimentally [5-7]. The study of HFEs with Cl atom is also important in the marine regions, which can not be ignored. There are very limited studies are reported in the literature in this regard.

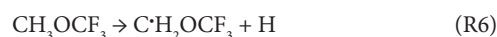
In the present work, we aim to address the degradation pathways of the trifluoromethyl methyl ether (CH_3OCF_3) with Cl atom using the quantum chemical method. The reaction between CH_3OCF_3 and Cl atom will proceed by H-atom abstraction as well as Cl atom addition and C-O bond breaking, leading to the formation of alkyl

and alkoxy radicals. The following reactions are considered for the study and shown in Scheme 1.

Furthermore we will also determine the heat of formation ($\Delta_f H_{298}^\circ$) and Bond Dissociation Energy (BDE) of CH_3OCF_3 molecule by using quantum chemical method. Here, we will determine heat of formation of CH_3OCF_3 molecule by using isodesmic reaction method [8] at the same level of theory. As the isodesmic reaction is a relatively inexpensive and accurate method to predict the enthalpy of formation because the conservation of the number of electron pairs in the reactants and products and the similarity of bond type cancel the possibilities of systematic errors in the calculations. Here, we predict the heat of formation for CH_3OCF_3 molecule, using the following isodesmic reactions:

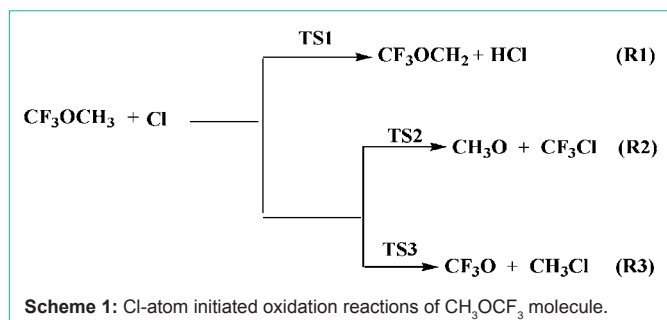


Bond dissociation energy (BDE) is an important parameter in understanding the progress of a chemical reaction. So, we are considered to obtain BDE of species using the following reaction



Computational Details

Electronic structures and thermochemical calculations are performed using the Density Functional Theory (DFT) method as given in Gaussian 09 software package [9]. We have used M06-2X functional [10] of DFT method along with 6-31+G(d) basis set to obtain optimized geometry of all species. It is important to note that 2X in M06-2X represented the double the amount of nonlocal exchange, and it is parametrized mainly for non-metals [11]. This functional has been chosen for the calculations as it served better



results for thermochemistry, kinetics, and barrier height on related systems [1,12,13]. Further, we have performed vibrational frequencies calculations for all the species at the same level of theory. Frequency results stand hold of the stable minima that correspond to the real and positive values except for transition states. Transition states have been identified by only one imaginary frequency. Intrinsic Reaction Coordinate (IRC) calculations have been performed to testify the transition states smoothly connecting the reactant and product [14].

The Heat of reaction is calculated by using the expression:

$$\Delta H_r^\circ = \sum H^\circ (\text{Products}) - \sum H^\circ (\text{Reactants}) \quad (1)$$

Heat of reaction also expressed as:

$$\Delta H_r^\circ = \Delta H_f^\circ (\text{Products}) - \Delta H_f^\circ (\text{Reactants}) \quad (2)$$

Where H denotes enthalpy of the species and ΔH_f° change of heat of formation of species

BDE of C-H bonds are calculated by using the given equation:

$$\text{BDE} (\text{A}-\text{B}) = \text{H}(\text{A}^\bullet) + \text{H}(\text{B}^\bullet) - \text{HA}-\text{B} \quad (3)$$

where H's are the enthalpy of the corresponding species. A^\bullet and B^\bullet are the radical species formed as a result of the homolytic fission of the covalent bond.

