Theoretical study on mechanism, kinetics, and thermochemistry of the gas phase reaction of 2,2,2-trifluoroethyl butyrate with OH radicals at 298 K

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Abstract. A theoretical investigation has been carried out on the mechanism, kinetics, and thermochemistry of gas-phase reaction of 2,2,2-trifluoroethyl butyrate (TFEB, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CF}_3$) with OH radicals using a modern DFT functional. The involvement of pre- and post-reactive complexes was explored and the reaction profiles were modeled. Energetic calculations were performed using the M06-2X/6-31+G(d,p) method. The intrinsic reaction coordinate (IRC) calculation has been performed to confirm the smooth transition from the reactant to product through the respective transition state. It has been found that the dominant path of the H-atom abstraction takes place from the $-\text{CH}_2-$ position, which is attached with the methyl group at the one end of TFEB. Theoretically calculated rate constant at 298 K using canonical transition state theory (CTST) is found to be in reasonable agreement with the experimental data. Using group-balanced isodesmic procedure, the standard enthalpy of formation for TFEB is reported for the first time. The branching ratios of the different reaction channels are also determined. The atmospheric lifetime of TFEB is determined to be 6.8 days.

Keywords. Fluoroesters; M06-2X; IRC; rate constant; atmospheric lifetime.

1. Introduction

Recently, hydrofluoroethers (HFEs) are widely used as new-generation alternatives to chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs) in many industrial applications, such as cleaning agents in electronic industry, heat-transfer fluid in refrigeration, carrier fluid for lubricants, and foam-blowing agents.^{1–3} HFEs possess similar properties to that of CFCs but the former have additional advantages that they do not have any harmful effect to the environment in the form of global warming and ozone depletion. It is because HFEs do not possess any chlorine atom. This shows that the HFEs would have little impact on the stratospheric ozone. It is well established that the fluorinated esters (FESs) are the primary products of the atmospheric oxidation of HFEs.^{4–6} Like HFEs, FESs also undergo photochemical oxidation in troposphere with atmospheric oxidants, OH radicals, or Cl atoms. The degradation of FESs produces an environmentally burdening product like trifluoroacetic acid (TFA) and COF_2 . TFA detected in surface

water has no known sink apart from rainwater and this species may have deleterious effect on agricultural and aquatic systems.⁷ Thus, it is important to study the kinetics and mechanistic degradation pathways of FESs for the complete assessment of atmospheric chemistry as well as to explore the impact of FESs on the environment. Considerable attention has been paid in recent years to perform experimental and theoretical studies on the decomposition kinetics of FESs.^{8–19} In this work, kinetic and mechanistic studies have been performed at 298 K for the reaction of 2,2,2-trifluoroethyl butyrate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ (TFEB) with OH radicals. To the best of our knowledge, there is only one experimental study reported by Blanco *et al.*¹² They studied the hydrogen abstraction reactions of OH radicals with TFEB using relative rate method at 298 K and reported a rate constant of $(1.3 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. However, this study provided only the total rate constant and it is difficult to predict the detailed mechanism, thermochemistry, and contribution of each reaction channel toward overall rate constant. Therefore, the present study deals with a detailed theoretical study for the first time on the H-abstraction reactions of TFEB mentioned above. The reaction of OH

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radicals with $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ (TFEB) is envisaged to occur via hydrogen atom abstraction from $\text{C}(\text{O})\text{OCH}_2-$, $-\text{CH}_2\text{C}(\text{O})\text{O}$, $-\text{CH}_2-$ or $-\text{CH}_3$ positions. Thus, four plausible reaction channels for $\text{TFEB}+\text{OH}$ are considered as follows:

The present investigation aims to have more accurate thermochemical data on a sound theoretical basis. In addition, our attempt is to find out the contribution of the individual channel to the overall rate constant in order to provide a detailed understanding of the kinetics involved during its oxidation. The knowledge of accurate enthalpy of formation (ΔH_f°) for TFEB and radicals generated is of vital importance for determining the thermodynamic properties. Here, we predict the enthalpies of formation of the title molecule using isodesmic reactions by performing a single-point energy calculation at M06-2X/6-311++G(d,p) using the optimized geometry obtained at the M06-2X/6-31+G(d,p) level.

