

Article

Comprehensive Theoretical Studies on the Reaction of 1-Bromo-3,3,3-trifluoropropene with OH Free Radicals

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Abstract: The potential energy surfaces (PES) for the reaction of 1-bromo-3,3,3-trifluoropropene (CF₃CHCBrH) with hydroxyl (OH) free radicals is probed theoretically at the CCSD/aug-cc-pVDZ//B3LYP/6-311++G(d,p) level of theory. All the possible stationary and first-order saddle points along the reaction paths were verified by the vibrational analysis. The calculations account for all the product channels. Based on the calculated CCSD/aug-cc-pVDZ potential energy surface, the possible reaction mechanism is discussed. Six distinct reaction pathways of 1-bromo-3,3,3-trifluoropropene (BTP) with OH are investigated. The geometries, reaction enthalpies and energy barriers are determined. Canonical transition-state theory with Wigner tunneling correction was used to predict the rate constants for the temperature range of 290–3,000 K without any artificial adjustment, and the computed rate constants for elementary channels can be accurately fitted with three-parameter Arrhenius expressions. OH addition reaction channel and the H atom abstraction channels related to the carbon-carbon double bond are found to be the main reaction channels for the reaction of 1-bromo-3,3,3-trifluoropropene (CF₃CHCBrH) with hydroxyl (OH) free radicals while the products leading to CF₃CHCH + BrOH and COHF₂CHCBrH + F play a negligible role.

Keywords: quantum chemical calculations; reaction mechanism; transition states; potential energy surface; reaction rate constants

1. Introduction

Ever since Halon 1301 (CF_3Br) was viewed as a serious ozone-depleting substance, the development and manufacture of non-ozone-depleting replacement agents has attracted wide research interests. As Halon alternatives, inert gases and halocarbon fire extinguishing agent are now commonly used because of their cleanliness, effectiveness and non-conductive characteristics. One class of suppressants currently under consideration is the bromofluoroalkene family [1]. The presence of a carbon-carbon double bond is expected to render these substances highly reactive toward the hydroxyl radical, OH, resulting in an extremely short tropospheric lifetime, thereby limiting their delivery of bromine to the stratosphere where it can participate in ozone-destroying catalytic reactions. At the same time, the presence of a Br atom suggests that these compounds will also have a high degree of fire suppression efficiency [2], so the bromocarbon-containing carbon-carbon double bond is tropodegradable and maintains high fire suppression efficiency [3].

1-Bromo-3,3,3-trifluoropropene (BTP) is composed with molecular structures containing both a carbon-carbon double bond and a bromine atom. Some researchers have proved that the ozone destroying potency and the globe potency of BTP is zero [4], so BTP represents one of the greatest hopes for the eventual identification of a practical Halon 1301 replacement. There have been several recent studies that have attempted to deduce the chemical behavior of BTP under different conditions [5–12]. BTP suppresses flames by both chemical and physical mechanisms. BTP is able to extinguish flames physically by removing thermal energy from the flame. It is thought that BTP suppresses flames chemically by removing important species that are necessary for flame propagation. The reactions of OH are extraordinarily important in atmospheric chemistry and in combustion science. However, the reaction mechanism between BTP and hydroxyl (OH) free radical is still unclear except some studies on the 1-bromo-3,3,3-trifluoropropene (BTP) thermal decomposition [11] and experimental study of the fire-extinguishing effectiveness of 1-bromo-3,3,3-trifluoropropene [12].

In this work, the CCSD/aug-cc-pVDZ//B3LYP/6-311++G(d,p) theory was used for the first time to directly compute the reaction barriers of all reaction channels without any further adjustments of the energies. The energetics of these reactions was used together with the transition state theory (TST) [13–20] to compute rate constants in the temperature range 290–3,000 K without the need of empirical and complicated extrapolation procedures based on the low temperature data. Possible reaction channels between BTP and OH are considered and discussed exhaustively. The relative importance of the elementary pathways is discussed quantitatively. The computed results provide the best available estimate for BTP extinguishing mechanism in use of research in the related field, and the comparison with future experimental measurements can provide a test to the predictive ability of the reaction computational theory.

