

On the search of environmentally friendly refrigerant: Reaction of •OH with CH₂=C(CH₃)-CX₃, X=(H,F)

Olivier Holtomo ^{a,b,*}

^a Department of Physics, Faculty of Science, The University of Bamenda, *Bambili P. O. Box 39, Cameroon*

^b Department of Physics, Faculty of Science, The University of Maroua, *Maroua P. O. Box 814, Cameroon*

*E-mail: holtomoo@gmail.com

Abstract

Refrigerants with high global warming potentials (GWPs) and high ozone depletion potential, were phase out by the Montreal protocol. Therefore, expansion of research in this direction were done these recent years. The present investigation aimed to give the insight of the atmospheric implications on the hydrofluoroolefins 2-methylpropene (MP) and 2-trifluoromethylpropene (tFMP) using quantum chemistry tools. These compounds are the modified structures of the existing refrigerant. The thermochemistry of the process of atmospheric removal of gases was studied using the PW6B95/Def2-TZVP. This has resulted in the exothermic and spontaneous reactions of both compounds with •OH radicals known as the detergent of the atmosphere. The enthalpy and free energy of reactions as well as the bond dissociations show that the methyl group, -CH₃, easily releases the hydrogen atom than the other sites of hydrogen abstraction. The kinetics of the said reactions were performed through the MPWB1K/Def2-QZVPP//Def2-TZVP method. The rate coefficient was calculated over a temperature ranging in 200 – 400 K. At ambient temperature, the rate coefficient yielded 9.28×10⁻¹⁴ and 2.16×10⁻¹³ cm³molecule⁻¹s⁻¹ for MP and tFMP, respectively. These results are decisive for atmospheric lifetime calculations, which gave 124.7 and 53.6 days, respectively. The climate forcing efficiencies (REs) were estimated through the IR absorption cross section using the B3LYP/6-31G (3df,p) level of theory. The global warming potentials (GWPs) of MP and tFMP, obtained using the atmospheric lifetimes and REs, yielded low values over the time horizon times 20, 100, and 500 years. The functional group -CF₃ showed lowering effect of GWP when moving from MP to tFMP. The estimates of the photochemical ozone creation potential (POCP) are also low for title compounds, indicating their very low contribution to ozone production in the troposphere. Therefore, MP and tFMP are both environmentally friendly compounds.

Keywords: Hydrofluoroolefins, Rate coefficient, Radiative forcing, GWP, POCP

INTRODUCTION

Hydrofluoroolefin (HFO) is the fourth-generation refrigerant and the most attractive these recent years, owing to its short atmospheric lifetime and low radiative forcing efficiency [1-4] which are the primary metric used to evaluate earth atmospheric friendly gases. As such, the present study concerns two olefins namely: 2-methylpropene or isobutylene (CH₂=C(CH₃)-CH₃) and 2-trifluoromethyl-1-propene (CH₂=C(CH₃)-CF₃) denoted MP and tFMP, respectively (Fig. 1). MP is currently used in the polymer, adhesive, sealant and laboratory chemical products. tFMP is a colorless liquid at room temperature and is known as distinctive odor. It is utilized in various applications such as production of pharmaceuticals, agrochemicals, and specialty chemicals. The presence of fluorine atoms is the potential enhancement of its reactivity in certain reactions [CymitQuimica.com]. These chemicals as well as HFO in general degrade rapidly when released in the atmosphere. This is due to their reactions with •OH radicals and other compounds like chlorine atom, NO₃•, etc. [1-4] which appear with lower concentration than •OH. Therefore, the title molecules as well as HFOs in general are potential replacements of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) in their technological applications as cleaning agents, foam blowing, refrigerants, fire extinguisher, alternatives to medical propellants, etc. [1-5]. Irrespectively of the large industrial applications of these halocarbons, they are being phased out through the Montreal protocol and still make significant contribution to climate change as a result of their long lifetime [6]. More precisely, when such compounds are released to the lower troposphere they move to the upper troposphere and stratosphere where in the presence of UV radiation, they are broken down to produce chlorine atoms hence initiating the depletion of the ozone layer [1,5].

Objectives

- Determine the impact of MP and tFMP in the lower atmosphere using the descriptors as atmospheric lifetime, climate forcing efficiency (RE), global warming potential (GWP) and photochemical ozone creation potential (POCP).