2. Computational Methods

Geometry optimization of the species were made using the density functional theory (DFT) using M06-2X functional²⁰ with 6-31+G(d,p) basis set. Previous studies have shown that the M06-2X hybrid density functional provides reliable results for thermochemistry and kinetics.^{21–25} It is known that the formation of pre- and post-reaction complexes modifies the shape of the potential energy surface for the hydrogen abstraction reactions. This in turn affects the tunneling factor^{26,27} resulting in a significant change in the rate constant. Thus, a great effort has been made to locate the pre- and post-reactive complexes along the entry and exit channels of the reaction path. To determine the nature of different stationary points on the potential energy surface, calculations of vibrational frequencies were performed using the same level of theory at which the optimization was made. Furthermore, calculations of intrinsic

reaction coordinate (IRC)²⁸ were also performed in order to ascertain that the identified transition states connected reactants and products smoothly. All calculations were performed with the Gaussian 09 suite of program.²⁹

3. Results and Discussion

The results obtained during detailed thermodynamic calculation performed at M06-2X/6-31+G(d,p) level for reaction enthalpies ($\Delta_r H_{298}^\circ$) free energies ($\Delta_r G_{298}^\circ$) and free energy of activation ($\Delta G_{298}^\ddagger$) associated with reaction channels (1–4) are listed in table 1. Results show that all the four reaction channels are exergonic ($\Delta_r G_{298}^\circ < 0$). The enthalpy of reaction ($\Delta_r H_{298}^\circ$) values shows that each reaction channel is exothermic in nature and thermodynamically facile. Geometry optimization of TFEB molecule predicts three possible conformers (SC1, SC2, and SC3) and their structures are shown in figure 1. The three conformers differ mainly in the orientation of the C–C–O–C backbone. The energy difference of SC2 and SC3 conformers is found to be more than 1 kcal mol^{−1}, which implies that both of them have no contribution to the title reaction according to the Boltzmann population distribution law given as $(1/(1+\exp(-\Delta E/RT)))$, where ΔE is the energy difference between the conformers. Hence, the most stable conformer SC1 is considered for detailed study and thus the transition states are located from SC1 conformer. It can be seen from the geometrical parameters and stereographical orientation that the hydrogen atoms in the $-\text{CH}_3$ group are not equivalent. The stereographic environment of one H-atom is different from the other two in the $-\text{CH}_3$ group of TFEB, as shown in figure 1. Therefore, two transition states should be located for $\text{TFEB}+\text{OH}$ reactions. However, the transition states obtained for two different H-atoms were found almost structurally and energetically same. Therefore, we have presented only one transition state for hydrogen abstraction from $-\text{CH}_3$ group of TFEB molecule. An extensive search of pre- and post-reactive

Table 1. Thermochemical data for reaction channels (1–4) calculated at the M06-2X/6-31+G(d,p) and M06-2X/6-311++G(d,p) (values in parentheses) levels of theory. All values are in kcal mol^{−1}.

Reaction channel	$\Delta G^\ddagger$	$\Delta_r G_{298}^\circ$	$\Delta_r H_{298}^\circ$
1	10.9 (9.9)	−18.3 (−19.8)	−17.0 (−16.8)
2	8.7 (7.6)	−24.2 (−25.8)	−23.3 (−23.1)
3	6.8 (6.0)	−19.1 (−21.0)	−17.6 (−17.7)
4	9.5 (8.5)	−16.4 (−18.3)	−14.9 (−15.0)

Figure 1. Optimized geometries of species involved in H-atom abstraction reactions of TFEB with OH radical at the M06-2X/6-31+G(d,p) level. Bond length is in Å.

Figure 1. (continued.)

complexes led to the existence of three pre-reactive complexes (RC1, RC2, and RC3) at the entrance of the reaction channels (1–3), respectively. Similarly, three product complexes (PC1, PC2, and PC3) were also located at the exit of the reaction channels (1–3) that were formed before the formation of the final reaction products. In the pre-reactive complexes, hydrogen bonds are formed between the oxygen atom of the hydroxyl radical with the hydrogen atom in TFEB with bond distances of 2.56, 2.60, and 2.59 Å for reaction channels (1–3), respectively, while the other bond lengths are almost similar to the equilibrium structure of the TFEB molecule. At the same time, the post-reaction hydrogen bonded complexes (PC1, PC2, and PC3) having energy less than the corresponding products located at the exit of the reaction channels (1–3) can be identified with relatively strong C–H...O and O–H...O bonds, as shown in figure 1. Thus, it is evident that the reaction channels (1–3) proceed via an indirect mechanism. The optimized structure of the species involved during the present study were obtained at the M06-2X/6-31+G(d,p) level of theory and are shown in figure 1. The location of the transition state was searched along the minimum energy path on a relaxed potential energy surface. Visualization of the optimized geometries of transition states (TS1–TS4) corresponding to reaction channels (1–4) reveals that the breaking C–H bonds are elongated by 10–15%, whereas the newly formed H–O bond is increased by 27–36%. Elongation of the forming bond is larger than that of the breaking bond. This indicates that the reaction would proceed via early transition state having a reactant-like structure, which is in consonance with Hammond’s postulate³⁰ applied to an exothermic reaction.