Results and Discussion

Electronic Structures and Energy Profile Diagram

We have first optimized the geometry of CH_3OCF_3 molecule at M06-2X/6-31+G(d) level of theory and found that hydrogen atoms present in $-\text{CH}_3$ sites are equivalent. Thus, we have considered only one H-abstraction reaction from $-\text{CH}_3$ sites of CH_3OCF_3 . In addition to this, we have also considered Cl-atom addition to CH_3 - and CF_3 -site of CH_3OCF_3 molecule and C-O bond cleavage reactions. All the possible reaction channels (R1-R3) are shown as Scheme 1.

Considering these reaction pathways, the geometries of all the species including Reaction Complexes (RC), Transition States (TSs), Product Complex (PC) and products are optimized at M06-2X/6-31+G(d) level of theory and are presented in Figure 1 along with the bond lengths (in Å).

We have observed from Figure 1 that in the case of H-abstraction by Cl-atom as given in R1, the C-H bond distances of TS1 increase from 1.088 Å to 1.430 Å with respect to equilibrium C-H bond of CH_3OCF_3 . In R2, Cl-atom addition occurs at $-\text{CF}_3$ site of CH_3OCF_3 molecule and simultaneously C-O bond breaks and thus leading to the formation of $\text{CH}_3\text{O} + \text{CF}_3\text{Cl}$ via TS_2 . In TS_2 , the Cl is at a distance of 2.44 Å from

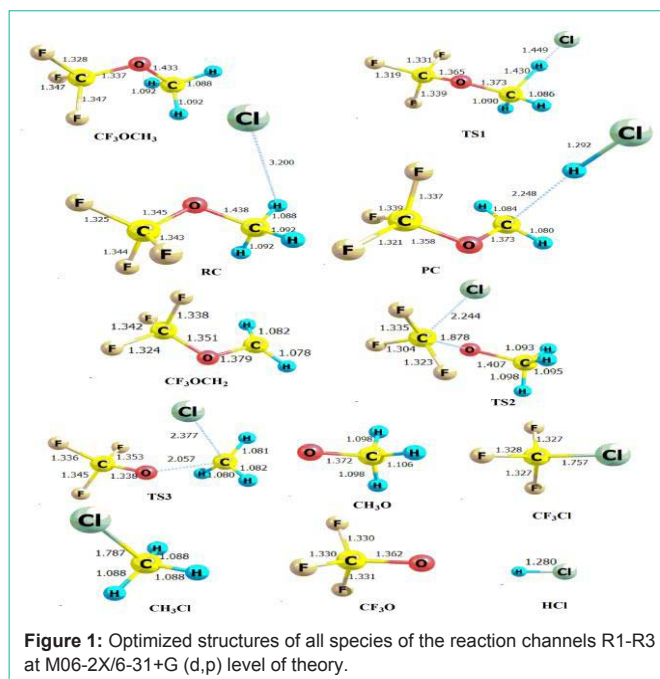


Figure 1: Optimized structures of all species of the reaction channels R1-R3 at M06-2X/6-31+G (d,p) level of theory.

Table 1: Zero-point corrected total energy (E_0) for species and transition states along with the relative energy (R.E) at M06-2X/6-31+G (d,p) levels of theory.

Reaction Species	E_0 (in Hartree)	R.E. (in kcal mol ⁻¹)
$\text{CH}_3\text{OCF}_3 + \text{Cl}$	-912.6752994	0
RC	-912.680852	-3.48
TS1	-912.6747171	0.37
TS2	-912.5540586	76.08
TS3	-912.5793497	60.21
PC	-912.678111	-1.76
$\text{CF}_3\text{OC}^\bullet\text{H}_2 + \text{HCl}$	-912.6748833	0.26
$\text{CH}_3\text{O} + \text{CF}_3\text{Cl}$	-912.6427967	20.40
$\text{C}^\bullet\text{F}_3\text{O} + \text{CH}_3\text{Cl}$	-912.6511897	15.12

Table 2: Thermochemical data (in kcal mol⁻¹) for reaction channels (R1-R3) calculated at M06-2X/6-31+G(d,p) levels of theory.

