Theoretical studies of the reactions of $\text{O}^{(3}\text{P})$ with halogenated methyl (I)

—Reaction mechanism of the $\text{O}^{(3}\text{P}) + \text{CH}_2\text{Cl}$ reaction

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Received April 13, 1999

Abstract The reaction of $\text{O}^{(3}\text{P})$ with $\text{CH}_2\text{Cl}$ radical has been studied using $ab\ initio$ molecular orbital theory. G2 (MP2) method is used to calculate the geometrical parameters, vibrational frequencies and energies of various stationary points on the potential energy surface. The reaction mechanism is revealed. The addition of $\text{O}^{(3}\text{P})$ with $\text{CH}_2\text{Cl}$ leads to the formation of an energy rich intermediate $\text{OCH}_2\text{Cl}$ which can subsequently undergo decomposition or isomerization to the final products. The calculated heat of reaction for each channel is in agreement with the experimental value. The production of $\text{H} + \text{CHClO}$ and $\text{Cl} + \text{CH}_2\text{O}$ are predicted to be the major channels. The overall rate constants are calculated using transition state theory on the basis of $ab\ initio$ data. The rate constant is pressure independent and exhibits negative temperature dependence at lower temperatures, in accordance with the experimental results.

Keywords: $ab\ initio$, potential energy surface, $\text{O}^{(3}\text{P})$ atom, $\text{CH}_2\text{Cl}$ radical.

Incineration is an effective method for the management of halogenated hydrocarbons wastes\[1\]. How to control secondary pollution during the incineration is an important subject. It is necessary to understand the reaction mechanism of the combustion process. Halogenated methyl is highly reactive when the hydrogen atoms in the methyl are substituted by halogen atoms. $\text{O}^{(3}\text{P})$ atoms can rapidly react with halogenated methyls. The reactions are highly exothermic and play an important role in the combustion process. To date, there are few experimental and theoretical studies of this type of reactions.

The reaction of $\text{O}^{(3}\text{P}) + \text{CH}_2\text{Cl}$ is important in the incineration of the chlorinated hydrocarbons wastes\[2\]. It was not until 1997 that this reaction began to be examined. Overall rate constants were obtained by Seetula et al.\[2\] using a heatable tubular reactor coupled to a photoionization mass spectrometer and were set to $k = (1.49 \pm 0.34) \times 10^{-10} \exp \left[ \left(1.46 \pm 0.38 \text{ kJ \cdot mol}^{-1}/RT\right) \right] \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ over the temperature range 297—823 K. $\text{CHClO}$ and $\text{CH}_2\text{O}$ were found to be the major products. They indicated that $\text{CHClO}$ and $\text{CH}_2\text{O}$ were generated from the decomposition of an energy rich intermediate, $\text{OCH}_2\text{Cl}$. Until now, there has been no theoretical study of this reaction. In this paper we examine this reaction using $ab\ initio$ methods on the lowest-lying doublet potential energy surface. The reaction mechanism is illustrated in detail. The rate constants are calculated by transition state theory (TST).

1 Computation methods

The geometries of reactants, products, intermediates and transition states are optimized at the UMP2(full)/6-31G(d) level of theory. Based on the optimized structures, the high-level energies of the stationary points are calculated at QCISD(T)/6-311G(d,p) and UMP2/6-311 + G(3df,2p) level
els of theory, respectively. The total energies are obtained using the G2MP2 scheme\textsuperscript{[3]} To obtain reliable vibrational frequencies and zero-point energies, frequency analysis is carried out at the UMP2 (full)/6-31G(d) theory. All calculations are performed using Gaussina 94 programs\textsuperscript{[4]}.

2 Results and discussion

The optimized geometries of reactants, intermediates, transition states and products are shown in fig. 1. The corresponding frequencies and zero-point energies are listed in table 1, with only one neg-

![Diagrams of molecular structures and bond lengths](image)

Fig. 1. The UMP2(full)/6-31G(d) optimized geometries of the various forms of the reaction O(\textsuperscript{3}P) + CH\textsubscript{3}Cl. Bond lengths in nm and angles in degree.