Results obtained during frequency calculations for species involved in reaction channels (1–4) are recorded in table S1 of the Supporting Information. These results show that all the species belonged to stable minima on their potential energy surface characterized by the occurrence of only real positive vibrational frequencies, while transition states TS1, TS2, TS3, and TS4 were characterized by the occurrence of only one imaginary frequency observed at 1213*i*, 1075*i*, 854*i*, and 814*i* cm^{−1}, respectively. Visualization of the imaginary frequency revealed a qualitative confirmation of the existence of transition states connecting reactants and products. Calculations of IRC²⁸ performed for each transition state at the same level of theory as shown in figures S1 and S2 of the Supporting Information reveal that the transition state structures smoothly connect the reactant and the product sides.

Total energy (including zero-point energy) for all the species is determined with respect to the reactants,

setting it arbitrarily at zero, and the results are recorded in table S2 of the Supporting Information. The energy barriers associated with reactions (1–4) are also recorded in table S2. A schematic potential energy diagram of the TFEB + OH reactions with ZPE-corrected total energy obtained at M06-2X /6-31+G(d,p) level are plotted in figure 2. The results show that reactions (1–4) possess barrier heights of 2.7, 0.2, −1.9, and 1.6 kcal mol^{−1}, respectively. Moreover, spin contamination is not important for the TFEB + OH reactions because $\langle S^2 \rangle$ is found to be 0.76 at M06-2X/6-31+G(d, p) before annihilation, which is only slightly larger than the expected value of $\langle S^2 \rangle = 0.75$ for doublets.

The rate constant for the reaction channels involved during the H-atom abstraction from TFEB by OH radical are calculated using the canonical transition state theory³¹ given by the following expression:

$$k = \sigma \kappa(T) \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} \exp \frac{-\Delta E^\ddagger}{RT} \quad (5)$$

where σ is the reaction path degeneracy, $\kappa(T)$ is the tunneling correction factor at temperature T . Q_{TS} , Q_A , and Q_B are the total partition functions (per unit volume) for the transition state and reactants, respectively. $\Delta E^\ddagger$ is the barrier height, including zero-point energy correction, k_B and h are the Boltzmann and the Planck’s constants, and R represents the universal gas constant. The tunneling correction factor $\kappa(T)$ is defined as the ratio of the quantum mechanical to the classical mechanical barrier crossing rate. The tunneling correction $\kappa(T)$ was estimated by using the Eckart’s asymmetric barrier method.³² In this method, the reaction path through TS is fitted first in a model potential function:

$$V = -\frac{Ay}{1-y} - \frac{By}{(1-y)^2} \quad (6)$$

where $y = -\exp(2\pi x/L)$ and x is the variable measured along the reaction coordinate and L is the characteristic length. All vibrational modes, except for the lowest vibrational mode, were treated quantum mechanically as separable harmonic oscillators, whereas for the lowest-frequency mode, the partition function was evaluated by the hindered-rotor approximation as proposed by Chuang and Truhlar.³³ The total partition function is approximated by the product of translational, rotational, vibrational, and electronic partition functions. Several low-frequency vibrational modes were identified as internal rotations. The total partition function of reactants and transition states were corrected for hindered rotor. The rotations of OH at TS are also treated as hindered rotor. In the calculation of reactant electronic partition function, due care was taken to consider the splitting of the ground-state

Figure 2. Energy diagram for the TFEB + OH reactions obtained at the M06-2X/6-31+G(d,p) level.