Reaction Channels	$\Delta_f H^\circ$	$\Delta_f G^\circ$
$\text{CH}_3\text{OCF}_3 + \text{Cl} \rightarrow \text{CF}_3\text{OCH}_2 + \text{HCl}$ (R1)	0.90	-1.45
$\text{CH}_3\text{OCF}_3 + \text{Cl} \rightarrow \text{CH}_3\text{O} + \text{CF}_3\text{Cl}$ (R2)	20.47	16.74
$\text{CH}_3\text{OCF}_3 + \text{Cl} \rightarrow \text{CF}_3\text{O} + \text{CH}_3\text{Cl}$ (R3)	15.26	32.64

C atom of CF_3 site and at the same time C-O bond distance increases from 1.337 Å to 1.878 Å in TS_2 with respect to CH_3OCF_3 molecule. In the same way, in R3 pathway, Cl-atom addition occurs at $-\text{CH}_3$ site of CH_3OCF_3 molecule and breaking of the C-O bond is also observed simultaneously, leading to the formation of $\text{CF}_3\text{O} + \text{CH}_3\text{Cl}$ via TS_3 . In TS_3 , the Cl-atom is at a distance of 2.38 Å from C atom of CH_3 site and at the same time C-O bond of TS_3 increases with respect to CH_3OCF_3 from 1.43 Å to 2.37 Å.

Frequency calculations of all species have also been performed at M06-2X/6-31+G(d,p) level of theory. Vibrational frequency results signify the existence of stable minima, having real positive frequencies for all the species except the transition states. Transition

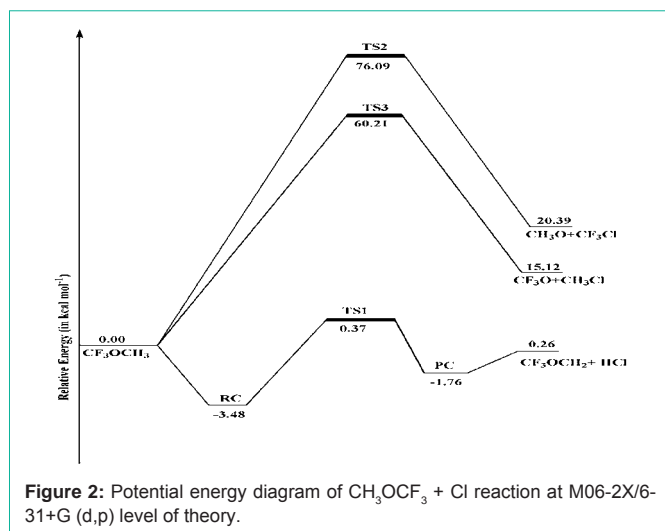


Figure 2: Potential energy diagram of $\text{CH}_3\text{OCF}_3 + \text{Cl}$ reaction at M06-2X/6-31+G(d,p) level of theory.

Table 3: Value of enthalpies (in Hartree) for all species present in R4-R6 at M06-2X/6-31+G(d,p) level of theory.

Species	Enthalpy (H)
CH_3OCF_3	-452.568
CH_4	-40.4389
CH_3OCH_3	-154.869
CHF_3	-338.106
CH_3F	-139.644
CF_4	-437.339
$\text{C}_2\text{H}_2\text{OCF}_3$	-451.913
H	-0.494

states TS1, TS2 and TS3 are characterized by the occurrence of only one imaginary frequency observed at 760i, 543i and 724i cm^{-1} . Visualization of the imaginary frequency has revealed a qualitative confirmation of the existence of transition states connecting reactants and products. Intrinsic reaction coordinate (IRC) calculations have been performed for each transition state at the same level of theory. Results show that each transition state connects the reactant and the product sides smoothly.

We have also explored the reaction pathways to determine the kinetically favorable one. Zero-point corrected total energy for all species and TSs along with the relative energy barrier are presented in Table 1.

A Potential Energy Diagram (PES) of the title reaction is constructed with the help of data reported in Table 1 and shown in Figure 2.

