Computational study on kinetics and mechanism of Cl-initiated hydrogen abstraction of methyl fluoroacetate

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A B S T R A C T

A theoretical investigation has been performed on the mechanism, kinetics and thermochemistry of the gas phase reactions of methyl fluoroacetate $CH_2FC(O)OCH_3$ (MFA) with Cl atoms. Geometry optimization and frequency calculations have been made at the MPWB1K/6-31+G(d,p) level of theory and energetic information is further refined by calculating the energy of the species using G2(MP2) theory. The rate constant for reactions of MFA with Cl atoms are reported over wide range of 250–450 K using the Canonical Transition State Theory (CTST). The atmospheric lifetime of $CH_2FC(O)OCH_3$ was estimated to be around 1.21 years with respect to reaction with Cl atoms. The rate constant obtained is compared with literature values for other similar species to establish reactivity trends. It is shown that the F-atom substitution decrease the reactivity of C–H bond of esters.

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1. Introduction

Hydrofluoroethers (HFEs) have been the focus of intense attention as replacement materials for CFCs and hydrochlorofluorocarbons (HCFCs) in industrial applications such as heat-transfer fluid in refrigeration systems, cleaning agent in electronic industry, foam-blowing and also for lubricant deposition [1,2]. It has been reported that fluorinated esters (FESs) are the primary products of the atmospheric oxidation of HFEs [3]. For instance, the fluoroakylformates $C_4F_9OC(O)H$ and n-$C_3F_7OC(O)H$ are the major degradation products of HFE-7100 ($C_4F_9OCH_3$) and HFE-7000 ($C_3F_7OCH_3$), respectively [4,5]. Similarly, methyl trifluoroacetate $CH_3OC(O)CF_3$ is the major degradation product of OH-initiated oxidation of $CH_3OCH(CF_3)_2$ [6]. These fluorinated compounds find wide applications in biochemistry, medicinal chemistry, pharmacology and related fields [7,8]. The substitution of hydrogen by fluorine in pharmacologically active organic molecules can have profound effects on the activity [9]. Fluoroacetate (FA; CH_2FCOOR) is highly toxic towards humans and other mammals through inhibition of the enzyme aconitase in the tricarboxylic acid cycle, caused by 'lethal synthesis' of an isomer of fluorocitrate (FC) [10]. The

degradation of FESs produce environmentally burdened product like trifluoroacetic acid (TFA) which may impact on agricultural and aquatic systems [11]. Thus, it is important to study the kinetics and mechanistic degradation pathways of FESs for complete assessment of atmospheric chemistry as well as to explore the impact of FESs on the environment. Considerable attention has been paid in recent years to perform experimental and theoretical studies on the decomposition kinetics of FESs [12–24].

It is known that MFA was a substance of great toxicity, with very interesting pharmacological properties [25]. Like most volatile organic compounds (VOCs), reaction with OH radicals is considered to be the dominant removal process of esters in the troposphere [26]. Although global atmospheric abundance of OH radicals is around 2 orders of magnitude greater than that of chlorine atoms, Cl reactions are generally faster than OH reactions, so their contribution to the degradation of VOCs may be not negligible compared to the role of OH [27]. This contribution of Cl could be significant in areas where the concentration of Cl precursor species has been reported to be high, such as the coastal boundary layer [28]. In fact, chlorine atoms have been monitored in concentrations in the order of 10^5 molecule cm^{-3} over the marine boundary layer [29]. Thus, chlorine atom also plays an important role in atmospheric chemistry [30]. In earlier report [31] we theoretically investigated the product distribution of MFA by OH-initiated oxidation. The rate constant for the hydrogen abstraction by OH radicals

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were estimated over the temperature range of 250–450 K and reported rate constant at 298 K as 2.44×10^{-13} cm^3 molecule^{-1} s^{-1}. The OH-driven atmospheric lifetime of MFA was estimated to be 24 days. To the best of our knowledge, no experimental study has been reported for hydrogen abstraction by Cl atom with $CH_2FC(O)OCH_3$. Thus, the question arises: which is the major channel for the $CH_2FC(O)OCH_3 + Cl$ reactions? Are the reaction mechanisms similar to those of the $CH_2FC(O)OCH_3 + OH$ reactions? In addition, no experimental information is available on the branching ratios of the title reactions. In this work, kinetic and mechanistic studies have been performed for the reactions of Cl atoms with MFA. Our calculation indicates that two reaction channels each from –CH$_3$ and –CH$_2$F groups are feasible for the $CH_2FC(O)OCH_3 + Cl$ reactions as given below:

$$CH_2FC(O)OCH_3 + Cl \rightarrow {}^*CH_2OC(O)CH_2F + HCl \qquad (1)$$

$$CH_2FC(O)OCH_3 + Cl \rightarrow {}^*CHFC(O)OCH_3 + HCl \qquad (2)$$
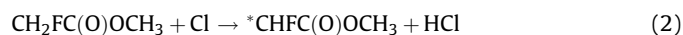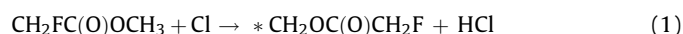
To the best of our knowledge this is the first detailed theoretical study on Cl-initiated hydrogen abstraction reactions of MFA. This work provides the first kinetic data for the reactions of $CH_2FC(O)OCH_3$ with Cl atom at 298 K. The data obtained in this work were used to estimate the effective lifetime in the troposphere of the studied compound.