Fig. 1. Equilibrium geometries of MP and tFMP at the B3LYP/6-31G(3df,p). Further on the kinetics study, (3) indicates the site of radical adduct

METHODOLOGY

The quantum chemistry tools were employed in the present work to better describe the geometrical structures and IR absorption cross section of MP and tFMP molecules. The B3LYP/6-31G(3df,p) method was performed for this issue. Then the composite method MPWB1K/Def2-QZVPP//Def2-TZVP was performed for potential energy surfaces of reactions involving title molecules and OH radicals. All calculations were carried out through the Gaussian 16 suite of programs.

The rate coefficients of reactions were calculated using transition state theory [xxx] implemented in our homemade FORTRAN.

A simple method for determining the RFE was created by Pinnock et al. (1995). Their method allows to assess this physical quantity from the IR spectrum of gas without the use of a complex radiative transfer model. In this approach, the RFE is stated as follows:

$$RFE = \sum_{i=1}^{250} 10\sigma_i(\omega_i)F_i(\omega_i)$$

where $\sigma_i(\omega_i)$ is the absorption cross section (cm²molecule⁻¹) averaged over a 10 cm⁻¹ interval around the frequency ω_i and $F_i(\omega_i)$ is the instantaneous cloudy sky radiative forcing per unit cross section in Wm⁻² (cm²molecule⁻¹cm⁻¹)⁻¹ for a 0–1 ppbv increase in absorber. The values of $F_i(\omega_i)$ were reported by Pinnock et al. using their narrow band radiative transfer model in the frequency range 0–2500 cm⁻¹.

