ELSEVIER

Journal of Molecular Structure: THEOCHEM 730 (2005) 143–150

THEO CHEM

www.elsevier.com/locate/theochem

DFT study on the reaction mechanisms of polyfluorosulfonate ester with F^-

Li Guo[a], Zhong-Heng Yu[a,*], Shi-Zheng Zhu[b], Qing-Yun Chen[b]

[a]State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, Peoples's Republic of China

[b]Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200031, People's Republic of China

Received 15 March 2005; revised 10 June 2005; accepted 10 June 2005
Available online 2 August 2005

Abstract

Gas-phase reaction of $C(1)F_3S(2)O_2O(3)C(4)H_2C(5)F_3$ and $F^-(16)$ is investigated using DFT method. The geometries of various stationary points and their relative energies are obtained from 6-31+G*, 6-311G**, and 6-311++G** levels. In the S_N2(C) reaction leading to the cleavage of the C(4)–O(3) bond, the reaction complex results from attacking of F^- at a hydrogen atom H11 attached to carbon atom C(4). Afterward, F^- is attacking the atom C(4) from the backside of the atom O(3) with the help of the neighboring effect, and meanwhile a multi-membered ring, F(16)–H(11)–C(4)–C(5)–F(16), is being formed. The S_N2(C) reaction is irreversible. On the contrary, the S_N2(S) reaction leading to the cleavage of the S(2)–O(3) bond is reversible, and it is initiated by attacking of F^- at the atom S(2) from the backside of the atom O(3). The products of the reaction $CF_3SO_3CH_2CF_3$ $+F^-$ should be, thermodynamically, controlled due to the reversibility of the S_N2(S) reaction, and those result, chemospecifically, from the cleavage of the C–O bond. At last, the SCRF calculations confirm that the solvent effect is preferable to the S_N2(C) reaction.

Keywords: Polyfluoroalkylsulfonate; S_N2 reactions; DFT method; Chemospecific reaction

1. Introduction

The bimolecular nucleophilic substitution (S_N2) is an important reaction in organic chemistry, and it has been extensively studied both experimentally [1–5] and theoretically [6–12]. Hydrolysis of sulfonate ester RSO_2OR' is a S_N2 reaction [13] and the R′–O cleavage is much more likely than S–O cleavage when R′ is alkyl. On the other hand, the S–O bond is much more likely to cleave when R′ is aryl [13,14]. The nucleophilic substitutions at perfluoro- and polyfluoro-sulfonate ester were, experimentally, studied by Chen and Zhu [15] because the groups, such as $CF_3SO_3^-$, $n-C_4F_9SO_3^-$ and $CF_3CH_2SO_3^-$, were found to be better leaving-groups [13a]. Particularly, the nucleophilic substitutions at perfluoro- and polyfluoro-sulfonate ester are chemospecific. In the S_N2 reaction (I), as shown by the experiments [15a], the nucleophile, such as F^-, attacks $R_FSO_3CH_2R'_F$ at the α-carbon atom, leading to the C–O cleavage exclusively:

$$R_FSO_3C\mathbf{H}_2R'_F + F^- \xrightarrow[\text{cleavage}]{\text{C-O}} R_FSO_2O^- + R'_FC\mathbf{H}_2F \qquad \text{(I)}$$

$$R_FSO_3C\mathbf{F}_2R'_F + F^- \xrightarrow[\text{cleavage}]{\text{S-O}} R_FSO_2F + R'_FC\mathbf{F}_2O^- \qquad \text{(II)}$$

$$R'_FC\mathbf{F}_2O^- \xrightarrow{\text{(III)}} F^- + R'_FCOF$$

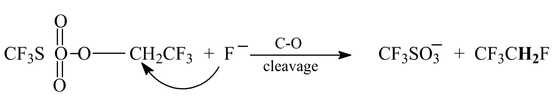
But the reaction (II) leads to the S–O cleavage solely [15b]. The chemospecificity of the S_N2 reaction at perfluoro- and polyfluoro-sulfonate ester should be more interesting than the chemoselectivity of the reaction at sulfonate ester RSO_2OR'. Yoshida ascribed such chemospecificity to the great electronegativity of the fluorine atom [16]. On the basis of the experimental works [15], Chen and Zhu deduced that the screen effect, associated with the electron repulsion interaction between F^- and the fluorine atoms (denoted as F11 and F12 in Fig. 1) attached to the α-carbon atom, plays an important role in determining the chemospecificity of reaction (II). However, in the transition

* Corresponding author. Tel.: +86 1062564822; fax: +86 1062557393.
E-mail address: yuzh@iccas.ac.cn (Z.-H. Yu).

