



Study of the halon C_2BrClF_4 , reaction rate and properties

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Abstract. *In this work, we present the rate constant and the thermodynamic properties of the halon 1-Bromo-2-Chlorotetrafluoroethane (C_2BrClF_4) reacting with dihydrogen (H_2), where we found three geometry variations for the singlet state (1A). The optimized geometries and frequencies were determined at B3LYP/6-311g(2d,d,p) internal to CBS-QB3 methods. The reaction rates are calculated using the APUAMA code, applying the tunneling correction of Wigner, Eckart and small curvature transmission coefficient (SCT), the reaction rate for VI (first geometry variation) is presented in the Arrhenius form as $k_{(VI)}(cm^3 mol^{-1} s^{-1}) = 5.22 \times 10^4 T^{2.37} exp(1.01 \times 10^5 kcal mol^{-1} / RT)$.*

Keywords: Rate constant; Quantum chemistry; C_2BrClF_4 ;
1-Bromo-2-Chlorotetrafluoroethane (R-114B1).

1. Introduction

The group of halogenated organic compounds are extensively used as pesticides, anesthetics, fire extinguishers, refrigerants, etc (HORVATH, 2001). A large number of this organic compounds are theoretically possible by different combination of fluorine, chlorine, bromine and iodide with carbon atoms. However, all of them have not been published in the literature. Even many of the reported compounds do not have all their physicochemical properties listed (HORVATH, 1992). In our knowledge, there is no reference data to the halon 1-Bromo-2-Chlorotetrafluoroethane (C_2BrClF_4), that is the object of this work.

In this paper we present three geometry variations for the C_2BrClF_4 and the respective reaction rates with H_2 , by optimizing the geometries (interatomic distances and angles), calculating frequencies and energy of the species. For the reaction rate, we have used the APUAMA code (EUCLIDES; BARRETO, 2017) with the transition state theory (TST) applying tunneling correction of Wigner (WIGNER, 1932), Eckart (ECKART, 1930) and SCT (GONZALEZ-LAFONT; TRUONG; TRUHLAR, 1991) in a temperature range of 200–4000K (which is the standard temperature range used in APUAMA). We also calculate thermodynamic properties, such as enthalpy, entropy and heat capacity.

Section 2 describes our electronic structure calculations, section 3 discuss the results and 4 presents concluding remarks.



2. Methodology

2.1. *Ab initio* calculations

For the *ab initio* calculations we used B3LYP/6-311g(2d,d,p) method internal to CBS-QB3 which computes very accurate energies. For all species used: reactants, products and transition state structures, the geometries and frequencies was determined and the energy was calculated. The number of imaginary frequencies, 1 or 0, determine if we have a transition state or the reactants and products, respectively. All this calculations were performed using the GAUSSIAN09 program.

2.2. Reaction rate with APUAMA

We use the APUAMA (EUCLIDES; BARRETO, 2017) code to calculate the thermodynamic properties and reaction rate using TST (transition state theory). The equation of TST is given:

$$k(T) = \frac{k_B T}{h} \frac{Q_{X^\ddagger}}{Q_A Q_{BC}} \exp\left(-\frac{V_a^{G^\ddagger}}{RT}\right) \quad (1)$$

Where the constants are k_B for Boltzmann, h for Planck and R for gas constant, the partition functions Q_{X^\ddagger} , Q_A and Q_{BC} are given by the products of partition functions of translation, rotation, vibration and electronic. The entry for APUAMA (EUCLIDES; BARRETO, 2017) are all the properly defined species and their data, like the mass, external symmetry, geometry, frequencies, energy and imaginary frequency for transition state. The outputs of the program are: the rate with three types of tunneling: Wigner (WIGNER, 1932) which uses a parabolic potential for the nuclear motion near the transitions structure, taking into account only the imaginary frequency and not the reaction coordinate; Eckart (ECKART, 1930) which is the ratio between the coefficients of quantum and classical reaction; and small curvature transmission coefficient (SCT) (GONZALEZ-LAFONT; TRUONG; TRUHLAR, 1991) which is approximated by the ratio of the fundamental state probabilities by the classical state. The rate is presented in the Arrhenius form (ARRHENIUS, 1889), the thermodynamic properties such as entropy, enthalpy and heat capacity are calculated, the MEP (minimum energy path) with ZPE (zero-point energy) correction and the reaction barriers as well.