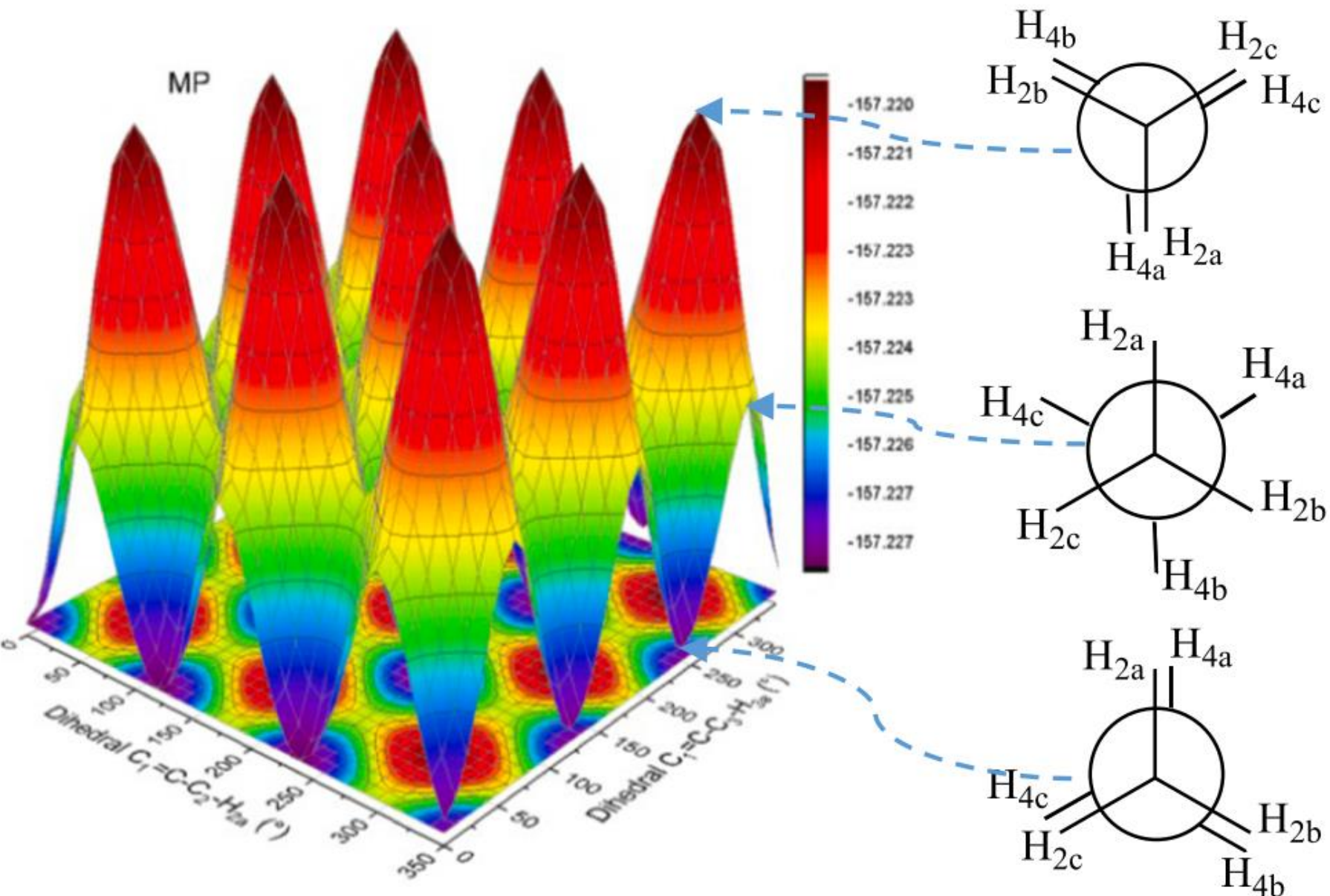


Fig. 2. 3D-Potential energy surface from the rotation of two dihedral angles C₁=C-C₂-H_{2a} and C₁=C-C₃-H_{4a} for MP (upper panel) and C₁=C-C₂-H_{2a} and C₁=C-C₃-F₁ for tFMP (lower panel). The eclipsed and staggered conformationals are identified