Figure 1. Cont.

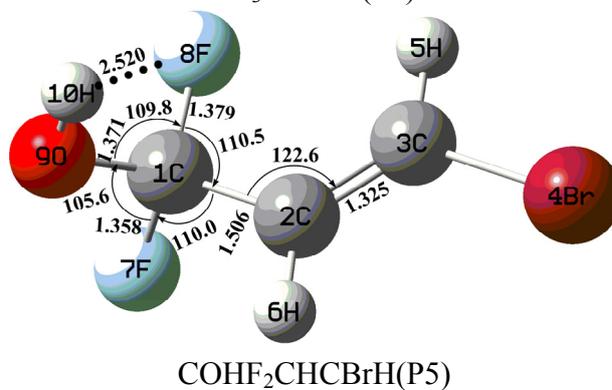
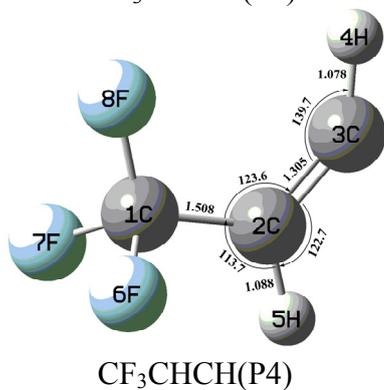
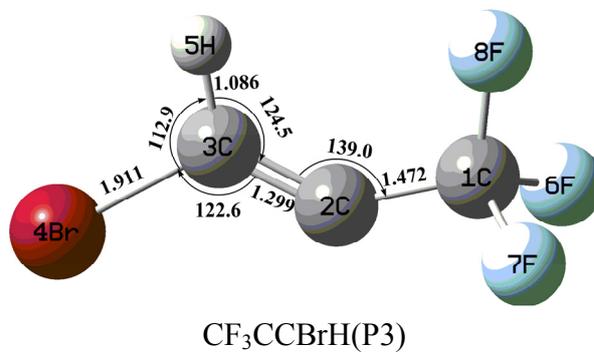
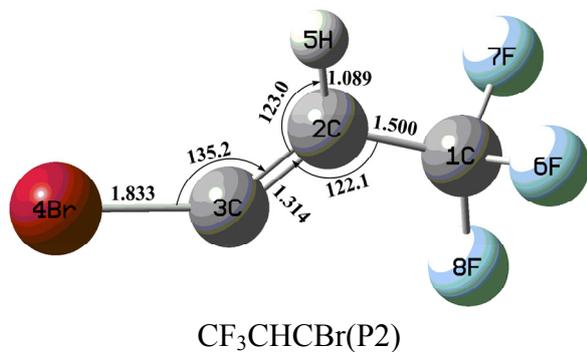
