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Night-time reaction of 2-chloroethyl methyl ether ($CH_3OCH_2CH_2Cl$) initiated by NO_3 radical: A theoretical insight

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ABSTRACT

Night-time gas-phase reaction of $CH_3OCH_2CH_2Cl$ initiated by NO_3 radical has been carried out using dual-level of quantum methods. Optimization and frequency calculations are performed at hybrid density functional M06-2X/6-31+G(d,p) level of theory and energy calculations are further refined at CCSD(T)/6-311++G(d,p) level of theory. All the stationary points (both minima and saddle points) have been located and characterized on the potential energy surfaces. The result shows that H-atom abstraction from the —OCH_2 site of $CH_3OCH_2CH_2Cl$ initiated by NO_3 radical is thermodynamically and kinetically more favorable reaction pathways than other reaction channels. The atmospheric lifetime, radiative efficiency and global warming potentials (GWPs) have also been reported in this work.

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1. Introduction

Hydrochloroethers (HCEs) is considerable part of oxygenated volatile organic compounds (OVOCs) which have been widely used in agricultural and industrial purpose [1,2] and their continuous release into the atmosphere has been considered as a major problem to human health and environment. These compounds are emitted directly into the atmosphere from biogenic and anthropogenic sources and are also formed in situ from the oxidation of all atmospheric hydrocarbons [3,4]. Due to presence of the ether linkage (—O—), may lead to an even greater reactivity of HCEs in the troposphere [5]. They also contain Cl atom which can destroy the ozone layer and facilitate the global warming. Therefore, it is important to study the kinetics and mechanistic degradation pathways of HCEs in troposphere for complete assessment of atmospheric chemistry. In the troposphere, they can be initiated by wet and dry deposition and by photolytic degradation with OH radicals (during the day-time), with Cl atoms in coastal, marine and industrial regions (during daylight hours) and with NO_3 radicals (during night-time). Although, reaction with the OH radicals is the dominant degradation process during the day due to high concentration of OH radicals [6] and numerous experimental and theoretical investigations have been done on HCEs initiated by OH radicals and Cl atom in the recent years [7–12]. However, NO_3 radicals are important oxidants in the atmosphere at night, and their reactivities are comparable to those of OH radicals in the atmosphere during the day time [13]. Its average concentration is found to be 5×10^8 to 2×10^9 molecule cm^{-3} in the night-time atmosphere [14,15] measured by long path spectroscopic techniques. Therefore, in the recent years, researchers have paid attention towards performing kinetics of volatile organic compounds (VOCs) initiated by NO_3 radical [16–19]. It was observed in the previous studies that NO_3 night-time degradation in urban zones with a large concentration of ether and its derivatives. The NO_3 radicals contribute to the oxidation of HCEs and to the formation of HNO_3 which is also related to particulate formation and harmful health effects. In addition, reactions of NO_3 with biogenic hydrocarbons are particularly efficient and are responsible for the production of organic nitrates and secondary organic aerosols [20–22]. Chen et al. [19] first experimentally studied the kinetics of gas-phase reactions of ethers and its derivative with NO_3 radicals using relative rate technique at 298 K. However, neither theoretical nor experimental studies have been performed for the reaction of HCEs initiated by NO_3 radicals. In this work theoretical investigation has been carried out on the kinetics, mechanism and thermochemistry of $CH_3OCH_2CH_2Cl$ initiated by NO_3 radicals in night-time atmospheric reaction for complete assessment of atmospheric chemistry.

The H-atom abstraction take place from $CH_3OCH_2CH_2Cl$ initiated by the NO_3 radicals may occur from either one of the follow-

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ing positions —CH_2Cl, —OCH_2 and —OCH_3 which lead to three possible reaction channels:

$$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_3OCH_2C^{\cdot}HCl + HNO_3 \quad (R1)$$

$$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_3OC^{\cdot}HCH_2Cl + HNO_3 \quad (R2)$$

$$CH_3OCH_2CH_2Cl + NO_3 \rightarrow C^{\cdot}H_2OCH_2CH_2Cl + HNO_3 \quad (R3)$$

The main aim of this manuscript is to characterize of all the stationary points (both minima and saddle points) involved in the reaction channel (R1-R3) on potential energy surface and also evaluate more accurate thermochemistry and kinetics data of the reaction channels by means of dual level of quantum chemical calculations. However, experimental result gives only the average rate constant and doesn't provide any idea about the detailed mechanism, thermochemistry and various reaction channels involved in the process. In order to overcome these experimental shortcomings, a well-defined theoretical approach is highly solicited to acquire complete information. Here, dual-level of quantum calculation procedure was chosen in which geometry optimizations and frequency calculations were carried out at a lower level of method followed by energetic calculations at a higher level as proposed by Truhlar and co-workers [23–25]. Thus, the optimizations and frequency calculations were performed at hybrid density functional M06-2X [25] followed by a energetic calculation at CCSD (T) level [26].