RESULTS

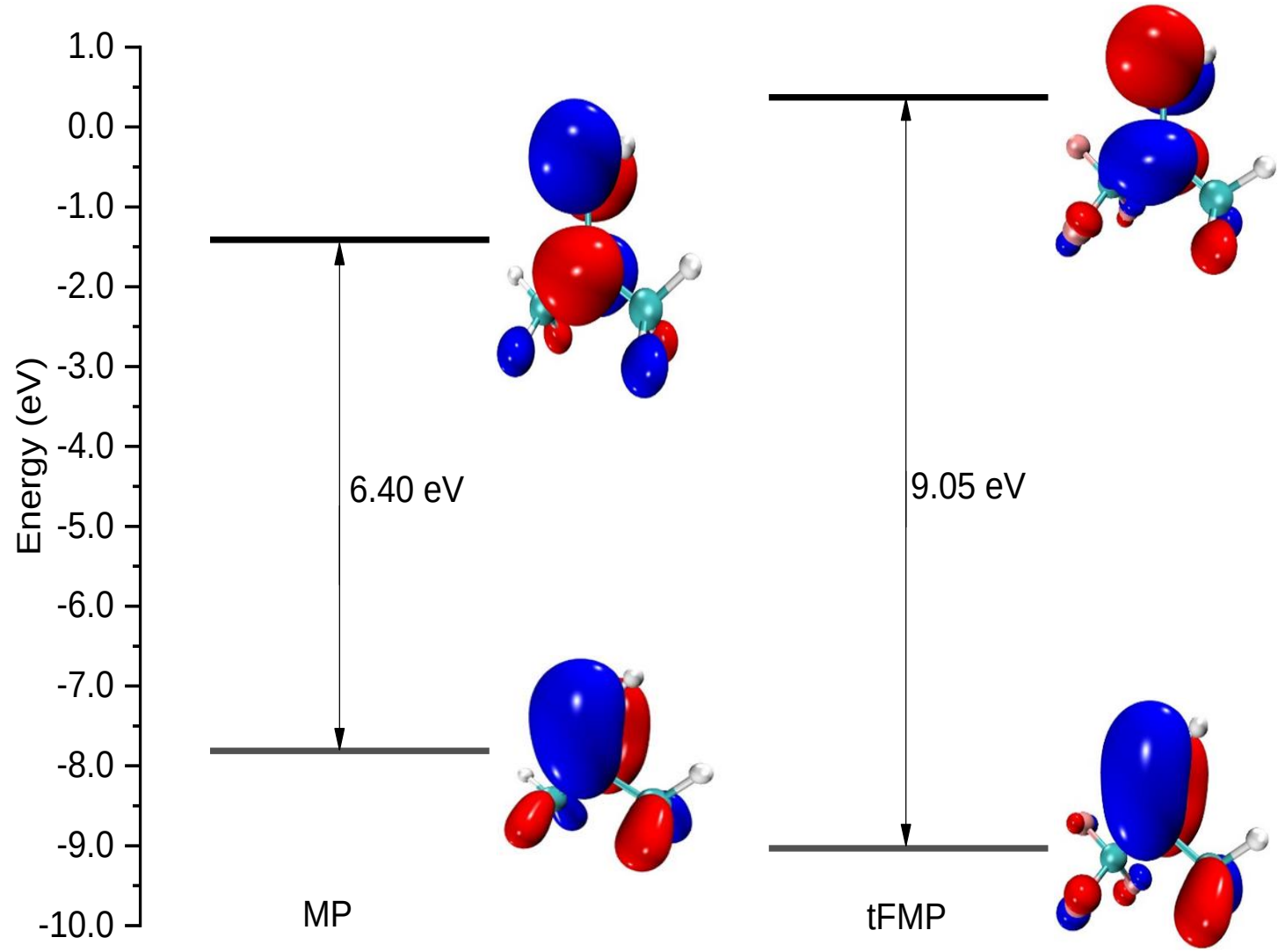


Fig. 3. HOMO – LUMO diagram of MP and tFMP molecules

The reaction of the •OH radicals with MP and tFMP can result into four different processes as presented in reactions (R1) – (R4). The structure of MP is symmetric while the structure of tFMP is asymmetric due to the -CF₃ group. As such, reaction (R3) for tFMP is counted as different channel for both hydrogen (CH₂=).

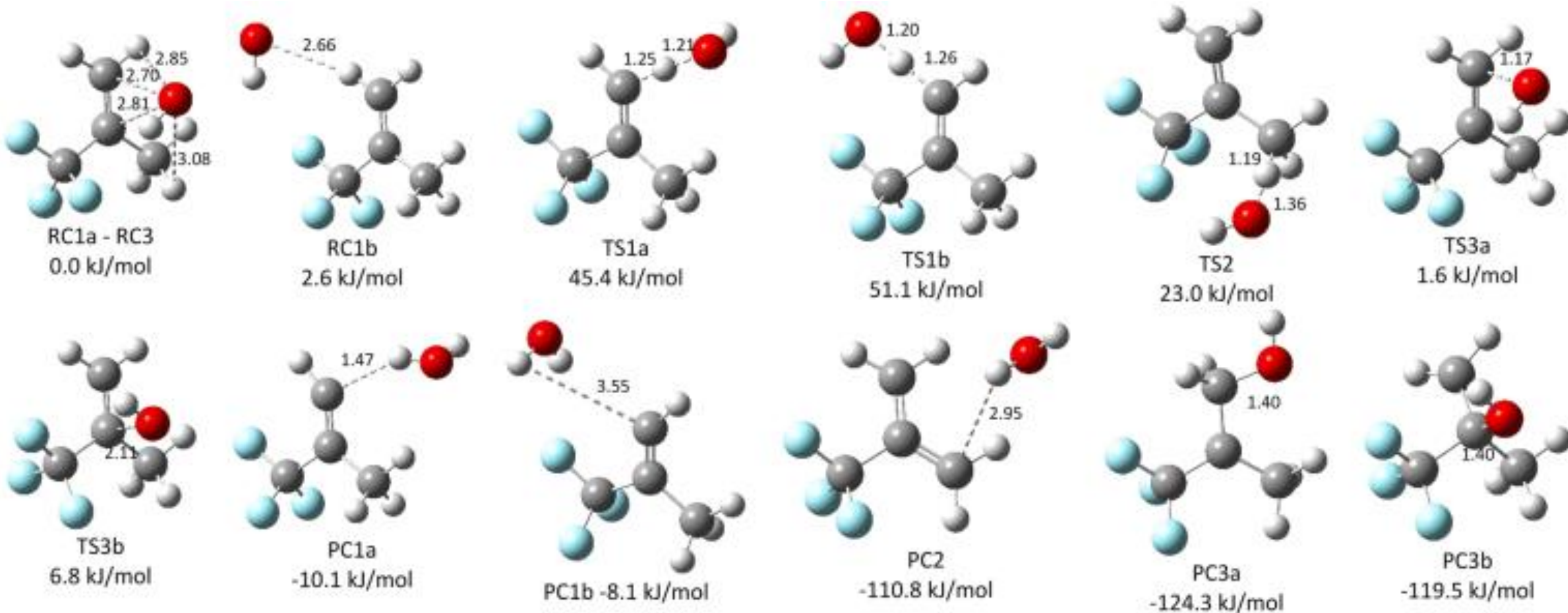
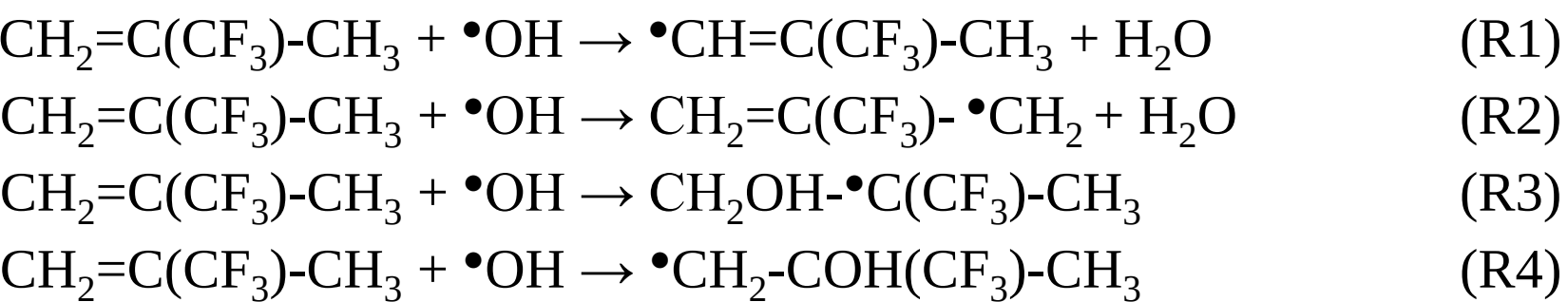


