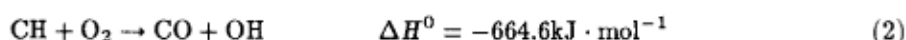[通 讯]

Ab initio Study on the Reaction of CH Radical with O_2*

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The reaction of the methylidyne radical $CH(X^2\Pi)$ with the oxygen molecule($X^3\sum_g^-$) is well known to be of great importance in combustion chemistry. Experiments[1] have suggested that the reaction has two main channels:

$$CH + O_2 \rightarrow CO_2 + H \qquad \Delta H^0 = -758.1 kJ \cdot mol^{-1} \qquad (1)$$

$$CH + O_2 \rightarrow CO + OH \qquad \Delta H^0 = -664.6 kJ \cdot mol^{-1} \qquad (2)$$

The purpose of the present study is to give theoretical descriptions of the mechanisms for the reactions (1) and (2). In the literature no theoretical work directly on the $CH + O_2$ reactions has been reported except some preliminary calculations on the reaction(1) presented in an experimental paper of Okada et al.[2].

The mechanisms of the $CH + O_2$ reactions are complicated compared with those of many other radical reactions since the first excited state $^1\Delta_g$ of O_2 is involved (see below). We would first present our analyses for the general situation based on the symmetry considerations similar to those presented in a theoretical study of Walch[3] for the $CH_3 + O_2$ reactions. The $CH + O_2$ reaction system is considered to have a symmetry plane containing all the four atoms (this has been confirmed in our calculations). The lowest $^2A''$ potential energy surface of $CH + O_2$ corrleates with O_2 in the $X^3\sum_g^-$ state and the lowest $^2A'$ surface with O_2 in the $^1\Delta_g$ state. The final products of reaction (1) are apparently of the $^2A'$ symmetry. Reaction (2) is analogous to the $CH_3 + O_2 \longrightarrow CH_2O + OH$ reaction studied in ref.[3], and the final products (CO + OH) are also related to the $^2A'$ surface[3]. It is expected that the surface crossing occurs along the reaction paths from the original reactants ($CH + O_2(X^3\sum_g^-)$, in the $^2A''$ surface) to the final products (in the $^2A'$ surface) of the two reactions.

Our calculations were performed at the (U)MP2/6-31G** level with the GAUSSIAN 92 program package[4]. Figure 1 shows a schematic diagram of the calculated reaction paths for reactions (1) and (2). The intermediates and transition states along the paths are denoted as IMn (n=1-4) and TSn (n=1-5), respectively, and the values in the parentheses are the relative energies in kJ·mol^{-1} with respect to CH + O$_2(X^3\sum_g^-)$. The optimized geometries for IMn and TSn (except TS2) are given in Fig.2.

As shown in Fig.1, the $^2A'$ path branches at IM3 and splits up into two paths, one leading to CO$_2$ + H and the other to CO + OH. The $^2A''$ path, starting from the original reactants, "crosses" the $^2A'$ path in the region between IM2 and TS2. The right portion of the $^2A''$ path to the crossing region is not interesting for the present study. The occurrence of reactions (1) and (2) requires a surface hopping from the $^2A''$ to $^2A'$ surface. The mechanisms of reactions (1) and (2) are therefore described by the following scheme (see Fig.1):
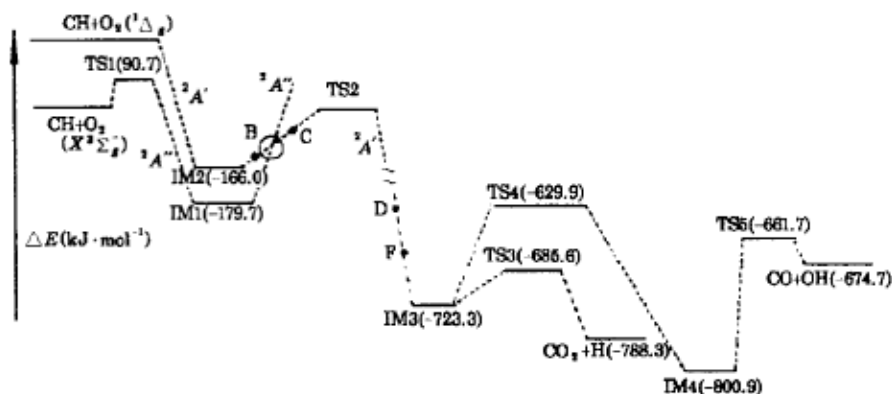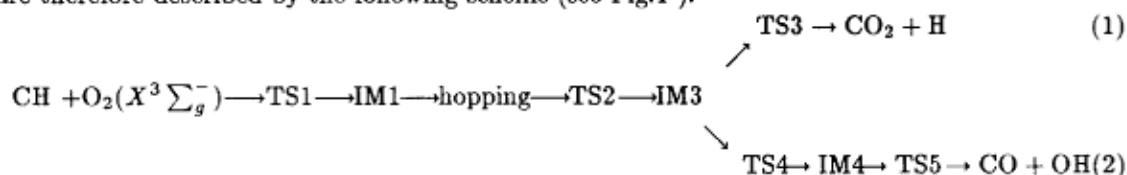
$$
\text{CH} + O_2(X^3\textstyle\sum_g^-) \longrightarrow \text{TS1} \longrightarrow \text{IM1} \longrightarrow \text{hopping} \longrightarrow \text{TS2} \longrightarrow \text{IM3} \Big\langle
\begin{array}{l} \text{TS3} \to \text{CO}_2 + \text{H} \qquad (1) \\[4pt] \text{TS4} \to \text{IM4} \to \text{TS5} \to \text{CO} + \text{OH} (2) \end{array}
$$