2. Results and discussion

2.1. Structure and energetics

Geometry optimization of MFA molecule predicts two possible conformers (SC1 and SC2) which differ mainly in the orientation of C2–F1 bond relative to the F–C–C–O backbone and their structures are shown in Fig. 1. These two conformers of MFA molecule are in accordance with the observation reported by Abraham et al. [7] and Sahnoun et al. [8] by means of theoretical tools. Meanwhile, for hydrogen abstraction by Cl atoms, the same transition state was found from both conformers of MFA. Therefore, we have presented only transition states from the most stable conformer (SC1). There are two hydrogen abstraction sites of MFA, namely the –CH$_3$ and –CH$_2$F group. Two transition states (TSs) are therefore located from conformer (SC1) for the two reactions. The detailed
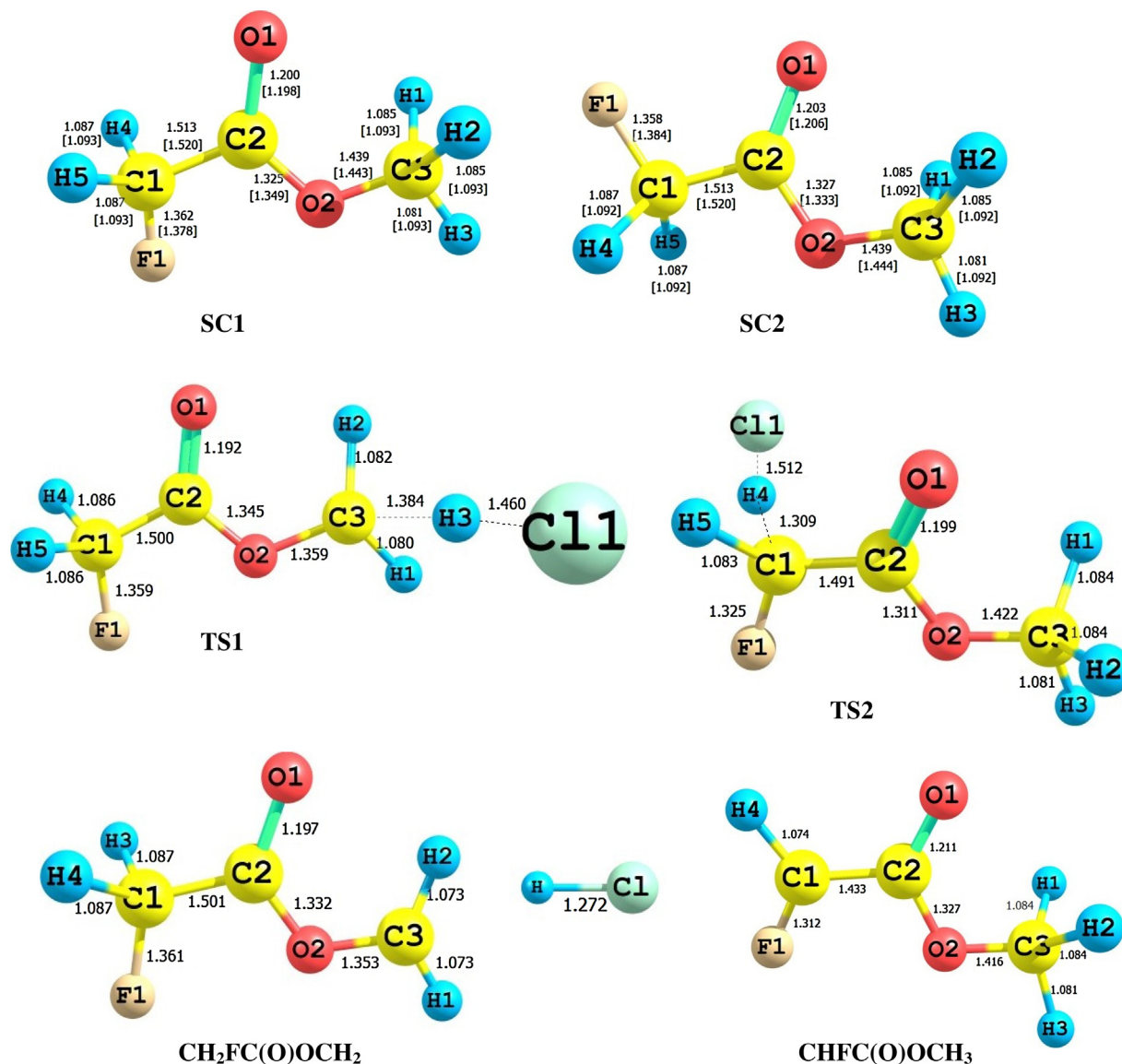
Fig. 1. Optimized geometries of reactants, products and transition state involved in the H-atom abstraction reaction of CH$_2$FC(O)OCH$_3$ by Cl atoms at MPWB1K/6-31+G(d,p) method. The values given in square bracket are taken from Ref. [7].