

A computational perspective of the competitive decomposition and isomerization of CH₃OCHFO radical

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Received 25 June 2012; Accepted (in revised version) 30 July 2012

Published Online 28 June 2013

Abstract. A detailed quantum chemical study is performed on the mechanism of the CH₃OCHFO radical formed during the photooxidation of CH₃OCH₂F (HFE-161), including the main decomposition and isomerization processes at the G2(MP2)/MPWB1K level of theory. The results clearly point out that the β -C-H bond scission is the dominant path involving the lowest energy barrier of 8.16 kcal mol⁻¹ calculated at G2(MP2) level of theory. On the basis of the results obtained during the present investigation, the thermal rate constant for the different reaction channels involved during the isomerization and decomposition processes of CH₃OCHFO are evaluated at 298 K and 1 atm using Canonical Transition State Theory. The results are compared with the data available in the literature.

PACS: 31.15.A, 31.15.E, 82.20.Kh, 82.30.Lp, 82.33.Tb

Key words: theoretical study, hydrofluoroethers, G2 method, isomerization, canonical transition state theory

1 Introduction

Concern over the global environmental consequences of fully halogenated chlorofluorocarbons (CFCs) has created a need to determine the potential impact of other halogenated organic compounds on stratospheric ozone. The absence of a H-atom in the CFCs does not allow them to be oxidized or photolyzed in the troposphere. Thus, such compounds are transported into the stratosphere and their subsequent decomposition can lead to chlorine catalyzed ozone depletion [1-4]. Because of the critical role played by CFCs in stratospheric ozone depletion, continuous efforts are being made to find replacement compounds. Recently, attention has been paid to hydrofluoroethers (HFEs) to be used as

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third generation replacements to CFCs and may find a place in the industry to be used as cleaning agents of electronic equipments, heat transfer agents in refrigeration systems and as carrier fluids for lubricant deposition [5,6]. One of the principal advantages of the HFEs is their shorter atmospheric lifetimes in comparison to HFCs which in turn lead to lower GWP [7]. The absence of chlorine atoms in HFEs would lead us to believe that such compounds have little impact on stratospheric ozone and that they would possess a negligible Ozone Depleting Potential (ODP) [8]. Several theoretical and experimental studies performed with a few HFEs have shown that HFEs possess physical and thermochemical properties similar to that of CFCs, HCFCs and HFCs. Thus, the former can find acceptability in a wide variety of Industrial applications [9-13]. The low ozone depleting potential and shorter atmospheric life time (0.112 years) [14] of fluoromethyl methyl ether $\text{CH}_3\text{OCH}_2\text{F}$ (HFE-161) and its comparable thermo-physical properties to CFCs regard it as the most suitable replacement for CFCs as a refrigerant. A general mechanism of tropospheric degradation of HFE-161 is shown in Fig. 1 which is based on the fact that initial attack of OH radical leads to the formation of haloalkyl radical ($\text{CH}_3\text{OCHF}^\bullet$). The latter reacts with atmospheric O_2 to produce peroxy radicals ($\text{CH}_3\text{OCFHO}_2^\bullet$). In a polluted atmosphere the peroxy radicals thus formed may further react with other oxidizing species such as NO_2 and NO that ultimately leads to the formation of haloalkoxy radical. On the other hand, haloalkoxy radical may also be generated through another intermediate, the hydroperoxide ($\text{CH}_3\text{OCFHO}_2\text{H}$) formed by the reaction of $\text{CH}_3\text{OCFHO}_2^\bullet$ and HO_2 . The haloalkoxy radicals thus formed play a critical role in removing a variety of organic vapours present in the troposphere [15]. Therefore, it is pertinent to perform experimental and theoretical studies on the decomposition of HFEs in order to ascertain their suitability as replacement compounds of CFCs.

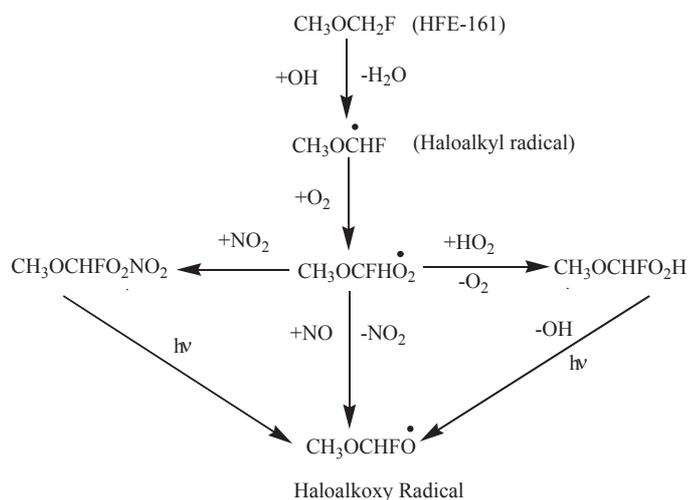


Figure 1: Tropospheric degradation mechanism of HFE-161.