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# Theoretical study on the kinetics and branching ratios of the gas phase reactions of 4,4,4-trifluorobutanal (TFB) with OH radical in the temperature range of 250–400 K and atmospheric pressure

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ABSTRACT

Qunatum mechanical calculations are carried out on the reactions of $CF_3CH_2CH_2CHO$ (TFB) with OH radical by means of meta hybrid DFT methods. The geometries of the reactants, reaction complex, products and transition states involved in the reaction pathways are optimized at MPWB1 K level of theory using 6-31G(d,p) basis set. Single point energy calculations are performed at MPWB1 K level using extended 6-311+G(3df,2pd) basis set. Using group balanced Isodesmic reactions enthalpy of formation at 298 K ($\Delta_f H_{298}{}^{\circ}$) of reactant and corresponding products are also estimated for the first time by using G2(MP)2 and CBS-QB3 methods. The hydrogen abstraction rate constant for the title reaction are calculated in the temperature range of 250–400 K and atmospheric pressure using the Canonical Transition State Theory (CTST) including tunneling correction. The percentage contributions of all three reaction channels are also reported within temperature range of 250–400 K and atmospheric pressure.

## 1. Introduction

Recognisation of the prominent adverse effect of Chlorofluorocarbons (CFCs) toward stratospheric Ozone depletion and global warming has led an international agreement (Montreal protocol) to phase out its commercial production as well as replace CFCs with environmentally more acceptable alternatives [1–4]. In order to minimize the stratospheric impact of CFCs a number of CFCs replaceable compound such as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) have been proposed. However, their strong infrared absorbance due to the C–F bonds and relatively long atmospheric lifetimes signifies the potential contribution of these ozone-friendly substances toward global warming [5]. Recently, hydrofluoroethers (HFEs) and partially fluorinated alcohols, $(CF_3(CH_2)_xCH_2OH$ where, $x = 1$ and 2) are widely recommended as a new generation alternatives for HFCs and HCFCs in many industrial applications such as cleaning of electronic equipments, heat transfer fluid in refrigerators, carrier fluid for lubricants and foam blowing agents [6–10]. Partially fluorinated alcohols do not contain chlorine and bromine atoms that cause the ozone depletion. In addition the rate constant for the reaction of partially fluorinated alcohols (PFAs) with OH radical suggest that their atmospheric lifetime should be relatively short and thus PFAs appear to have less impact for the global warming [11,12]. Nevertheless, the presence of C–F and C–O bonds in PFAs may enhance the absorption features in the atmospheric infrared region (800–1400 $cm^{-1}$) and could play a significant role as green house gases. The main degradation route for PFAs is expected to be their tropospheric removal initiated by hydroxyl (OH) radicals and Cl atom in marine troposphere and also possibly with chloride containing aerosol of highly industrialized urban areas [13]. Tropospheric degradation of PFAs is known to yield fluorinated aldehydes (FAs) as a major product [13–15]. The prospective atmospheric implications of PFAs are associated with their tropospheric degradation pathways, nature of products of these degradations, and atmospheric lifetimes of each newly formed species. Therefore, it is important to study the kinetic and mechanistic degradation pathways of Fluorinated aldehydes (FAs) for complete assessment of PFAs atmospheric chemistry as well as their impact on global warming and climate change.

In our present work, we pay attention to the mechanism and kinetics study of H-abstraction reaction between $CF_3CH_2CH_2CHO$ (TFB) with OH radical. TFB is expected to be produced in the atmosphere by OH and Cl initiated photo oxidation of $CF_3CH_2CH_2CH_2OH$ [16]. Besides atmospheric importance, use of TFB as precursor aldehydes for the synthesis of fluorinated alpha (α) amino acids also endorsed its significant contribution toward medicinal research domain [17]. For the reaction of TFB with

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OH-radical three H-abstraction channels are feasible which may proceed from beta (β)–$CH_2$ group, alpha (α)–$CH_2$ group, and aldehydic (–CHO) group. Therefore, knowledge of branching ratios for these three pathways are important as H-abstraction from each reaction channels yield different products. So the three primary processes have been considered for the title reaction as given by reactions ((R1)–(R3)) during the present investigation.

