

Ab initio Mechanism Study on the Reaction of Chlorine Atom with Formic Acid

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The potential energy surface (PES) for the reaction of Cl atom with HCOOH is predicted using *ab initio* molecular orbital calculation methods at UQCISD(T, full)/6-311++G(3df, 2p)//UMP2(full)/6-311+G(d, p) level of theory with zero-point vibrational energy (ZPVE) correction. The calculated results show that the reaction mechanism of Cl atom with formic acid is a C-site hydrogen abstraction reaction from *cis*-HOC(H)O molecule by Cl atom with a 3.73 kJ/mol reaction barrier height, leading to the formation of *cis*-HOCO radical which will react with Cl atom or other molecules in such a reaction system. Because the reaction barrier height of O-site hydrogen abstraction reaction from *cis*-HOC(H)O molecule by Cl atom which leads to the formation of HCO₂ radical is 67.95 kJ/mol, it is a secondary reaction channel in experiment. This is in good agreement with the prediction based on the previous experiments.

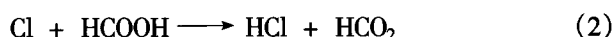
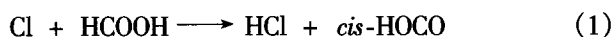
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Introduction

The reactions of chlorine atoms with hydrocarbons are important to our understanding of atmospheric chemistry. Chlorine atoms are widely used in many studies of the atmospheric degradation mechanism of organic compounds.¹ To facilitate the design and interpretation of some experiments, kinetic and mechanistic data concerning the reaction of Cl atoms with some hydrocarbons are needed. Information concerning the reactivity of the desired products and key intermediates with Cl atoms is needed to design and optimize industrial processes. Therefore, Cl atoms play important roles in many reactions and processes. The kinetics and mechanisms of the reactions of chlorine atoms with many hydrocarbons have been studied using experimental and theoretical methods.^{1,4}

The hydroxy formyl radical HOCO is of great interest as a transitory intermediate in many important reactions,^{5,6} and plays an important role in many kinetic experiments. In the reaction of Cl atom with HCOOH, which has proved to be a

useful source of relatively unexcited HOCO radicals in laboratory studies of their kinetics,^{3,4,7} two possible reaction channels were predicted,⁸⁻¹⁰



and the products, *cis*-HOCO or HCO₂, will react with other molecules in such a reaction system.

In 1991, Tyndall⁸ studied the reaction, and thought that reaction (2) contributes at most 4% with channel (1) accounting for over 96% of the reaction. Miyoshi and Matsui⁹ successfully used the reaction to produce the HOCO radical by a photoionization mass spectrometry in gas phase. More recently, Li and coworkers¹⁰ studied rate constants for the gas-phase reactions of Cl atoms with HCOOH and with HOCO radicals using absolute and relative rate techniques, and thought that the channel (1) is the dominant mechanism. For understanding the detailed mechanisms of the experimental reaction of Cl and HCOOH, an *ab initio* molecular orbital calculation has been performed for predicting the particular schematic potential energy surface (PES).

Computational methods

The geometries of the reactants, products, intermediates and transition states were optimized using the second-order Moller-Plesset perturbation (UMP2) method^{11,12} with 6-311+G(d, p) basis set. Vibrational frequencies, calculated at UMP2(full)/6-311+G(d, p) level of theory, were used for the characterization of stationary points. Zero-point vibrational energy (ZPVE) correction was gained at UMP2(full)/6-311+G(d, p) level of theory. All the stationary points were positively identified for minimum (number of imaginary frequen-

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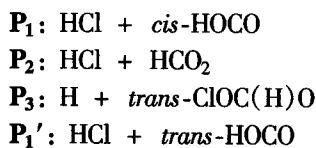
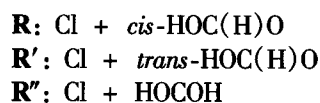
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cies $N = 0$) or transition state ($N = 1$). The geometries of the reactants, products, intermediates and transition states at UMP2(full)/6-311 + G(d,p) level of theory were used for calculating single-point energies using configuration interaction method [UQCISD(T,full)]^{13,14} with 6-311 ++ G(3df,2p) basis set. All the energies quoted and discussed in the present article are at UQCISD(T,full)/6-311 ++ G(3df,2p)//UMP2(full)/6-311 + G(d,p) level of theory with ZPVE correction, except that stated otherwise. In order to confirm whether the obtained transition states connect the right reactants and products, the intrinsic reaction coordinate (IRC) calculations^{15,16} were carried out at the UMP2(full)/6-311 + G(d,p) level of theory. All calculations are carried out using the GAUSSIAN98 package¹⁷ running on the SGI/O-
rigin300 Server.