3. Results and Discussions

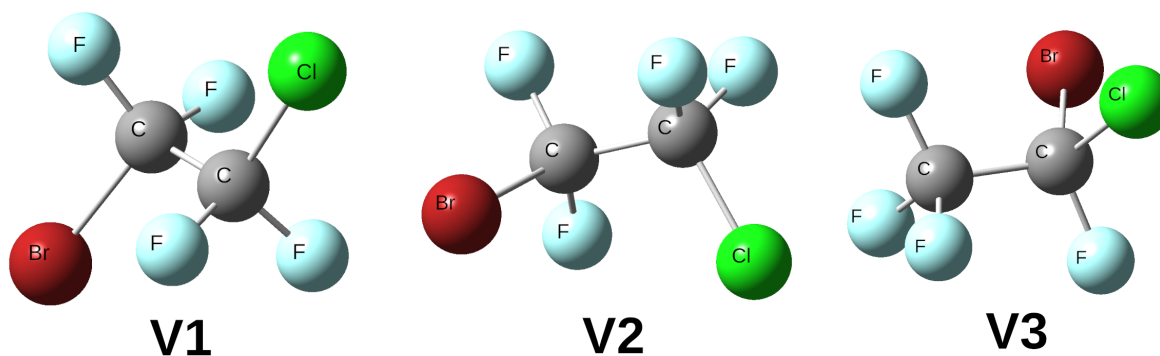


Figure 1. The three geometry variations for C_2BrClF_4

Through electronic structure calculations we found three geometry variations for C_2BrClF_4 (named V1, V2 and V3), as shown in figure 1. V1 and V2 has similar geometries, only differing



in the dihedral angle between the atoms Cl-C-C-Br, where V1 has a *trans* isomerism with 180.0° in dihedral angle and V2 a *cis* with 0.0°, while V3 has both atoms, Cl and Br, bounded in the same carbon atom. With the lowest energy among the reactants, the geometry V3 is the equilibrium state of C₂BrClF₄, where we have a energy barrier of 3.27 kcal mol⁻¹ for V1 and 3.65 kcal mol⁻¹ for V2. The same analysis can be make for the products, in this case geometry V2 is the equilibrium state for C₂HBrClF₃, with a energy barrier of 0.09 kcal mol⁻¹ for V1 and 2.29 kcal mol⁻¹ for V3.

