

Theoretical Study of the Thermal Decomposition of Chlorofluoromethanol (CHClFOH)

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Abstract: A complete potential energy surface for the CHClFOH system was calculated at the G3(MP2) level. The calculations reveal that the four-center 1,2-HX (X=F, Cl) elimination mechanism rather than the bond scission mechanism dominate decomposition of CHClFOH. The results are valuable to understand the atmospheric chemistry of HCFC-31.

Keywords: Chlorofluoromethanol, reaction mechanism, potential energy surface.

Introduction

Hydrochlorofluorocarbons (HCFCs) have been widely used as replacements of chlorofluorocarbons (CFCs). The insertion of O (¹D) into the CH bond of HCFC forms the activated alcohol. It has been shown that these hot alcohols play an important role in the degradation mechanism of atmospheric compounds¹.

Chlorofluoromethanol (CHClFOH) appears in the reaction of O (¹D) with CH₂ClF (HCFC-31)². Neither experimental nor theoretical study of this species was available to date. Using the *ab initio* G3(MP2)³, we report nearly all the possible decomposition pathways of CHClFOH.

Computations

The geometries of the reactants, products, and transition states were optimized at the MP2(full)/6-31G(d) level. The vibrational frequencies were obtained at the same level. All transition states were subjected to intrinsic reaction coordinate (IRC) calculations. The energetics were obtained *via* the G3(MP2) method, which performs well for both reaction heat and barrier height^{3,4} with an accuracy of ± 2 kcal/mol.

Results and Discussion

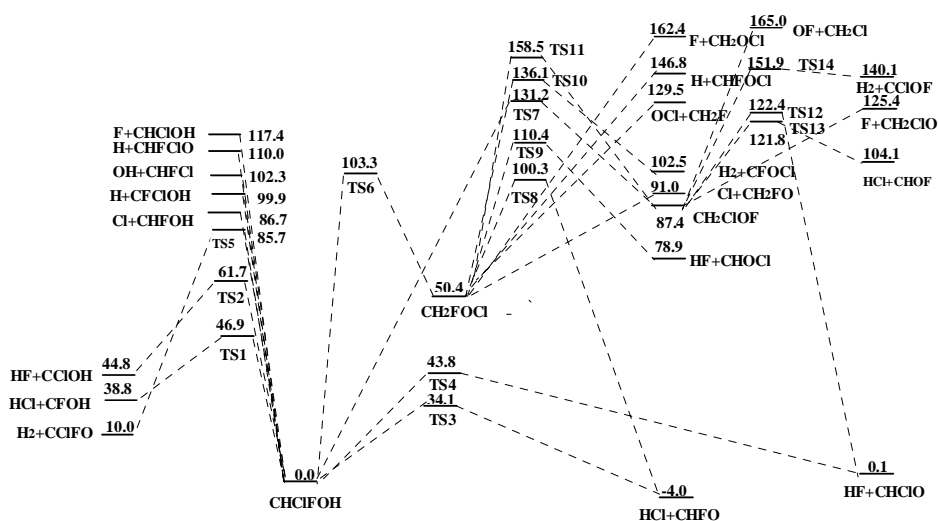
The calculated potential energy surface (PES) is shown in **Figure 1**. The highly endothermic CF, CCl, OH, CO, and CH simple bond scissions proceed without transition

state and are less important. The three-center decompositions of CHClFOH produce HCl + CFOH and HF + CClOH *via* transition states TS1 and TS2, respectively. Their activation barriers (46.9 and 61.7 kcal/mol) are of significance.

The four-center 1,2-HX (X=F, Cl) elimination from CHClFOH becomes more feasible in view of lower barriers. The HCl + CHFO channel not only possesses the lowest energy barrier (TS3, 34.1 kcal/mol), but is slightly exothermic (-4.0 kcal/mol). The HF + CHClO channel is nearly thermally neutral with a barrier of 43.8 kcal/mol (TS4). The forming HCl bond in TS3 and HF bond in TS4 are 52% and 28% longer than their respective equilibrium distances. The four-center 1, 2-HH elimination channel involves a much higher barrier of 85.7 kcal/mol (TS5). These findings are apparently consistent with the feature of PES for the CH₂FOH and CH₂ClOH molecules.

CHClFOH rearranges to CH₂FOCl or CH₂ClOF *via* the concerted H, X-migration, but again the barriers (TS6, TS7) exceed 100 kcal/mol. Thus the reaction cannot occur to any extent despite many open channels of the isomers.

Figure 1. The overall profile of the PES (in kcal/mol) for the CHClFOH system.



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