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Study of the halon $C_2BrCl_2F_3$

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Abstract
In this work, we present the rate constant and the thermodynamic properties of the halon bromodichlorotrifluorethane ($C_2BrCl_2F_3$) reacting with dihydrogen (H_2), where we found six 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 (V1) $C_2BrCl_2F_3 + H_2$ is presented in the Arrhenius form as $k_{(V1)}(cm^3mol^{-1}s^{-1}) = 1.46\times10^6\, T^{2.45} \exp(-117.42\ kcal\ mol^{-1}/RT)$.

Introduction

The group of halogenated organic compounds are extensively used as pesticides, anesthetics, fire extinguishers, refrigerants, etc [1]. 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 [2]. In our knowledge, there is no reference data to the halon bromodichlorotrifluorethane ($C_2BrCl_2F_3$), that is the object of this work.
In this work we present six geometry variations for the $C_2BrCl_2F_3$ 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 [3] with the transition state theory (TST) applying tunneling correction of Wigner, Eckart and SCT 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.

Methodology

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 were determined as well as energies. All this calculations were performed using the GAUSSIAN09 program.

Results

A total of six geometries were found for halon X and can be seen in fig1, where the first and fifth variations (V1 and V5) are similar and vary in dihedral angle, V1 with cis isomerism and V5 trans; the same happens with the geometry variations V2 (CAS: 2106-94-7), V3 and V6, they are similar and differ in the dihedral angle Cl-C-C-Cl, in this case V2 is the equilibrium geometry for having the lowest energy, V3 has trans isomerism and V6 cis; and lastly, V4 (CAS: 354-50-7) has the three halogens of the same type bonded to the same carbon atom. The geometries variations V1, V3, V5 and V6 do not have a CAS registration.

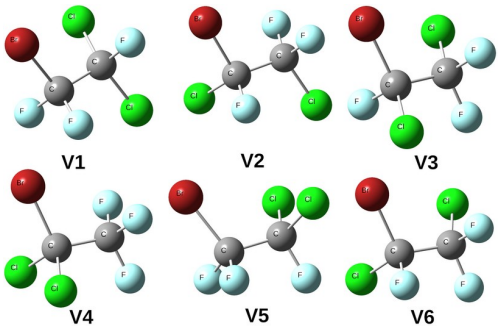

Fig1 – The six geometry variations for $C_2BrCl_2F_3$

Each geometry variation of $C_2BrCl_2F_3$ was reacted with H_2 and resulted in seven different products, as shown in Fig2. The product VX correspond to the respective variation X of the halon reacting with dihydrogen, in the V6 case, where we have 2 products, the notation 6.1 and 6.2 was used. In this figure, one can observe that some of the products formed are new halons, as $C_2HBrCl_2F_2$, and the others species formed are known molecules, as HBr, HCl, HF and the halon HCF_3 (CAS: 75-46-7) which is a HFC found in refrigerants.

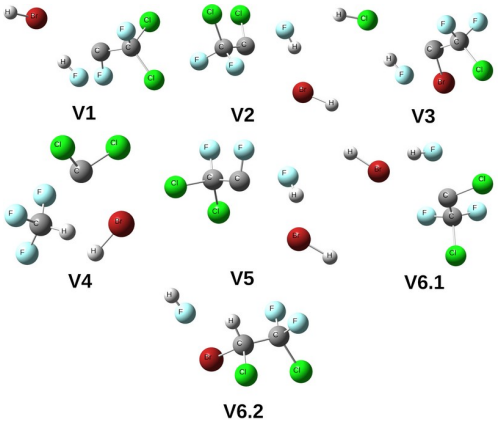

Fig2 – The seven products of $C_2BrCl_2F_3 + H_2$

The reaction rate was determined using the APUAMA code, the Fig3 shows the rate constant for the (V1) $C_2BrCl_2F_3 + H_2 \rightarrow C_2Cl_2F_2 + HF + HBr$, this figure compares the rate in logarithm, and tunneling corrections with the reciprocal temperature (10000/T).

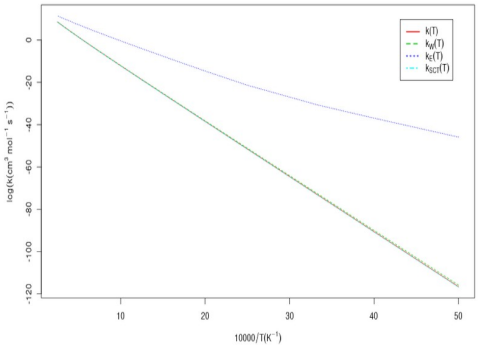

Fig3 – Reaction rate for (V1) $C_2BrCl_2F_3 + H_2$

Conclusions

In this work, we have used the transition state and electronic structure theory to describe the bromodichlorotrifluorethane 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 seven reaction rates ($cm^3mol^{-1}s^{-1}$) can be represented in Arrhenius form as:

$k_{(V1)} = 1.46\times10^6 T^{2.45} \exp(-117.42 /RT)$
$k_{(V2)} = 1.27\times10^6 T^{2.42} \exp(-110.03 /RT)$
$k_{(V3)} = 1.13\times10^6 T^{2.54} \exp(-112.58 /RT)$
$k_{(V4)} = 3.80\times10^6 T^{2.38} \exp(-99.63 /RT)$
$k_{(V5)} = 4.37\times10^6 T^{2.46} \exp(-118.03 /RT)$
$k_{(V6.1)} = 2.50\times10^6 T^{2.43} \exp(-110.08 /RT)$
$k_{(V6.2)} = 2.01\times10^5 T^{2.43} \exp(-98.11 /RT)$

Acknowledgements

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References

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