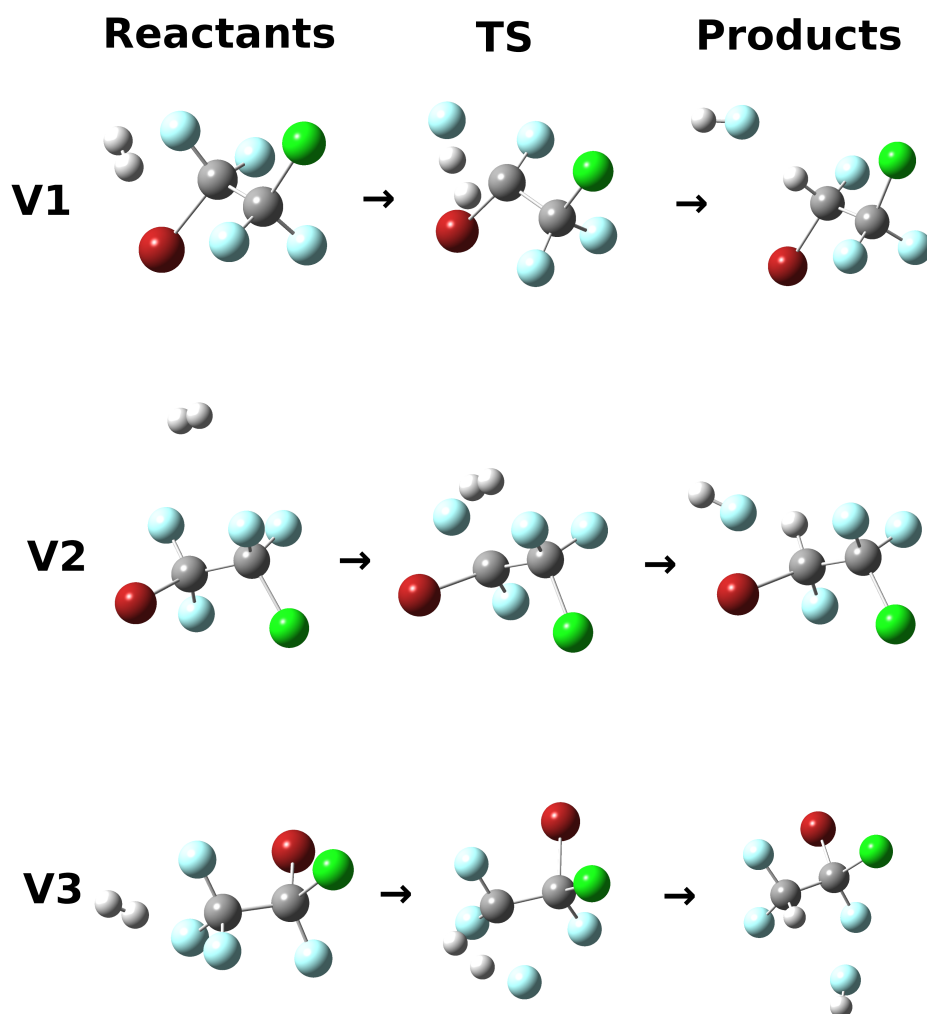


Figure 2. Reaction schematic for the three variations of the $C_2BrClF_4 + H_2 \rightarrow C_2HBrClF_3 + HF$

These three variations was reacted with H₂, in all cases we obtained, as result of the reaction, different geometries of C₂HBrClF₃ + HF as shown in figure 2. The reaction paths was confirmed via IRC (intrinsic reaction coordinate) calculations and are shown in figure 3, we can observe that either a), b) or c) the pattern is repeated, where we see the increase of R_{CF} and R_{HH'}, breaking CF and HH' bonds and forming HF through the decrease of R_{HF}.

The table 1 shows the vibrational frequencies, ZPE and energy, calculated in B3LYP/6-311g(2d,d,p) for all species and TS (transition structure) in the reaction schematic for



C_2BrClF_4 . We can observe that TS(V1) has the highest imaginary frequency with $1823.8i\text{ cm}^{-1}$, followed by TS(V2) with $1773.7i\text{ cm}^{-1}$ and lastly TS(V3) with $1607.8i\text{ cm}^{-1}$. As expected, the ZPEs of TSs are larger (in order of 22 kcal mol^{-1}) because the transition structures have more vibrational frequencies, totaling 23, while the reactants and products have 18 vibrational frequencies and the ZPEs are in order of 15 kcal mol^{-1} and 20 kcal mol^{-1} , respectively.

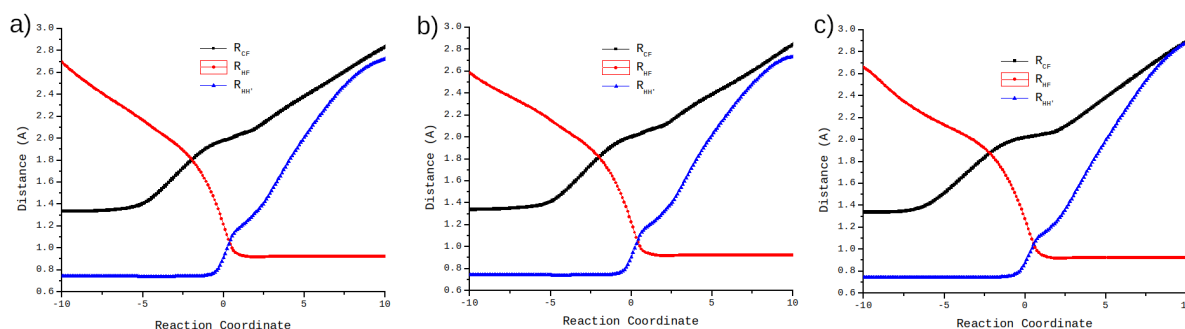


Figure 3. The bond lengths changes along the reaction coordinate of the C_2BrClF_4 for a) TS(V1), b) TS(V2) and c) TS(V3)

Table 1. Vibrational frequencies (cm^{-1}), ZPE (kcal mol^{-1}) and Energy (Hartree) for all species and TS of C_2BrClF_4