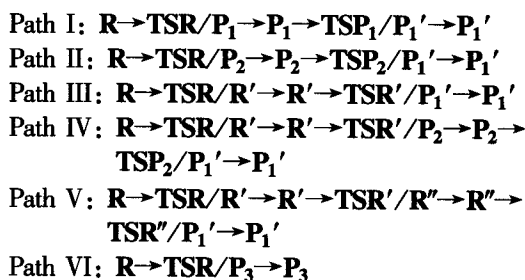
Results and discussion

The geometries of the reactants, products, intermediates and transition states on the potential energy surface (PES) of Cl + HCOOH system are found at UMP2(full)/6-311 + G(d,p) level. These structures are displayed in Figs. 1 and 2, while their total energies, single-point energies and zero-point energies are listed in Table 1. Furthermore, a schematic potential energy surface (PES) of Cl + HCOOH system is shown in Fig. 3. Starting from the reactant **R** (Cl + *cis*-HOC(H)O), several possible channels are considered in this paper. These reactants and products are as follows:



Reaction channels

From the original reactants **R**, five reaction channels are found on the PES. These reaction channels are as follows:



The Path I includes two transition states, **TSR/P**₁ and **TSP**₁/**P**_{1'}. First, we consider the process **R** → **P**₁. The IRC computations indicate that it is a reaction process by abstraction of the *C*-site hydrogen atom from *cis*-HOC(H)O molecule by Cl atom with a 3.73 kJ/mol reaction barrier height. If the *C*-site H atom is abstracted by Cl atom, *cis*-HOCO and HCl molecules are formed. The next process is from **P**₁ to **P**_{1'}, which leads to the formation of *trans*-HOCO molecule from *cis*-HOCO molecule. The *cis-trans* isomerization barrier is 96.51 kJ/mol. The calculated results show that *trans*-HOCO molecule is lower in energy than *cis*-HOCO molecule by 7.16 kJ/mol. This is in agreement with the previous experimental and theoretical results.^{6,9}

Table 1 Calculated total energies (a. u.), single-point energies (a. u.) and zero-point energies (kJ/mol) of reactants, products, intermediates and transition states in the reaction of Cl atom with formic acid

Species	UMP2(full)/6-311 + G(d,p)	UQCISD(T,full)/6-311 ++ G(3df,2p)	ZPVE
<i>cis</i> -HOC(H)O	-189.418751	-189.573293	89.85
<i>trans</i> -HOC(H)O	-189.411350	-189.566543	88.80
HOCOH	-189.348594	-189.506392	89.63
<i>trans</i> -CIOC(H)O	-648.435401	-649.199754	61.42
<i>trans</i> -HOCO	-188.759328	-188.909190	55.71
<i>cis</i> -HOCO	-188.755701	-188.906220	55.04
HCO ₂	-188.724457	-188.882373	52.27
H	-0.499810	-0.499810	0.00
HCl	-460.294207	-460.420483	18.46
Cl	-459.635377	-459.754901	0.00
TSR/P ₃	-648.905883	-649.198659	65.92
TSR''/P _{1'}	-649.002853	-649.245766	79.00
TSR/P ₁	-649.040549	-649.320420	73.16
TSR/P ₂	-649.001925	-649.292047	62.82
TSR'/R'	-189.291152	-189.445545	72.78
TSR/R'	-189.397715	-189.552881	84.28
TSP ₁ / P _{1'}	-188.742685	-188.868067	51.32
TSP ₁ / P ₂	-188.695240	-188.848254	39.45
TSR'/P ₂	-649.014692	-649.301526	61.36
TSR'/P _{1'}	-649.041442	-649.314215	80.70