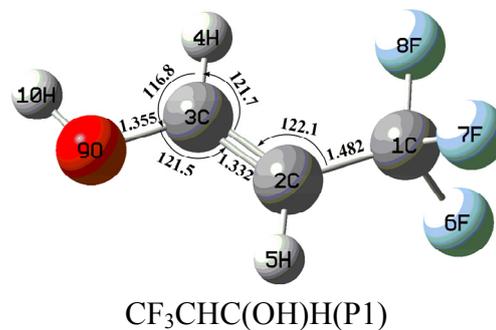
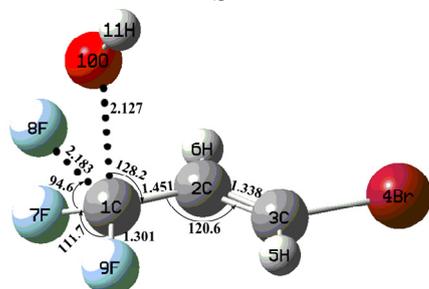
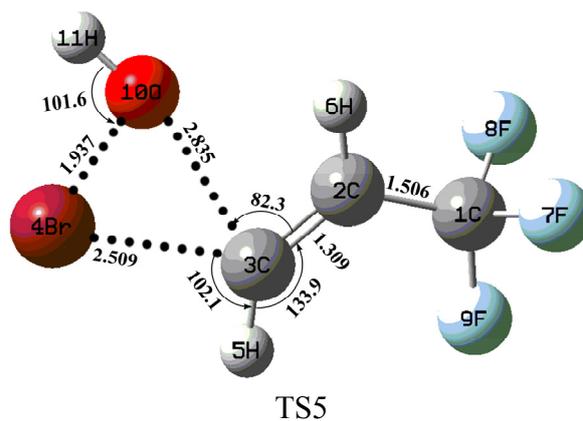
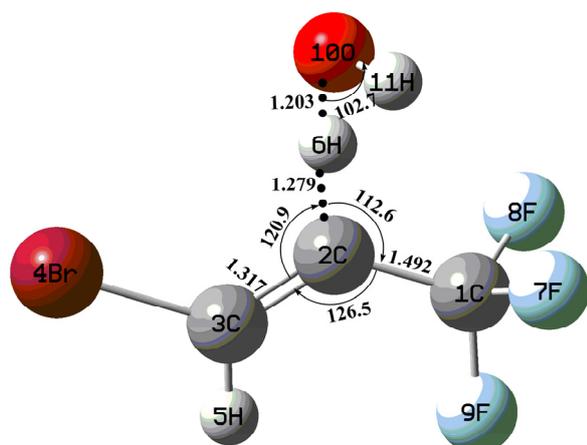
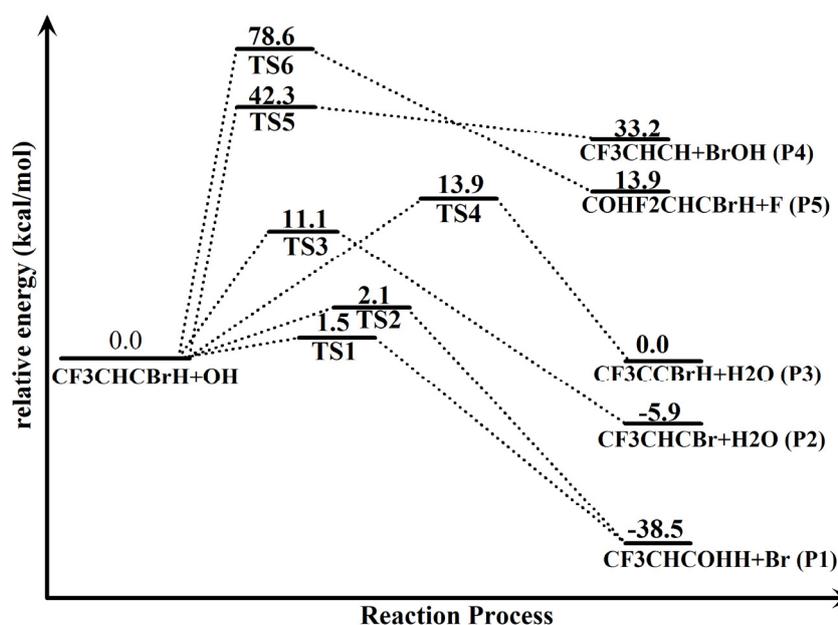