$$CF_3CH_2CH_2CHO + OH \rightarrow CF_3CH_2CH_2CO + H_2O \tag{R1}$$

$$CF_3CH_2CH_2CHO + OH \rightarrow CF_3CH_2CHCHO + H_2O \tag{R2}$$

$$CF_3CH_2CH_2CHO + OH \rightarrow CF_3CHCH_2CHO + H_2O \tag{R3}$$

Antinolo et al. [18] first experimentally studied rate constant for the reaction of TFB with OH radical by pulsed UV laser photolysis (PLP) technique and reported a rate constant of $1.28 \pm 0.24 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and pressure (51–204 Torr of He). However, experimental studies provided only the total rate constant and it is difficult to predict the detailed mechanism, thermo chemistry and contribution of each reaction channels toward overall rate constant. Thus, for better understanding of mechanistic pathways, kinetics and thermo chemistry we must rely on quantum chemical methods. Canonical Transition State Theory (CTST) [19,20] is also utilized to predict the rate constant of the title reactions on the basis of meta hybrid density functional MPWB1 K 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 reaction of TFB.

## 2. Results and discussion

The detailed thermodynamic calculations for enthalpy of reactions ($\Delta_rH^\circ$), reaction free energies ($\Delta_rG^\circ$) and Gibbs free energy of activation ($\Delta G^\#$) performed at 298 K for the reaction of $CF_3CH_2CH_2CHO$ with OH radical are recorded in Table 1. Thermal corrections for zero point vibration energy (ZPVE) at 298 K were included in the determination of thermodynamic functions. Calculated free energy value shows that all three reaction channels are exergonic ($\Delta G < 0$). The reaction enthalpy ($\Delta_rH^\circ$) values for reactions ((R1)–(R3)) given in Table 1 show that all three reaction channels are significantly exothermic in nature and thus thermodynamic facile. The optimized geometries and structural parameters for reactants ($CF_3CH_2CH_2CHO$ and OH), hydrogen bonded reaction complex, products ($CF_3CH_2CH_2CO$, $CF_3CH_2CHCHO$, $CF_3CHCH_2CHO$ and $H_2O$) and the transition states ($TS_1$, $TS_2$ and $TS_3$) involved in the reactions ((R1)–(R3)) obtained at MPWB1 K/6-31G(d,p) level are shown in Fig. 1 with available limited experimental values for OH and $H_2O$ [21,22]. The existence of one hydrogen bonded reaction complex ($HBRC_1$) on the reactant side of reaction (R1) was validated at the MPWB1 K level. Thus, for reaction (R1) indirect mechanism has been proposed. In the optimized geometry of $HBRC_1$ the bond distance between hydrogen and oxygen atom with oxygen and hydrogen atom of hydroxyl radical are 1.94 and 2.59 Å, respectively while the other bonds are similar to the reactant. From Fig. 1, we can predict that in the optimized structure of $TS_1$, the length of the breaking C–H bond increases from 1.102 to 1.149 Å (almost an 4% increase) whereas the newly formed OH bond is increased from 0.953 to 1.525 Å resulting in an increase of about 60%. For the transition state ($TS_2$), the length of the breaking C–H bonds increases from 1.090 to 1.208 Å (almost a 10% increase) whereas the newly formed OH bond is increased from 0.953 to 1.304 Å resulting in an increase of about 36%. Similarly, in the $TS_3$ the breaking C–H bond and forming O–H bond are found to be 14% (1.085 to 1.246 Å) and 28% (0.953 to 1.225 Å) longer than the isolated C–H and O–H bonds of $CF_3CH_2CH_2CHO$ and $H_2O$, respectively.