2. Computational details

The geometry of reactants, transition states, and products involved in the reaction channels (R1-R3) were optimized using hybrid density functional M06-2X with 6-31+G(d, p) basis set. In order to evaluate various stationary points on the potential energy surface, vibrational frequency calculations were also performed using the same level of theory at which the optimizations were carried out. We have used M06-2X functional because this provides reliable results for thermochemistry and kinetics [27–30]. As higher order correlation corrected relative energies along with the density functional energies are necessary to obtain theoretically consistent reaction energies. Therefore a potentially high-level CCSD(T) method was employed for energetic calculations using 6-311++G(d,p) basis set. This dual level of method i.e. CCSD (T)/M06-2X have been found to be better results as compared to be individual M06-2X functional [31,32]. Galano et al. have proposed that the T1 diagnostic seems not a settled issue to judge multi reference character in CCSD(T) wave function. Probably the most frequently used is the T1 diagnostic in several diagnostics available, which gives a qualitative assessment of the significance of non-dynamical (or static) correlation. The literature information has been proposed that T1 values $\geq$0.02 and 0.045 indicate a significant multi reference character for closed-shell and open-shell systems, respectively [33,34]. In this work, the T1 values are smaller than 0.02 for closed-shell systems and smaller than 0.045 for open-shell systems, show that the multi reference character is not an issue. However, it has been reported that these threshold values are not rigorously defined and can be system- and method-dependent. The transition states in reaction channels (R1-R3) were obtained using synchronous transition-guided quasi-Newton (STQN) method [35,36]. All the species were identified with zero imaginary frequency (NIMAG = 0), while TSs (TS1–TS3) were identified with only one imaginary frequency (NIMAG = 1). In order to confirm whether the identified transition states were correctly connected reactants and products smoothly we have carried out intrinsic reaction coordinate (IRC) calculations [37]. As higher order correlation corrected relative energies along with the density functional energies are necessary to obtain theoretically consistent reaction energies. Therefore a potentially high-level CCSD(T) method was employed for energetic calculations using 6-311++G(d,p) basis set. We were done all the optimization and energetic calculations using Gaussian 09 program package [38].

3. Results and discussion

The values reaction enthalpies $\Delta H^{\circ}_{r,298}$ and Gibbs free energies $\Delta G^{\circ}_{r,298}$ (in kcal mol^{-1}) for the reaction channels (R1-R3) calculated at M06-2X/6-31+G(d,p) and CCSD(T)/6-311++G(d,p)//M06-2X/6-31+G(d,p) levels of theory as described in the computational details was recorded in Table 1. Form Table 1, it is very clear that all of the hydrogen abstraction pathways considered during the present study are significantly exothermic in nature ($\Delta H^{\circ}_{r,298} < 0$) and thus thermodynamically facile ($\Delta G^{\circ}_{r,298} < 0$). The more negative value of $\Delta H^{\circ}_{r,298}$ and $\Delta G^{\circ}_{r,298}$ shows that the hydrogen atom abstraction for R2 may be thermodynamically more favorable than other reaction channels. The optimized geometries along with bond parameter (in angstrom) for reactants ($CH_3CH_2OCH_2Cl$ and NO_3), TSs (TS1, TS2 and TS3) and products ($CH_3OCH_2C^{\cdot}HCl$, $CH_3OC^{\cdot}HCH_2Cl$, $CH_3C^{\cdot}HOCH_2CH_2Cl$, $C{\cdot}H_2OCH_2CH_2Cl$ and HNO_3) obtained at DFT (M06-2X)/6-31G+(d,p) level of theory are shown in Fig. 1. From the optimized geometry of TSs (TS1–TS3) for reaction channels (R1-R3), the percentage elongation of C—H (bond breaking) and O—H (bond making) bonds with respect to their corresponding equilibrium bond distances are calculated and are found to be 7.7%, 3.7% and 3.6 % respectively for the former case while they are found to be 49.5%, 71.9% and 75.3 % respectively for the latter case. The fact that the percentage elongation of bond distances in bond making is larger than that in the bond breaking indicates that the barrier of the reaction is near the corresponding reactants. This means the reaction will proceed via early transition state structure which is in consonance with Hammond's postulate [39] applied to an exothermic hydrogen abstraction reaction.

Vibrational frequency values obtained during frequency calculations for all the species at same level of theory are recorded in Table 2. From Table 2, it is clear that all the species correspond to stable minima having real positive vibrational frequencies except transition states. Transition state structures (TS1, TS2 and TS3) are identified by only one imaginary frequency at 710*i* cm^{-1}, 255*i* cm^{-1} and 326*i* cm^{-1} respectively. Visualization of vibrations of these imaginary frequencies have been observed using ChemCraft program [40]. To confirm the smooth connection of transition state with reactants and products, intrinsic reaction coordinate (IRC) calculations are also performed at the same level of theory.

Energetic calculations of various species involved in the hydrogen atom abstraction reactions are further refined using CCSD (T)/6-311++G(d,p) level of theory at M06-2X/6-31+G(d,p) opti-

Table 1
Reaction enthalpies ($\Delta H^{\circ}_{r,298}$) and Gibbs free energies ($\Delta G^{\circ}_{r,298}$) values (in kcal mol^{-1}) for reaction channels (R1-R3) calculated at M06-2X/6-31G(d,p) and CCSD(T)/6-311++G(d,p)//M06-2X/6-31+G(d,p) and level of theories.

Reaction channels	M06-2X	CCSD(T)
$\Delta H^{\circ}_{r,298}$		
$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_3OCH_2CHCl + HNO_3$ (R1)	−9.96	−4.87
$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_3OCHCH_2Cl + HNO_3$ (R2)	−16.61	−10.32
$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_2OCH_2CH_2Cl + HNO_3$ (R3)	−11.89	−7.13
$\Delta G^{\circ}_{r,298}$		
$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_3OCH_2CHCl + HNO_3$ (R1)	−10.18	−5.09
$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_3OCHCH_2Cl + HNO_3$ (R2)	−16.89	−10.60
$CH_3OCH_2CH_2Cl + NO_3 \rightarrow CH_2OCH_2CH_2Cl + HNO_3$ (R3)	−11.43	−6.67

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