Specie	6-311G(2d,d,p)	
H_2	ν_i	4414.2230
	ZPE	6.31045
	Energy	-1.163732
HF	ν_i	4115.7921
	ZPE	5.88382
	Energy	-100.357569
$C_2BrClF_4(V1)$	ν_i	58.4, 141.3, 216.7, 219.9, 293.9, 317.7, 352.1, 359.8, 423.6, 528.6, 594.2, 691.0, 779.9, 1008.0, 1129.8, 1179.9, 1190.3, 1252.4
	ZPE	15.35163
	Energy	-3507.735980
$C_2BrClF_4(V2)$	ν_i	60.9, 135.7, 193.5, 280.2, 288.4, 312.5, 332.5, 382.3, 429.2, 472.4, 607.4, 660.0, 873.8, 1007.1, 1103.0, 1167.2, 1175.2, 1244.7
	ZPE	15.33491
	Energy	-3507.735375
$C_2BrClF_4(V3)$	ν_i	65.8, 149.1, 187.2, 226.1, 286.7, 305.2, 322.5, 386.1, 471.4, 545.2, 580.1, 719.4, 825.5, 915.7, 1107.2, 1204.7, 1225.6, 1262.3
	ZPE	15.42049
	Energy	-3507.741206
$C_2HBrClF_3(V1)$	ν_i	61.3, 144.8, 217.3, 236.5, 299.8, 353.7, 416.2, 463.3, 618.1, 687.3, 773.0, 952.9, 1106.4, 1153.5, 1230.8, 1253.9, 1367.2, 3143.7
	ZPE	20.70143
	Energy	-3408.565513
$C_2HBrClF_3(V2)$	ν_i	67.6, 142.4, 193.2, 285.5, 296.0, 365.2, 418.7, 484.8, 610.1, 636.5, 763.4, 1038.7, 1107.8, 1143.8, 1175.3, 1257.0, 1363.6, 3121.4
	ZPE	20.68845
	Energy	-3408.565659
$C_2HBrClF_3(V3)$	ν_i	80.2, 153.9, 184.4, 225.7, 306.0, 316.9, 408.7, 491.3, 560.3, 611.4, 842.3, 1041.1, 1102.9, 1142.2, 1171.6, 1374.9, 1377.9, 3089.7
	ZPE	20.70365
	Energy	-3408.562008
TS(V1)	ν_i	1823.8i, 50.7, 92.3, 152.3, 217.8, 237.3, 307.4, 350.5, 358.1, 378.6, 427.7, 455.5, 528.0, 594.3, 668.0, 743.6, 793.0, 1036.5, 1096.0, 1112.3, 1188.4, 1203.1, 1232.7, 2244.8
	ZPE	22.11543
	Energy	-3508.735416
TS(V2)	ν_i	1773.7i, 61.2, 105.4, 152.0, 195.7, 281.1, 292.9, 336.1, 351.1, 387.9, 391.3, 427.3, 490.2, 575.6, 653.0, 687.0, 823.6, 989.1, 1083.9, 1173.8, 1188.2, 1212.2, 1238.1, 2249.6
	ZPE	21.94066
	Energy	-3508.735857
TS(V3)	ν_i	1607.8i, 79.8, 101.5, 155.9, 190.8, 234.2, 241.1, 318.0, 332.8, 354.2, 406.6, 472.6, 532.9, 603.0, 661.9, 733.8, 818.7, 930.2, 1044.2, 1137.3, 1186.0, 1252.8, 1339.9, 2530.0
	ZPE	22.38637
	Energy	-3508.736232



3.1. Reaction rate and thermodynamic properties

For all three $C_2BrClF_4 + H_2$ reactions the rate constant was determined using the APUAMA (EUCLIDES; BARRETO, 2017) code, the figure 4 shows the reaction rates for each geometry variation of C_2BrClF_4 , fig.4a) $C_2BrClF_4(V1) + H_2$, fig.4b) $C_2BrClF_4(V2) + H_2$ and fig.4c) $C_2BrClF_4(V3) + H_2$. This figure compares the rate in logarithm, and tunneling corrections with the reciprocal temperature ($10000/T$). The minimum energy path was also calculated with the APUAMA, figure 5 shows the MEP for V1, V2, and V3 reactions. In fig5a) and b) we can observe exothermic reactions with similar energy barriers, 103.5373 kcal mol⁻¹ for V1 and 102.7275 kcal mol⁻¹ for V2, and enthalpy of formation -10.52409 kcal mol⁻¹ and -10.99123 kcal mol⁻¹, respectively. For V3 in fig5c) we also have an exothermic reaction, with an enthalpy of formation of -5.11201 kcal mol⁻¹ and a large barrier of 275.3449 kcal mol⁻¹, indicating that this reaction is less probable to occur.