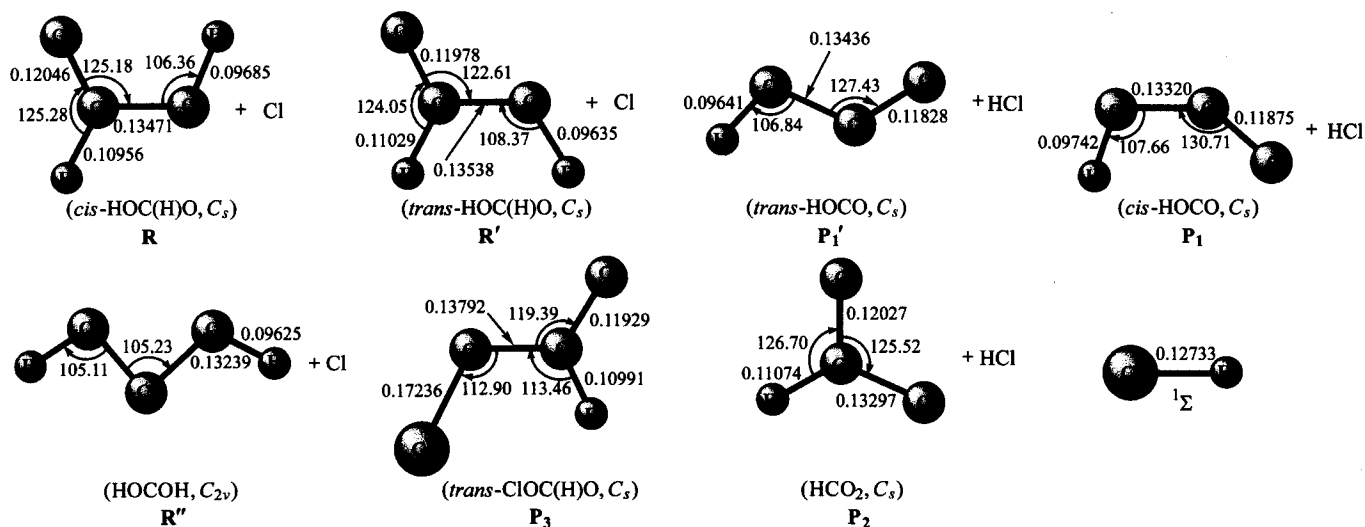


Fig. 1 Predicted geometries of reactants, products and intermediates at UMP2(full)/6-311 + G(d,p) level (Bond lengths are in nanometers and bond angles in degrees).