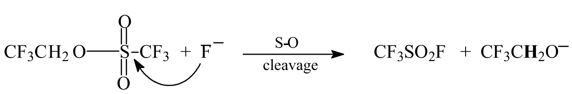
0166-1280/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2005.06.013

state of reaction (II), the nucleophile F^- should have greater leaving-group ability than the group $R'_FCF_2O^-$ [17]. It is due to reaction (III) that reaction (II) leads, specifically, to the S–O cleavage. In appearance, the behavior of the atoms on α-carbon atom plays an important role in determining the mechanism of reaction (II) besides the screen effect. In fact, as will be shown in this work, the neighboring effect also plays an important role in determining the mechanism. In addition, as emphasized by the experimental researchers [15a], perfluoro- and polyfluoro-sulfonate ester can be used as an excellent alkylating agent because $R_FSO_3^-$ is a good leaving group. Therefore, it is necessary to theoretically understand the chemospecificity of reactions (I) and (II) as well as to detail the roles of the α-group and β-group. In this work, the reaction, $CF_3SO_3CH_2CF_3 + F^-$, is investigated using DFT (density functional theory), and the theoretical research on the reaction (II) will be published elsewhere.

There are two possible ways for F^- to attack CF_3SO_2-OCH_2CF_3: (i) at the α-carbon atom from the backside of the oxygen atom [reaction (IV)]; (ii) at the sulfur atom from the backside of the oxygen atom [reaction (V)].



(IV)



(V)

2. Calculation method

All computations are done using Gaussian 98 program package [18]. Various species involved in the reactions are optimized at B3LYP/6-311G**, 6-31+G* and 6-311++G** levels. The harmonic vibration frequencies are calculated, and each transition state is characterized by one imaginary frequency. Afterwards, the IRC (intrinsic reaction coordinate) method [19] is used to track minimum energy path from transition state to the corresponding local minima.

In S_N2 reactions (IV) and (V), the charge, which is located to F^- before reaction, becomes dispersed over a somewhat larger area in the reactant complex and transition state. To determine the effect of environment, the SCRF method [20] is used. Cyclohexane and dimethylsulfoxide (DMSO) are selected as the reaction fields.

3. Results and discussion

The reaction complex, transition state, product complex and two products ($CF_3SO_3^-$ and FCH_2CF_3), involved in reaction (IV), are denoted as RC-C, TS-C, PC-C, P1-C and P2-C, respectively, and those, involved in reaction (V), are symbolized as RC-S, TS-S, PC-S, P1-S (CF_3SO_2F) and P2-S ($^-OCH_2CF_3$).

According to the data presented in the Figures, the geometries of each of the neutral species, obtained from the

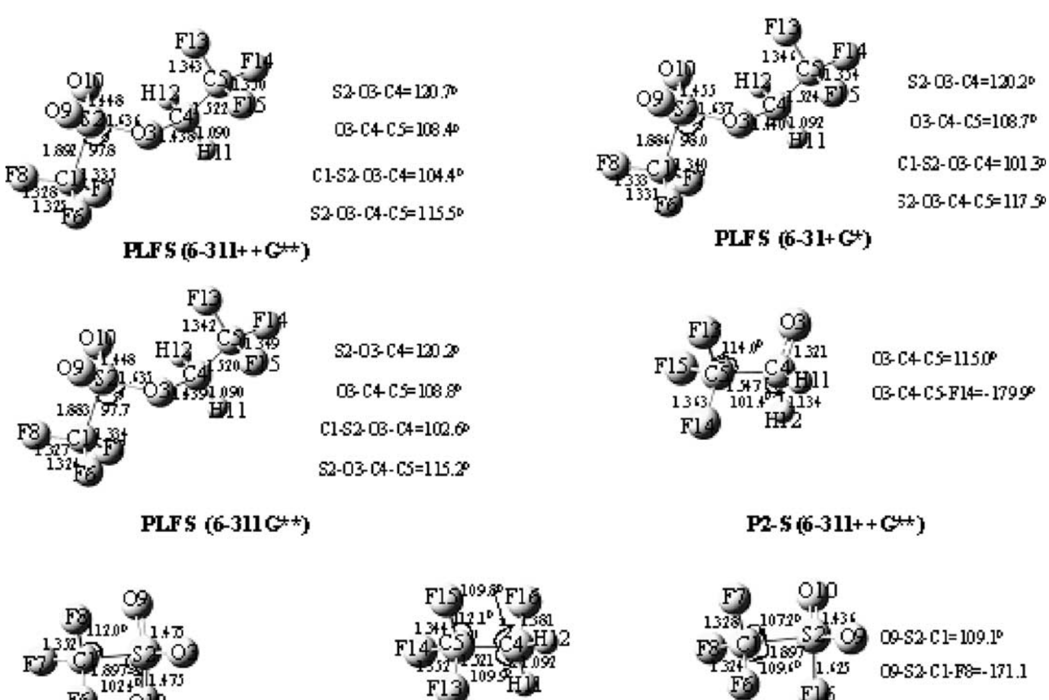


Fig. 1. Geometries of the reactant and products (bond length in Å, bond angle and dihedral angle in degree).