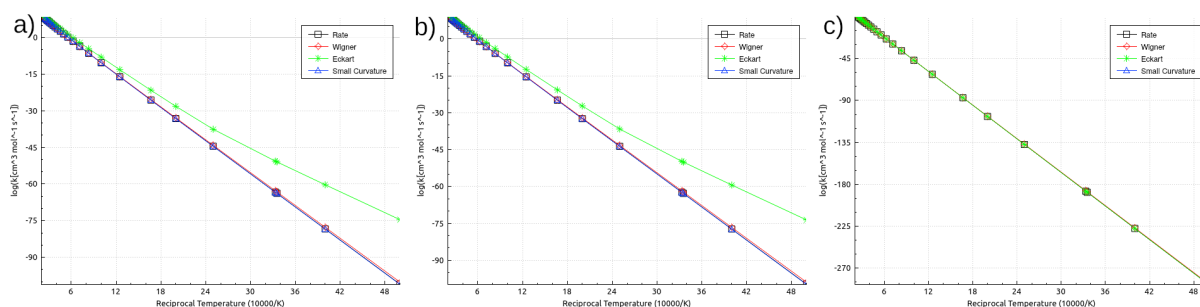


Figure 4. Reaction rate for V1, V2 and V3 of C_2BrClF_4 with H_2 via APUAMA

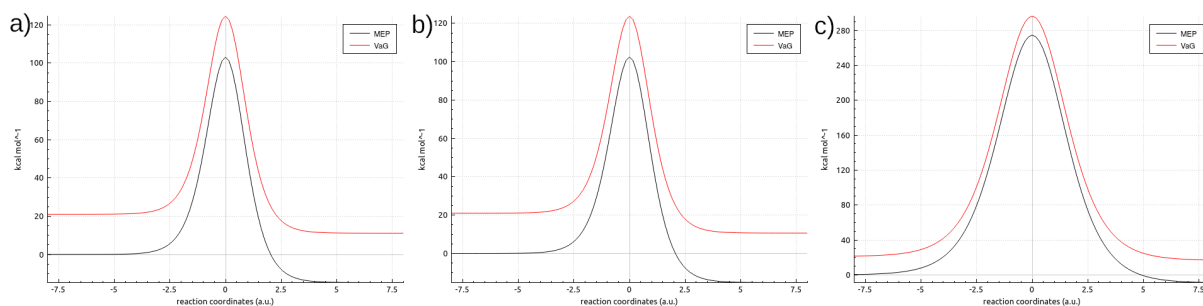


Figure 5. MEP for V1, V2 and V3 of C_2BrClF_4 with H_2 via APUAMA

Usually the most important information about the thermodynamic properties are the coefficient of the polynomial expression of heat capacity. APUAMA gives the set of seven (“old”-NASA type) and nine coefficient (“new”-NASA type) in two range of temperature of 200-1000K and 1000-6000K. The NASA 7-coefficient polynomial parameterization is used to compute the species reference-state thermodynamic properties and the NASA 9-coefficient polynomial parameterization is an extension of the NASA 7-coefficient polynomial parameterization which includes two additional terms in each temperature region, as well as supporting an arbitrary number of temperature regions(MCBRIDE; ZEHE; GORDON, 2002). The table 2 shows the “old”-NASA coefficients, whereas “new”-NASA coefficients are shown in table 3.