Table 1. The relative energies (in kcal/mol), ΔE (DFT), ΔE (CCSD) and ΔH_{298} (CCSD), as well as the zero-point vibration energies (ZPVEs) of species involved in the BTP reaction with OH.

Column heading	Species	ΔE (CCSD)	ΔE (DFT)	ZPE	ΔH_{298} (CCSD)
Reactants	<i>trans</i> -CF ₃ CHCBrH + OH	0.0	0.0	34.9	0.0
Transition states	TS1	1.5	-1.4	36.5	2.3
	TS2	2.1	-1.0	36.4	2.8
	TS3	11.1	3.5	32.8	8.4
	TS4	13.9	6.7	32.5	11.1
	TS5	42.3	36.5	36.5	42.6
	TS6	78.6	59.8	36.3	79.2
Products	CF ₃ CHC(OH)H + Br (P1)	-38.5	-38.8	38.2	-35.3
	CF ₃ CHCBr + H ₂ O (P2)	-5.9	-8.3	34.9	-5.6
	CF ₃ CCBrH + H ₂ O (P3)	0.0	-3.3	34.5	0.1
	CF ₃ CHCH + BrOH (P4)	33.2	31.2	34.9	32.8
	COHF ₂ CHCBrH + F (P5)	13.9	16.0	37.1	15.9

The stationary geometries were confirmed by harmonic vibration frequency analysis, *i.e.*, the reactants and products all possess real frequencies, whereas the transition structures possess only one imaginary frequency. The energy profiles of the potential energy surface for the reactions of 1-bromo-3,3,3-trifluoropropene (CF₃CHCBrH) with OH are plotted in Figure 2.

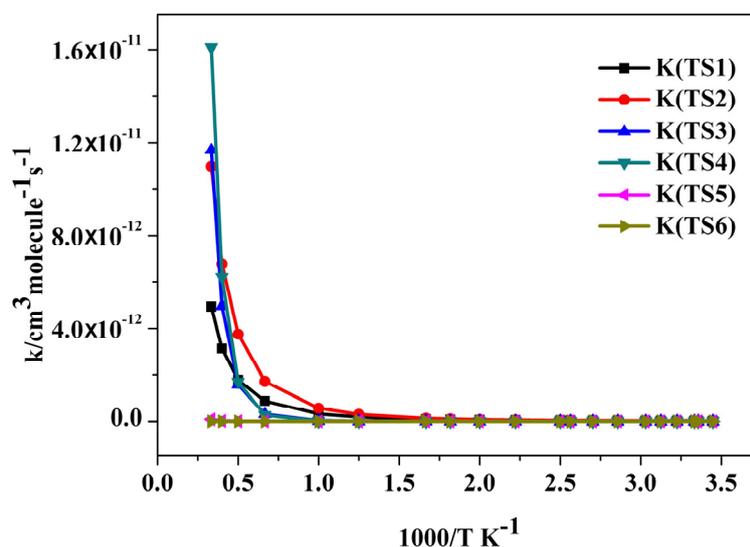
Figure 2. Potential energy surface for the reaction of *trans*-CF₃CHCBrH with OH free radical based on the relative energies obtained at the CCSD/aug-cc-pVDZ//B3LYP/6-311++G(d,p) level of theory. The energies of reactants CF₃CHCBrH + OH are set to zero.



The calculated rate constants of the main reaction channels for the *trans*-CF₃CHCBrH + OH reaction by the TST theory are showed in Figure 3. Roughly six distinct reaction pathways (A–F) for

the reaction of BTP with OH (see Figure 2) are investigated in the following and, unless noted otherwise, the CCSD/aug-cc-pVDZ//B3LYP/6-311++G(d,p) energies are used.

Figure 3. Theoretical rate constants for the reactions of *trans*-CF₃CHCBrH with OH free radical over the temperature range of 290–3,000 K.