energy of the OH radical due to spin-orbit coupling and separated at 140 cm^{-1} apart. The calculated total partition function and hindered-rotor corrected partition function for the reactants and transition states are recorded in table S3 in Supporting Information. The branching ratios for the reaction channels that represent their individual contribution toward overall reaction rate constant have been determined using the following expression:

$$\text{Branching ratio} = \frac{k}{k_{\text{total}}} \times 100 \quad (7)$$

The partial rate coefficients cannot be determined experimentally because reactions involved occur simultaneously, and in a few cases, they even lead to the same products. Thus, the experimental data mostly yield the overall reaction rate constant. Therefore, theoretical methods can be so valuable for the full understanding of a reacting chemical system. As stated earlier, TFEB + OH reactions may undergo four different channels (1–4) and the contribution from each of these channels needs to be taken into account while calculating the total rate coefficient (k_{OH}) for the titled reaction. The total rate coefficient (k_{OH}) is, therefore,

obtained from the addition of rate coefficients for the four channels: $k_{\text{OH}} = k_1 + k_2 + k_3 + k_4$. Our calculated total rate constant k_{OH} is found to be $2.7 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ using the M06-2X/6-31+G(d,p) level of theory, which is in reasonable agreement with the experimental value of $(1.3 \pm 0.3) \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ reported by Blanco *et al.*¹² using the relative rate method and FTIR detection technique and $1.77 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ derived by Kwok and Atkinson³⁴ using the structure–activity relationship (SAR) method. The branching ratio for reaction channels (1–4) is found to be 0.1%, 5.2%, 93.7%, and 1.0%, respectively, at 298 K. This clearly indicates the dominance of H-abstraction from $-\text{CH}_2$ group (reaction channel 3) of TFEB molecule. Hence, our study predicts reaction channel 3 to be the major reaction channel. This conclusion is in conformity with the observation made by Blanco *et al.*¹²

3.1 Atmospheric lifetime

The atmospheric sink of volatile organic compounds (VOCs) depends on various processes like photolysis,

wet and dry deposition, and reaction with atmospheric oxidants such as OH radicals, Cl atoms, and O₃ and NO₃ radicals. Previous reports^{35,36} reveal that photolysis and reactions with NO₃ and O₃ radicals are unimportant. The hydrophobic nature and volatility of ethers will render wet deposition and dry deposition an unlikely removal process. Thus, atmospheric lifetime (τ_{eff}) of VOCs is mainly controlled by OH-initiated hydrogen abstraction. To minimize the errors resulting from neglecting the specific temperature dependences, when calculating OH-based lifetimes, the use of 272 K as an average tropospheric temperature and methyl chloroform (CH₃CCl₃), as a chemical of well-known source and sink, has been suggested.³⁷ Thus, lifetime estimations for TFEB are generally calculated on the basis of gas-phase removal by OH only and with methyl chloroform (MCF) as reference:

$$\tau_{OH}^{TFEB} = \frac{k_{MCF}(272K)}{k_{TFEB}(272K)} \tau_{OH}^{MCF} \quad (8)$$

where τ_{OH}^{TFEB} is the lifetime for TFEB, k_{TFEB} and k_{MCF} are the rate constants for the reactions of OH radicals with TFEB and methyl chloroform (MCF), respectively, at $T = 272$ K and $\tau_{OH}^{MCF} = 5.99$ years.³⁷ Taking the values of rate constants for k_{MCF} 6.14×10^{-15} cm³ molecule⁻¹ s⁻¹ from Ref.³⁷ and calculated rate constant of $k_{TFEB} = 1.97 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 272 K, the estimated lifetime is found to be 6.8 days, which is in reasonable agreement with the reported value of 4 days by Blanco *et al.*¹²

The standard enthalpy of formation (ΔH_f°) for TFEB and the radicals CH₃CH₂CH₂C(O)OCHCF₃ (P1), CH₃CH₂CHC(O)OCH₂CF₃ (P2), CH₃CHCH₂C(O)OCH₂CF₃ (P3), and CH₂CH₂CH₂C(O)OCH₂CF₃ (P4) generated from hydrogen atom abstraction can be valuable information for understanding the mechanism and thermochemical properties of their reactions and most importantly for atmospheric modeling. These values are not known. The group-balanced isodesmic reactions, in which the number and types of bonds

are conserved, are used as working chemical reactions herein to calculate the ΔH_f° . The following two isodesmic reactions have been designed to calculate the enthalpy of formation of TFEB.