**Table 2. “old-”NASA coefficients for the polynomial fitting of the thermodynamic properties, c_p [kcal mol⁻¹ K⁻¹], S [kcal mol⁻¹ K⁻¹] and H [kcal mol⁻¹] for C₂BrClF₄ system**

H ₂				
3.38078127e+00	-4.33031725e-03	-1.04891143e-05	-1.42214205e-09	1.54314189e-11
-4.48233767e+02	1.42175741e+00	2.95092933e+00	-7.50187266e-04	3.77542986e-07
1.57959536e-12	-9.23802607e-15	-2.70023065e+03	-1.23679882e+00	
HF				
4.56521892e+00	-1.19291529e-02	1.96267571e-07	-1.98550205e-09	1.17476739e-11
-5.17453743e+02	1.11808886e+00	3.88003301e+00	-2.04407535e-03	7.73117113e-07
1.55214914e-12	-1.61214173e-14	-3.11286479e+03	-2.04371941e+00	
C ₂ BrClF ₄ (V1)				
1.50990916e+01	-2.13944588e-02	-5.22772956e-05	-1.30066350e-08	9.21651169e-11
-2.14515320e+03	8.96524316e+00	8.93704899e+00	1.68553336e-02	-5.31832558e-06
2.47613000e-11	8.70007826e-14	-1.56155311e+04	8.47757866e+00	
C ₂ BrClF ₄ (V2)				
1.51498860e+01	-2.17544992e-02	-5.17468167e-05	-1.30378441e-08	9.19807919e-11
-2.14808302e+03	8.95055284e+00	8.97239667e+00	1.68141204e-02	-5.30657199e-06
2.47705130e-11	8.68022207e-14	-1.56341526e+04	8.45368799e+00	
C ₂ BrClF ₄ (V3)				
1.48736981e+01	-2.01199932e-02	-5.39407885e-05	-1.28708670e-08	9.26326537e-11
-2.12996077e+03	9.00015079e+00	8.75273120e+00	1.71001504e-02	-5.39117129e-06
2.47450545e-11	8.82477523e-14	-1.55295851e+04	8.62490399e+00	
C ₂ HBrClF ₃ (V1)				
1.47263714e+01	-2.62334935e-02	-3.89534497e-05	-1.21305851e-08	8.21991654e-11
-2.02093310e+03	8.02114469e+00	8.63920950e+00	1.57098778e-02	-4.84235264e-06
2.31026776e-11	7.81712089e-14	-1.49014408e+04	7.54986905e+00	
C ₂ HBrClF ₃ (V2)				
1.46902319e+01	-2.61845985e-02	-3.88809471e-05	-1.21346886e-08	8.21251999e-11
-2.01758887e+03	8.01591932e+00	8.59640041e+00	1.57821122e-02	-4.86499036e-06
2.31131330e-11	7.85621648e-14	-1.48872838e+04	7.59498571e+00	
C ₂ HBrClF ₃ (V3)				
1.46135099e+01	-2.50666243e-02	-4.09279649e-05	-1.20658092e-08	8.30330365e-11
-2.01631884e+03	8.08994768e+00	8.58909911e+00	1.57449554e-02	-4.84922505e-06
2.30568359e-11	7.82616748e-14	-1.48665850e+04	7.56322524e+00	

**Table 3. “new-”NASA coefficients for the polynomial fitting of the thermodynamic properties, c_p [kcal mol⁻¹ K⁻¹], S [kcal mol⁻¹ K⁻¹] and H [kcal mol⁻¹] for C₂BrClF₄ system**