2.1. Conformational Surface

Figure 1 is the calculated equilibrium structure of BTP obtained from the B3LYP/6-311++G(d,p) optimization. The backbone of the molecule is formed by a chain of three carbon atoms. 1-Bromo-3,3,3-trifluoropropene (BTP) is composed with molecular structures containing both a carbon-carbon double bond and a bromine atom. In addition, two orientations of the hydrogen group in the BTP (CF₃CHCBrH) are involved, *i.e.*, the *cis*-CF₃CHCBrH and *trans*-CF₃CHCBrH, the detailed structure information please reference our previous work in ref. [11]. When the two hydrogen groups are oriented in the same direction relative to the double bond, the diastereomer is referred to as *cis*-CF₃CHCBrH, whereas, when the hydrogen groups are oriented in opposing directions relative to the double bond, the diastereomer is referred to as *trans*-CF₃CHCBrH. The energy difference between *cis*- and *trans*-CF₃CHCBrH is determined to be 3.0 kcal/mol, with *trans*-CF₃CHCBrH being slightly favored. The zero-point vibrational energies as well as the thermal correction energies by the B3LYP/6-311++G(d,p) calculations were found to be essentially the same for *cis*- and *trans*-CF₃CHCBrH. The vibrational frequencies for the reactant, transition state and products involved in the reaction of 1-bromo-3,3,3-trifluoropropene (CF₃CHCBrH) with OH are available by contacting the authors.

2.2. Reaction Mechanism of *Trans*-CF₃CHCBrH + OH

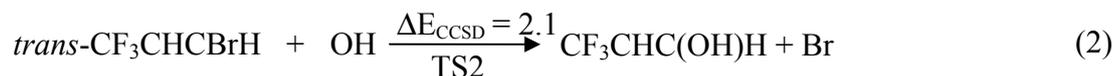
When OH radical and *trans*-CF₃CHCBrH approach each other, various possible products may be formed when OH radical interacts with different atoms of the CF₃CHCBrH molecules in the reaction. These different products are CF₃CHC(OH)H + Br (P1), CF₃CHCBr + H₂O (P2), CF₃CCBrH + H₂O (P3), CF₃CHCH + BrOH (P4) and COHF₂CHCBrH + F (P5). The mechanisms of their formation are as follows:

Pathway A



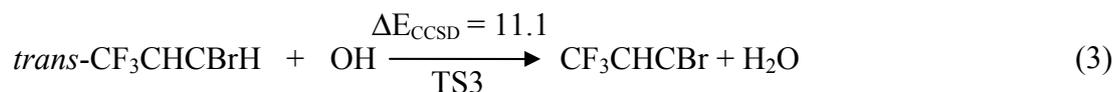
The O atom of OH attacks the C3 atom of the unsaturated *trans*-CF₃CHCBrH firstly and at the same time the Br atom on the *trans*-CF₃CHCBrH departs to form the products CF₃CHC(OH)H + Br. In this process, two possible reaction channels are detected because of the different attacking direction of the hydroxyl. In pathway A, the OH first addition to the carbon atom C3 related to the unsaturated double bond with the H atom on the OH directing to the Br atom of the *trans*-CF₃CHCBrH via TS1 (see Figures 1 and 2) with an imaginary frequency of 232i, whose barrier height (see Figure 2) is only 1.5 kcal/mol. Then the bromine departs from the C3 atom forming the products CF₃CHC(OH)H + Br. The energies of the products CF₃CHC(OH)H + Br are 38.5 kcal/mol below than that of the reactants and this reaction channel is the most exothermic pathway.

Pathway B



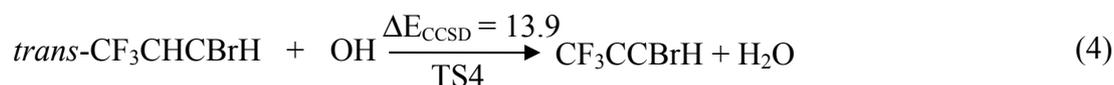
Analogous to pathway A, the products CF₃CHC(OH)H + Br may be produced in another way. The O atom of OH attacking the C3 atom of the unsaturated *trans*-CF₃CHCBrH in a different direction with the H atom on the OH directing to the F9 atom instead of directing to the Br atom of the *trans*-CF₃CHCBrH via TS2 (see Figure 1) with a slightly higher energy barrier of 2.1 kcal/mol than the pathway A. TS2 is a HO-BTP adduct with an imaginary frequency of 264i, whose barrier height (see Figure 2) is only 0.6 kcal/mol higher than TS1. Due to low reaction barriers and the most exothermic reaction, the two channels mentioned above play important roles in the overall reaction of *trans*-CF₃CHCBrH with OH.