Fig. 5. Equilibrium geometries of reaction complex (RC), transition states (TS1a, TS1b, TS2, TS3a, and TS3b), and product complexes (PC1a, PC1b, PC2, PC3a, and PC3b) for the reactions of •OH radical with tFMP at different reaction channels. The energy (kJ/mol) are the relative free energies carried out using mPWB1k/Def2-QZV2P//Def2-TZVP. The bond lengths in the active space of reaction are given in Å.

Table 1

Atmospheric lifetime τ (day), radiative forcing efficiency RFE (Wm⁻²ppbv⁻¹) over the frequency range 0-2500 cm⁻¹, and global warming potential GWP at time horizons 20, 100, and 500 years of MP and tFMP. UMG and NMG stand for uniform mixed gas and non-uniform mixed gas, respectively.

Gas	τ	RFE		GWP			POCP
		UMG	NMG	20	100	500	
MP	124.7	0.020	0.018	18.57	5.27	1.60	1.96
tFMP	53.6	0.207	0.068	52.24	14.84	4.51	2.22

The estimations show 124.7 and 53.6 days for MP and tFMP, respectively. The values of ALTs are of the order of days, meaning that, the concerned molecules tend to degrade near emission zone, showing a negligible impact on global warming. The presence of -CF₃, decreases significantly the ALT as compared with -CH₃. Hence there is a moderate and significant increase of ALT when moving from MP to tFMP. Comparing with other HFOs such as CF₃CF=CH₂ (HFO-1234yf), one of the most promising working refrigerants, having ALT of 11 days [26], the title molecules have greater ALTs.

Fig. 4. Equilibrium geometries of reaction complex (RC), transition states (TS1, TS2, TS3a, and TS3b), and product complexes (PC1, PC2, PC3a, and PC3b) for the reactions of •OH radical with MP at different reaction channels. The given energy (kJ/mol) are the relative free energies carried out using mPWB1k/Def2-QZV2P//Def2-TZVP. The bond lengths in the active space of reaction are given in Å.