H ₂				
-2.99664983e+03	-8.89068650e+01	2.87429599e+00	4.06188915e-03	-2.49770197e-05
-2.16493376e-11	2.07250140e-11	0.00000000e+00	-1.06241864e+02	1.89154523e+00
-5.90343924e+04	-3.15891435e+02	2.58342756e+00	4.28534361e-04	-6.69115893e-08
1.78127215e-13	3.23983781e-16	0.00000000e+00	-6.52433874e+02	-2.01287958e-03
HF				
-3.05928097e+03	-1.37163146e+02	3.80789722e+00	5.13043781e-04	-2.12291616e-05
-1.12029330e-10	1.97549779e-11	0.00000000e+00	3.51805568e+01	1.85499007e+00
-3.34216183e+05	-4.38247313e+02	3.22284058e+00	2.02299696e-04	-5.93302799e-08
3.08387787e-13	8.50621846e-16	0.00000000e+00	-6.11371878e+02	5.66699034e-02
C ₂ BrClF ₄ (V1)				
-2.14428077e+04	-9.07134566e+02	1.00718854e+01	6.12833879e-02	-1.94691957e-04
-3.94128743e-10	1.45245209e-10	0.00000000e+00	1.49035926e+03	1.38293898e+01
8.98202006e+06	-9.72787252e+02	1.31567033e+01	-1.70899194e-03	1.15203492e-06
-4.99750102e-12	-1.81625333e-14	0.00000000e+00	3.02045923e+03	-1.78718240e+00
C ₂ BrClF ₄ (V2)				
-2.14531114e+04	-9.09486304e+02	1.01103438e+01	6.11230632e-02	-1.94503868e-04
-4.00955872e-10	1.45193874e-10	0.00000000e+00	1.49757896e+03	1.38276608e+01
8.97643868e+06	-9.77378193e+02	1.31839517e+01	-1.72163459e-03	1.15328853e-06
-4.99554159e-12	-1.81527445e-14	0.00000000e+00	3.02524360e+03	-1.78587670e+00
C ₂ BrClF ₄ (V3)				
-2.13721028e+04	-8.96373238e+02	9.90330256e+00	6.16363666e-02	-1.94774756e-04
-3.74255634e-10	1.45101791e-10	0.00000000e+00	1.45948535e+03	1.38051700e+01
9.02669449e+06	-9.48319737e+02	1.30242688e+01	-1.65259790e-03	1.14791924e-06
-5.01653653e-12	-1.82452600e-14	0.00000000e+00	3.00174877e+03	-1.79705799e+00
C ₂ HBrClF ₃ (V1)				
-1.96179152e+04	-8.46075336e+02	1.00434195e+01	5.07560710e-02	-1.71556210e-04
-4.37094782e-10	1.31667516e-10	0.00000000e+00	1.37597736e+03	1.25608440e+01
8.25534731e+06	-9.60008033e+02	1.24479827e+01	-1.13639170e-03	1.02232309e-06
-4.57521824e-12	-1.66695805e-14	0.00000000e+00	2.67076441e+03	-1.64567044e+00
C ₂ HBrClF ₃ (V2)				
-1.96197697e+04	-8.45956997e+02	1.00078642e+01	5.07956828e-02	-1.71467883e-04
-4.41989433e-10	1.31587100e-10	0.00000000e+00	1.37877290e+03	1.25549480e+01
8.27287738e+06	-9.53946744e+02	1.24218007e+01	-1.12648773e-03	1.02224038e-06
-4.58339813e-12	-1.67029637e-14	0.00000000e+00	2.66769089e+03	-1.64941809e+00
C ₂ HBrClF ₃ (V3)				
-1.96203515e+04	-8.43053914e+02	9.94616551e+00	5.16714156e-02	-1.73100118e-04
-4.00765625e-10	1.32332125e-10	0.00000000e+00	1.36730117e+03	1.26128732e+01
8.24796766e+06	-9.53466653e+02	1.24004590e+01	-1.10488886e-03	1.01729574e-06
-4.56815531e-12	-1.66507631e-14	0.00000000e+00	2.65164098e+03	-1.64467879e+00

4. Conclusion

In this paper, we have used the transition state and electronic structure theory to describe the 1-Bromo-2-Chlorotetrafluoroethane in singlet state. The geometries of the species that compose the system were calculated with B3LYP in 6-311G(2d,d,p) basis set, where we can confirm the pathways using IRC calculation, and the energy was calculated at CBS-QB3 for higher



accuracy. The reaction rate was calculated in a temperature range of 200-4000K with APUAMA code. The reaction rates can be represented in Arrhenius form as:

$$k_{(V1)}(\text{cm}^3\text{mol}^{-1}\text{s}^{-1}) = 5.22 \times 10^4 T^{2.37} \exp(1.01 \times 10^5 \text{ kcal mol}^{-1}/RT)$$

$$k_{(V2)}(\text{cm}^3\text{mol}^{-1}\text{s}^{-1}) = 1.28 \times 10^5 T^{2.39} \exp(1.0 \times 10^5 \text{ kcal mol}^{-1}/RT)$$

$$k_{(V3)}(\text{cm}^3\text{mol}^{-1}\text{s}^{-1}) = 1.06 \times 10^6 T^{2.31} \exp(2.73 \times 10^5 \text{ kcal mol}^{-1}/RT)$$

We can observe that V1 rate is faster than V2 which is faster than that of V3, and the barriers of V1 and V2 are energetically equivalent in the order of $100 \text{ kcal mol}^{-1}$, whereas V3 has a large barrier in the order of $275 \text{ kcal mol}^{-1}$ which means a less probability to occur.

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