Pathway C



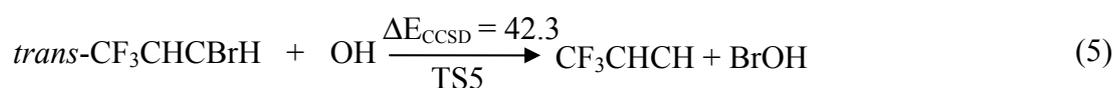
The O atom of OH may abstract the H atom of the *trans*-CF₃CHCBrH molecule to form CF₃CHCBr + H₂O via TS3 directly, whose barrier height (see Figure 2) is 11.1 kcal/mol. As shown in Figure 1, the breaking bond C3–H5 in TS3 is stretched to 1.240 Å, which is about 0.159 Å longer than that in parent *trans*-CF₃CHCBrH molecule. The forming O10–H5 bond is 1.255 Å, which is 0.293 Å longer than that in the H₂O product. The transition state TS3 has simple structure of C1 symmetry and is a true first-order saddle point with an imaginary frequency of 1325i. From Table 1 and Figure 2, the H-atom abstraction reaction of *trans*-CF₃CHCBrH by OH is an exothermic reaction. The total energy of products CF₃CHCBr + H₂O relative to the reactants *trans*-CF₃CHCBrH + OH is –5.9 kcal/mol.

Pathway D



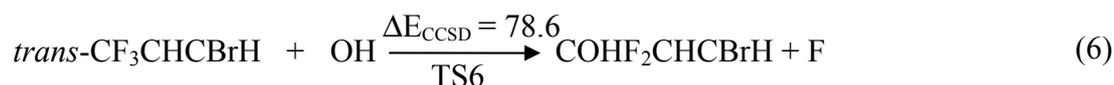
The free radical OH not only can abstract the H atom on C3 of the carbon-carbon double bond in the *trans*-CF₃CHCBrH molecule to form CF₃CHCBr + H₂O, but can also abstract the H atom on C2 of the carbon-carbon double in the *trans*-CF₃CHCBrH molecule to form the products CF₃CCBrH + H₂O via TS4 with a slightly higher barrier height of 13.9 kcal/mol, which is 2.8 kcal/mol higher than the H abstract channel on C3. The transition state TS4 has a simple structure of C1 symmetry and is a true first-order saddle point with an imaginary frequency of 1487i. The breaking C2–H6 bond in TS4 is 1.279 Å longer than that of *trans*-CF₃CHCBrH. Seen from Figure 1, the forming O10–H6 bond is 1.203 Å, which is 0.241 Å longer than that in the H₂O product. The energy of the products CF₃CCBrH + H₂O is just same with that of the reactants in this reaction channel.

Pathway E



The direct Br atom abstraction by OH free radical from *trans*-CF₃CHCBrH will produce the products CF₃CHCH + BrOH via a C3–Br4 bond fission transition state TS5. TS5 has a relatively high barrier height of 42.3 kcal/mol, which is 31.2 kcal/mol higher than the direct H abstract channel on C3. The C3–Br4 bond length is elongated by 0.616 Å in TS5 while the C2–C3 bond is shortened by 0.016 Å. TS5 has an imaginary frequency of 311i. The energy of CF₃CHCH + BrOH is 33.2 kcal/mol higher than that of the reactants *trans*-CF₃CHCBrH + OH. In view of the energetic, the energy barrier height of the Br abstract channel lies above that of the H abstract channel by 28.4 kcal/mol and 31.2 kcal/mol on C2 and on C3 respectively, the former is kinetically unimportant.