In the construction of the energy diagram, the ground state energies of the reactants are arbitrarily taken as zero. The calculated barrier heights for TS1, TS2 and TS3 are 0.37, 76.08 and 60.21 kcal mol^{-1} , respectively. So R1 channel is faster than the other two reaction channels (R2 and R3). In other words, we can say that Cl-initiated H-abstraction reaction is more dominant channel than the other two channels. We further observed that the product obtain corresponding to R1 channel is more stable than the other two products. Whereas in case Cl-atom addition and simultaneous C-O dissociation reactions

Table 4: Heat of formation and Bond Dissociation Energy (BDE) of CH_3OCF_3 is calculated at M06-2X/6-31+G(d,p) level of theory. All values in kcal mol^{-1} .

Molecule	Reactions	Heat of formation ($\Delta_f H_{298}^\circ$)	Literature values
CH_3OCF_3	R4	-212.70	
	R5	-215.77	
	Average	-212.74	(-212.7 ± 2.3) [15]
BDE			
CH_3OCF_3	R6	100.73	(102 ± 1) [16]

(R2 and R3), R3 pathway displayed more facile pathway to obtain CF_3O and CH_3Cl in comparison to R2 pathway.

Reaction energies (R1-R3), Heat of Formation and BDE of CH_3OCF_3 molecule

From frequency calculations, we have obtained absolute enthalpies and Gibbs free energies of all species (in Hartree). From these data, we have determined enthalpy and Free energy changes of the reaction channels (R1-R3) and are listed in Table 2.

Results show that the H-abstraction reaction i.e. R1 is slightly endothermic in nature with $\Delta_f H^\circ$ value of 0.90 kcal mol^{-1} but thermodynamically facile with $\Delta_f G^\circ$ value of -1.45 kcal mol^{-1} . On the other hand, Cl-atom addition and simultaneous C-O dissociation reactions (R2 & R3) are highly endothermic ($\Delta_f H^\circ > 0$) as well as thermodynamically not feasible ($\Delta_f G^\circ > 0$). These results are in accordance with the observed relative energy calculations.

In order to find heat of formation and bond dissociation energy of CH_3OCF_3 molecule, geometry optimizations of all species present in the reactions R4-R6 are performed. From this, we have obtained a global optimized structure corresponding to minimum energy and further performed frequency calculations of species to get thermochemical data of all the species present in reactions. The absolute enthalpies values of all the species are given in Table 3.

The reaction enthalpies of the reaction (R4 and R5) and heat of formation of CH_3OCF_3 molecule are calculated by using Equation.1 and Equation.2 (described in the computational details section) for isodesmic reactions R4 and R5. The experimental values of heat of formation ($\Delta_f H_{298}^\circ$) for all species involved in the above reaction have been taken from data available at NIST [12]. The value of heat of formation is given in Table 4.

Conclusions

We have systematically investigated the reaction mechanism and thermochemistry of trifluoromethyl methylether CH_3OCF_3 (HFE-143a) with Cl atom as well as Cl-atom addition and simultaneous C-O dissociation reaction with CH_3OCF_3 molecule at M06-2X/6-31+G(d,p) level of theory. From the energy profile diagram we found that hydrogen atom abstraction by Cl atom follows the lowest barrier path with an activation energy of 0.37 kcal mol^{-1} than the other two channels. The thermochemical analysis reveals that R1 channel is slightly endothermic ($\Delta_f H^\circ > 0$) and thermodynamically facile ($\Delta_f G^\circ < 0$), while R2 and R3 displayed highly endothermic nature ($\Delta_f H^\circ > 0$) and thermodynamically not feasible ($\Delta_f G^\circ > 0$). In addition to this, we have also obtained heat of formation of the CH_3OCF_3 molecule using isodesmic reaction schemes as well as bond dissociation energy of the molecule. These values are found to

be good agreement of experimentally reported values. The presented work would be very much helpful to understand oxidation pathways and thermochemistry of other such species. This study would also be helpful to determine kinetics, lifetime and global warming potential of HFEs.

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