**Table 1**
Thermochemical data for the H abstraction reaction channels of $CF_3CH_2CH_2CHO$ calculated at MPWB1 K/6-31G(d,p) level of theory. All values are in kcal mol$^{-1}$ considering thermal zero point vibrational energy (TZPVE) correction.

| Reaction channels | $\Delta_rH^\circ$ | $\Delta_rG^\circ$ | $\Delta G^\#$ |
|---|---|---|---|
| (R1) | −20.45 | -23.78 | 12.45 |
| (R2) | −19.85 | -21.64 | 15.52 |
| (R3) | −10.87 | -15.14 | 17.41 |

The fact that the elongation of forming bond is larger than that of the breaking bond indicates that the barrier of the reactions ((R1)–(R3)) is near the corresponding reactants. This means the reaction will proceed via early transition state structure which is in consonance with Hammond's postulate expected for exothermic hydrogen abstraction reaction [23]. Scaled harmonic vibrational frequencies obtained at MPWB1 K/6-31G(d,p) level for species involved in reactions ((R1)–(R3)) are recorded in Table 2 with limited experimental values [24]. These results show that the reactants, reaction complex and products have stable minima on their potential energy surface characterized by the occurrence of only real positive vibrational frequencies. Transition states (TS) are characterized by the occurrence of only one imaginary frequency at 310 cm$^{-1}$ for $TS_1$, 1204 cm$^{-1}$ for $TS_2$ and 1595 cm$^{-1}$ for $TS_3$ as recorded in Table 2. Visualization of the vibration corresponding to the calculated imaginary frequencies using ChemCraft [25] program shows a well defined transition state geometry connecting reactants and products during transition. The existence of transition state on the potential energy surface is further ascertained by intrinsic reaction coordinate (IRC) calculation performed at the same level of theory using the Gonzalez–Schlegel steepest descent path in the mass-weighted Cartesian coordinates with a step size of 0.01 (amu$^{1/2}$ bohr) [26]. The IRC plots for $TS_1$, $TS_2$ and $TS_3$ shown in Fig. 2 clearly authenticate a smooth transition from reactants to products along the potential energy surface.

Single point energy calculations of various species involved in the hydrogen abstraction reactions were further refined by using extended 6-311 + G(3df,2pd) basis set at MPWB1 K/6-31G(d,p) optimized geometries. Calculated total energies at MPWB1 K/6-311 + G(3df,2pd) and MPWB1 K/6-31G(d,p) level of theories are corrected with zero-point energy obtained at MPWB1 K/6-31G(d,p) level are recorded in Table 3. The associated energy barrier corresponding to the reactions ((R1)–(R3)) calculated from the results obtained at the above mentioned theoretical levels are also recorded in Table 3. A schematic potential energy surface of the $CF_3CH_2CH_2CHO + OH$ reactions are plotted and shown in Fig. 3. In the construction of energy diagram, zero-point energy corrected total energies as recorded in Table 3 are utilized and the ground state energies of the reactants are arbitrarily taken as zero. Literature survey reveals that there is no experimental data available for the comparison of the energy barrier for the H-atom abstraction reaction of $CF_3CH_2CH_2CHO$ by OH radical. The results given in Table 3 shows that the calculation performed during the present study utilizing MPWB1 K/6-311 + G(3df,2pd) stabilizes the $HBRC_1$ 2.90 kcal mol$^{-1}$ lower than the corresponding reactants. The apparent energy barriers ($\Delta E = E_{TS} - E_{TFB} - E_{OH}$) for reactions ((R1)–(R3)) are found to be −1.45, 1.40 and 2.31 kcal mol$^{-1}$, respectively at MPWB1 K/6-311 + G(3df,2pd) level. Since the apparent energy barrier for $TS_1$ is lesser in comparison to $TS_2$ and $TS_3$ therefore reaction R1 will be dominant reaction channel. However the effective energy barrier of $TS_1$ ($\Delta E^\# = E_{TS} - E_{HBRC1}$) calculated from indirect mechanism is found to be 1.44 kcal mol$^{-1}$ at MPWB1 K/6-311 + G(3df,2pd) level as given in Table 3. Spin contamination is not important for the present system because $<S^2>$ is found to be 0.76 at MPWB1 K/6-31G(d,p) before annihilation that is only slightly larger than the expected value of $<S^2> = 0.75$ for doublets. In our present study we made an