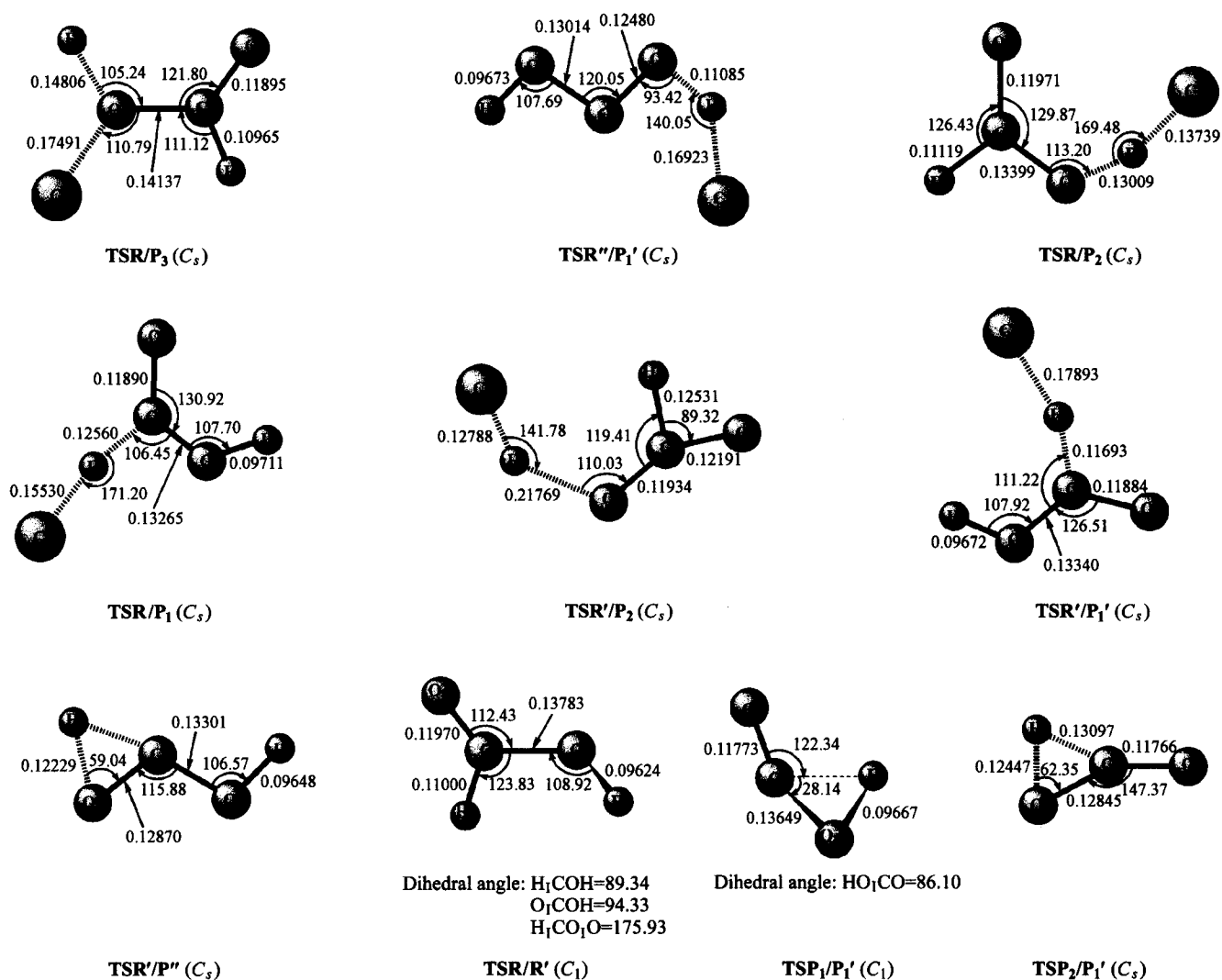


Fig. 2 Predicted structures of transition states at UMP2(full)/6-311 + G(d,p) level (Bond lengths are in nanometers and bond angles in degrees).

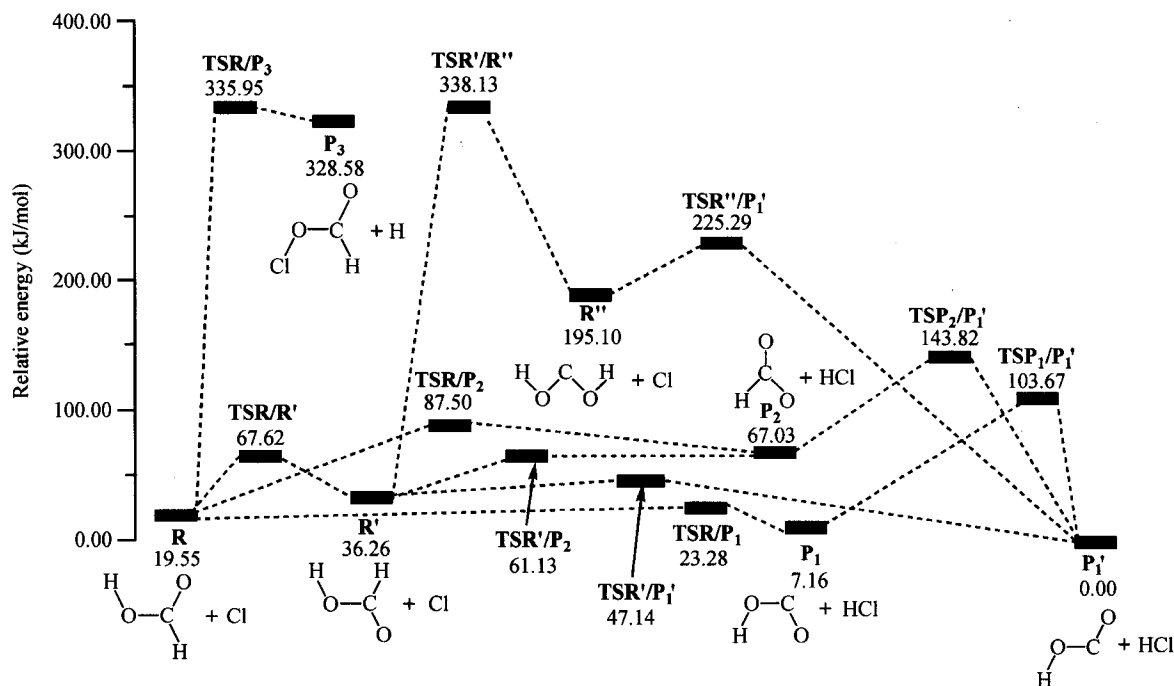


Fig. 3 A schematic potential energy surface of reaction of Cl atom with HCOOH at UQCISD(T, full)/6-311 ++ G(3df, 2p)//UMP2(full)/6-311 + G(d, p) level with zero-point energy correction.