Geometries of all the species involved in the isodesmic reactions (9–10) were first optimized at the M06-2X/6-31+G(d,p) level. Energies were further refined with an extended basis set (6-311++G(d,p)) using the same functional. At first, the reaction enthalpies (ΔH_r°) of the isodesmic reactions (9–10) are determined using the total energy of the species obtained at the M06-2X/6-311++G(d,p) level, including thermal correction to enthalpy estimated at the M06-2X/6-31+G(d,p) level. Since the ΔH_f° value corresponds to the difference in the enthalpies of formation (ΔH_f°) of the reactants and products, the (ΔH_f°) values of the reactant species can be easily evaluated by combining them with the known enthalpies of formation of the reference compounds involved in the isodesmic reaction schemes mentioned above (9–10). The experimental $\Delta_f H_{298}^\circ$ values in kcal mol⁻¹ for CH₄: -17.90,³⁸ CH₃CH₂C(O)OCH₃: -103.37,³⁹ CF₃CH₂CF₃: -336.49,⁴⁰ CH₃CH₂C(O)OCH₂CH₃: -112.02,⁴¹ CHF₃: -166.24,⁴² and CH₃CF₃: -178.20⁴³ were used to evaluate the required enthalpies of formation. The calculated values of ΔH_f° of TFEB obtained by two independent isodesmic reactions (9–10) are recorded in table 2. The results show that both yielded consistent values. The average values of ΔH_f° for TFEB calculated at M06-2X/6-311++G(d,p) and M06-2X/6-31+G(d,p) are found to be -277.3 and -277.4 kcal mol⁻¹, respectively. This shows that M06-2X functional yields

Table 2. Standard enthalpies of formation ($\Delta_f H_{298}^\circ$) for species in kcal mol⁻¹.

Species	Isodesmic reaction	M06-2X/6-311++G(d,p)	M06-2X/6-31+G(d,p)
TFEB	9	-276.7	-276.6
	10	-277.9	-278.2
Average		-277.3	-277.4
CH ₃ CH ₂ CH ₂ C(O)OCHCF ₃ (P1)		-227.6	-227.7
CH ₃ CH ₂ CHC(O)OCH ₂ CF ₃ (P2)		-233.9	-234.1
CH ₃ CHCH ₂ C(O)OCH ₂ CF ₃ (P3)		-228.2	-228.3
CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CF ₃ (P4)		-225.5	-225.6

reliable thermochemical values even with a moderate-size basis set. The $\Delta H_{f,298}^\circ$ values for radicals (P1, P2, P3, and P4) can also be easily calculated from the $\Delta_f H_{298}^\circ$ values for reactions (1–4) recorded in table 1 using the calculated $\Delta_f H_{298}^\circ$ value for TFEB and the experimental $\Delta_f H_{298}^\circ$ of H_2O ($-57.8 \text{ kcal mol}^{-1}$) and OH ($8.93 \text{ kcal mol}^{-1}$) radical⁴⁴. The $\Delta H_{f,298}^\circ$ values for radicals P1, P2, P3, and P4 determined from the energy data obtained at M06-2X/6-311++G(d,p) are found to be -227.6 , -233.9 , -228.2 and $-225.5 \text{ kcal mol}^{-1}$, whereas the same for M06-2X/6-31+G(d,p) are found to be -227.7 , -234.1 , -228.3 and $-225.6 \text{ kcal mol}^{-1}$, respectively. These data are not available in the literature and can therefore be useful for further thermochemical and kinetic modeling of reaction involving these species.

4. Conclusions

We present here the energy profile and the kinetic data of H-atom abstraction reaction of TFEB with OH radicals investigated at M06-2X/6-31+G(d,p) level of theory. Four different reaction channels have been considered. The barrier heights for reaction channels (1–4) were found to be 2.7, 0.2, -1.9 , and $1.6 \text{ kcal mol}^{-1}$, respectively. The overall rate constant for TFEB+OH was found to be $2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, which is in reasonable agreement with the available experimental value of $(1.3 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Based on the results obtained during the present study, it is concluded that the hydrogen abstraction from $-CH_2$ site attached to the methyl group at one end of TFEB molecule (reaction channel 3) is the dominant path, which is also in accord with the experimental observation. Our results also show that M06-2X functional coupled with 6-31+G(d,p) basis set is a reliable method for studying the kinetics and thermochemistry of hydrogen abstraction reactions. The $\Delta H_{f,298}^\circ$ values for TFEB and radicals (P1–P4) generated during hydrogen abstraction were found to be -277.4 , -227.7 , -234.1 , -228.3 and $-225.6 \text{ kcal mol}^{-1}$, respectively. The estimated atmospheric lifetime of TFEB was found to be 6.8 days. These data can be useful for further thermokinetic modeling of other reactions involving these species.

Supplementary Information

Harmonic vibrational frequencies of the species, relative energies, calculated partition functions, and IRC plots for transition states at the M06-2X/6-31+G(d,p) level of theory are available at www.ias.ac.in/chemsci.

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