Pathway F



When the O atom of OH attacks the C atom of *trans*-CF₃CHCBrH, other products COHF₂CHCBrH + F may be produced via the transition state TS6. TS6 exhibits a simple structure of C1 symmetry and is a true first-order saddle point with an imaginary frequency of 398i. O atom of OH attacks the C atom of the *trans*-CF₃CHCBrH, kicking off one F atom on the *trans*-CF₃CHCBrH. As can be seen from Figure 1, the bond length of C1–F8 in TS6 is stretched to be 2.183 Å, *i.e.*, it is a loose bond. The forming bond C1–O10 is 2.127 Å, which is 0.756 Å longer than that in the COHF₂CHCBrH product. The formation of COHF₂CHCBrH and F is endothermic by 13.9 kcal/mol. However, the energy barrier for the reaction is rather high, 78.6 kcal/mol, which is the highest energy barrier reaction in all the channels of the reaction *trans*-CF₃CHCBrH with OH. Clearly, this addition-elimination channel should play a negligible role in the reaction.

2.3. Reaction Rate Results

Due to the large differences in the reaction barrier heights of different reaction channels, the rate constant for the *trans*-CF₃CHCBrH + OH reaction can be viewed as contributed mainly from the HO-BTP adduct channel and H atom abstraction channels related to the unsaturated carbon-carbon

double bond, *i.e.* lead to the products $\text{CF}_3\text{CHC}(\text{OH})\text{H} + \text{Br}$, $\text{CF}_3\text{CHCBr} + \text{H}_2\text{O}$ and $\text{CF}_3\text{CCBrH} + \text{H}_2\text{O}$ for temperatures up to 1,000 K.

Figure 3 shows the calculated rate constants for the $\text{trans-CF}_3\text{CHCBrH} + \text{OH}$ reaction. The calculated rate constants exhibit a typical non-Arrhenius behavior. This non-Arrhenius behavior has frequently been observed in radical-molecule reactions studied over wide temperature ranges [21]. The calculated rate constants are fitted to a three-parameter formula over the temperature range of 290–3,000 K and are given in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as the following expressions:

$$K(\text{TS1}) = 2.257 \times 10^{-20} T^{2.4036} \exp\left(-\frac{163.53}{T}\right) \quad (7)$$

$$K(\text{TS2}) = 5.074 \times 10^{-20} T^{2.415} \exp\left(-\frac{468.091}{T}\right) \quad (8)$$

$$K(\text{TS3}) = 5.183 \times 10^{-22} T^{3.168} \exp\left(-\frac{4.525 \times 10^3}{T}\right) \quad (9)$$

$$K(\text{TS4}) = 9.943 \times 10^{-22} T^{3.187} \exp\left(-\frac{5.965 \times 10^3}{T}\right) \quad (10)$$

The products of TS5 and TS6 channels have a total energy higher than the energy of the $\text{trans-CF}_3\text{CHCBrH} + \text{OH}$ by a minimum of 13.9 kcal/mol and the reaction barrier is at least 42.3 kcal/mol by the two means. This is higher than the barrier height of 1.5 kcal/mol of the TS1 reaction channel by almost 40.8 kcal/mol and is well beyond the theoretical uncertainty. Therefore, our calculations have conclusively demonstrated that the TS5 results to $\text{CF}_3\text{CHCH} + \text{BrOH}$ channel and TS6 producing the $\text{COHF}_2\text{CHCBrH} + \text{F}$ channel of the reaction $\text{trans-CF}_3\text{CHCBrH} + \text{OH}$ is negligible in comparison with the first four reaction channels lead to the products $\text{CF}_3\text{CHC}(\text{OH})\text{H} + \text{Br}$, $\text{CF}_3\text{CHCBr} + \text{H}_2\text{O}$ and $\text{CF}_3\text{CCBrH} + \text{H}_2\text{O}$ temperature up to 1,000 K within a temperature range of our study. It is expected that the accurate future experiment measurement is very helpful in validating the theoretical model.