The Path II includes two transition states, **TSR/P₂** and **TSP₂/P₁'**, which connect actually two reaction channel processes, from *cis*-HOC(H)O to HCO₂ and from HCO₂ to *trans*-HOCO. From the form of transition state **TSR/P₂**, it can be easily known that it is a reaction channel by abstraction of the *O*-site hydrogen atom from *cis*-HOC(H)O molecule by Cl atom and leads to the formation of HCO₂ and HCl molecules. One of products in first step is HCO₂ radical, which is higher in energy than *cis*-HOCO and *trans*-HOCO by 59.87 and 67.03 kJ/mol, respectively. **TSP₂/P₁'** is a transition state that connects actually HCO₂ with *trans*-HOCO by a 76.79 kJ/mol reaction barrier height. The isomerization is a typical hydrogen shift reaction from C atom to O atom.

The Path III includes two steps. One is from *cis*-HOC(H)O molecule to *trans*-HOC(H)O molecule via transition state **TSR/R'** by a 48.07 kJ/mol reaction barrier height, and another reaction process happens via transition state **TSR'/P₁'** that connects actually Cl + *trans*-HOC(H)O (**R'**) with HCl + *trans*-HOCO (**P₁'**) by a 10.88 kJ/mol barrier height. The *cis*-HOC(H)O is slightly lower in energy than *trans*-HOC(H)O by 16.71 kJ/mol.

The Path IV includes three reaction processes via three transition states, **TSR/R'**, **TSR'/P₂** and **TSP₂/P₁'**. **TSR/R'** has been discussed in Path III. The IRC computations indicate that the reaction process via **TSR'/P₂** is associated with abstraction of the *C*-site hydrogen atom from *cis*-HOC(H)O molecule by Cl atom. If the *O*-site H atom is abstracted by the Cl atom, HCO₂ and HCl molecules will form. **TSR'/P₂** is higher in energy than **R'** by 24.87 kJ/mol. The next step following the formation of HCO₂ molecule in Path IV

is from HCO₂ molecule to *trans*-HOCO molecule via transition state **TSP₂/P₁'** with a 76.79 kJ/mol reaction barrier height, which has been previously described in Path II.

The Path V includes three transition states. The first transition state **TSR/R'** which connects *cis*-HOC(H)O with *trans*-HOC(H)O molecule has been previously described in Path III and Path IV. The second transition states **TSR'/R''** connects *trans*-HOC(H)O molecule with HOCOH, an isomer of formic acid. The isomer which has *C_{2v}* symmetry and ¹A₁ electronic state is higher in energy than *cis*-HOC(H)O and *trans*-HOC(H)O by 175.55 and 158.84 kJ/mol, respectively. The barrier height of hydrogen atom shift process from C atom to O atom via transition state **TSR'/R''** is 301.87 kJ/mol. The next process is hydrogen atom abstraction from HOCOH molecule by Cl atom via the third transition state **TSR''/P₁'**, which is slightly higher in energy than **R''** by 30.19 kJ/mol.

Furthermore, we also found a reaction pathway (Path VI) on the PES which is H atom loss from original reactant *cis*-HOC(H)O by Cl atom attack via a transition state **TSR/P₃**, which is higher in energy than **R** by 316.40 kJ/mol. This will lead to the formation of *trans*-ClOC(H)O, which is an isomer of chloroformic acid [*trans*-ClC(O)OH].

Reaction mechanism

By experiments and other reference data, Li and coworkers¹⁰ thought that the reaction of Cl atom with HCOOH has two possible channels, (1) or (2). Channel (1) that produces HCl + HOCO radicals is the dominant mechanism for the reaction, and the other pathway that produces HCl +