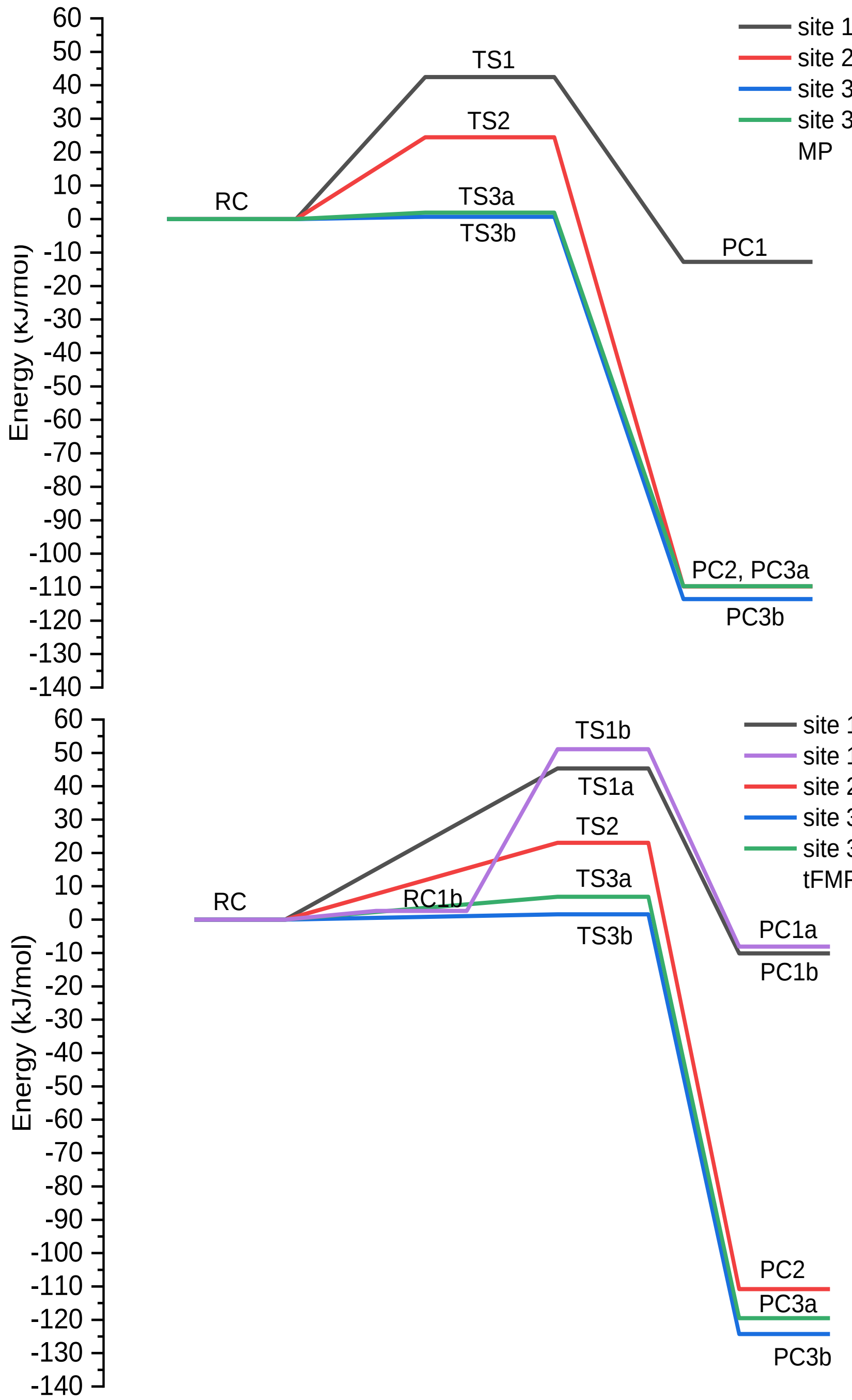


Fig. 6. Potential energy surface of the reaction of MP and tFMP with OH radical

CONCLUSION

The present work, plays a role of a solid foundation on which future experimental and theoretical work on MP and tFMP could be done to qualify a suitable gas for use as a refrigerant. It presents the first theoretical evaluation of parameters such as radiative forcing efficiencies, rate coefficients, atmospheric lifetimes, GWPs and POCP which are amongst the criteria for suitable refrigerant selection. It provides another variety of HFOs which have not been studied previously and serves as a solid foundation on which more research can be made. It broadens the scope of low-GWP HFOs refrigerants which is the main aim of the international regulations

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