3. Computational Methods

The geometries of all reactants, products and transition state structures have been fully optimized using the B3LYP [22,23] method with the 6-311++G(d,p) [24] basis set. Tran *et al.* have previously reported the success of the B3LYP method in predicting geometries of unsaturated chain structures, and this method produces optimized structures, at low computational cost, that compared favorably with higher level calculations [25]. Harmonic vibrational frequencies have been calculated at the same level to determine the nature of the various stationary points as well as the zero-point vibrational energies (ZPVEs). The stationary geometries were confirmed by harmonic vibration frequency analysis, *i.e.*, the reactants and products possess all real frequencies, whereas the transition structures possess only one imaginary frequency. Connections between reactants, transition structures and products were confirmed by intrinsic reaction coordinate (IRC) [26–29] calculations at the B3LYP/6-311++G(d,p) level. To improve the accuracy of the energies, subsequent single-point calculations were performed at the coupled-cluster level of theory with single and double excitations (CCSD) [30] with a diffuse functions basis set aug-cc-pVDZ [31].

The CCSD/aug-cc-pVDZ//B3LYP/6-311++G(d,p) theory was used for the reaction rate calculations. In order to find which reaction channel dominates kinetically at different temperatures in the reactions, the canonical transition state theory [13–20] (TST) including semiclassical multiplicative tunneling correction factors was used to predict the temperature dependence of the rate constants. Accordingly, the rate constants, $k(T)$, were computed using the following expression:

$$k = \Gamma(T) \frac{k_B T}{h} \frac{f^\ddagger}{\prod_B f_B} \exp\left(-\frac{E_0}{RT}\right) \quad (11)$$

where $\Gamma(T)$ is the transmission coefficient to correct the tunneling effect at temperature T , E_0 is the classical energy barrier including ZPE, *i.e.*, the enthalpy difference between reactants and transition states at 0 K, $\prod_B f_B$ are the continued product of the reactions partition function, f^\ddagger are the partition function of the transition state, k_B is the Boltzman's constant, and h is the Planck's constant.

The transmission coefficient was calculated by the Wigner method [32] as:

$$\Gamma(T) = 1 + \frac{1}{24} \left(\frac{h\nu^\ddagger}{k_B T} \right)^2 \quad (12)$$

where ν^\ddagger is the imaginary frequency at the saddle point. Choosing the simple and inexpensive Wigner method instead of the more sophisticated and computationally demanding algorithms such as the ones developed by Truhlar [33–37] and Miller [38,39] seems to be appropriate here as the tunneling corrections applied to the rate constants at typical combustion temperatures (typically above 2,000 K) are small to moderate (≤ 2) [40]. All the CCSD calculations were performed with the MOLPRO package [41] and all the B3LYP calculations were carried out with Gaussian 09 program [42].

4. Conclusions

Our CCSD/aug-cc-pVDZ//B3LYP/6-311++G(d,p) calculations provided detailed potential energy profile for the 1-bromo-3,3,3-trifluoropropene (CF_3CHCBrH) with hydroxyl (OH) free radical reaction. Six distinct reaction pathways of 1-bromo-3,3,3-trifluoropropene (BTP) with OH are investigated. The reaction enthalpies and energy barriers are determined. From the energetics, the most feasible reaction pathways for 1-bromo-3,3,3-trifluoropropene with OH are those that related to the unsaturated carbon-carbon double bond, *i.e.* lead to the products $\text{CF}_3\text{CHC(OH)H} + \text{Br}$, $\text{CF}_3\text{CHCBr} + \text{H}_2\text{O}$ and $\text{CF}_3\text{CCBrH} + \text{H}_2\text{O}$. Considering the extreme high flame temperature, the first four reaction pathways are competitive.

The rate constants for the main reaction channels were calculated by the TST theory. For the temperature range of 290–3,000 K, the calculated rate constants exhibit a typical non-Arrhenius behavior. Future experiment capable of reliably assessing the relative importance of the elementary reactions of the model combustion processes is necessary.

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Conflict of Interest

The authors declare no conflict of interest.

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