Fig.1 A schematic diagram of the UMP2/6-31G** potential energy curves for the CH + O$_2$ reaction (Values in the parentheses are the relative energies in kJ·mol^{-1})

In the following we would present the detailed results first for the right portion of the above scheme to IM3, and then for the left portion.

The relative energies of all the stationary points appearing after IM3 in the scheme are very large values with negative signs (see Fig.1). The geometry evolution from IM3 to CO$_2$ + H via TS3 indicates that the H-atom is leaving and the O-C-O part is becoming linear and symmetric. The final products CO$_2$ + H of reaction (1) are predicted to be 788.3kJ·mol^{-1} more stable than the original reactants, and this value is comparable with the experimental value of 769.0 kJ·mol^{-1} for the heat of reaction(1)[1]. Between IM3 and CO + OH along the other branch path (see Fig.1 or the above scheme), there are two transition states and one intermediate. The geometry evolution

from IM3 to IM4 via TS4 indicates a migration of the H-atom from the C-atom to one of the two O-atoms, and the rest part of this branch path describes the dissociation of IM4 into CO + OH. The final products of reaction (2) are predicted to be $674.7 kJ \cdot mol^{-1}$ more stable than the original reactants, and the value is close to the experimental value of $664.6 kJ \cdot mol^{-1}$ for the heat of reaction $(2)^{[1]}$.
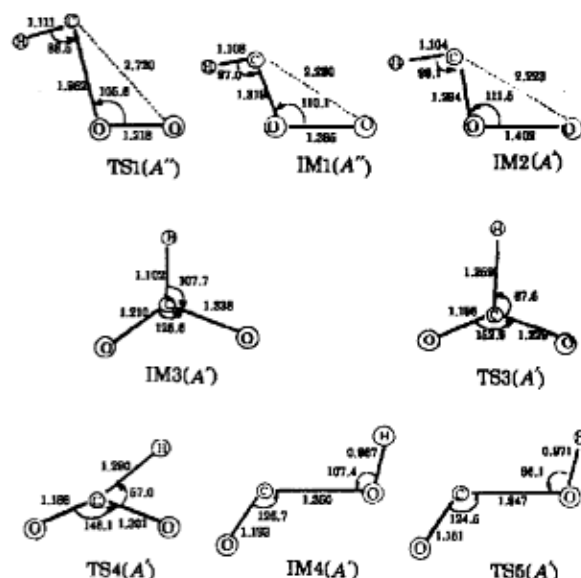

Fig.2 UMP2/6-31G** optimized geometries of the intermediates and transition states appearing in Fig.1. (bond distance in Å and angles in degrees)

The skeletons of the left portions of the curves (from CH + $O_2(X^3\sum_g^-$ and $^1\Delta_g$)to IM3) shown in Fig.1 are quite similar to the curves, describing the $CH_3 + O_2 \longrightarrow CH_2O + OH$ reaction, shown in Fig.2 of reference[3]. The adducts IM1 and IM2 are formed from CH + $O_2(X^3\sum_g^-)$(via TS1) and CH + O_2 $(^1\Delta_g$) in the $^2A''$ and $^2A'$ surfaces, respectively. The IM2-IM3 part of the $^2A'$ path curve was investigated by performing partial geometry-optimization calculations at a set of the fixed values (1.5Å(B), 1.4Å(C), 1.0Å(D), and 0.8Å(F), see Fig.1) of the parameter Z (the distance between the C-atom and the midpoint of the O-O distance). The parameters in partially optimized geometries change monotonously with the Z-value, but the change in energy is not monotonous ($E(B) < E(C)$ and $E(D) > E(F)$). These facts indicate that a transition state (TS2) exists after the adduct IM2 (between the points C and D) along the $^2A'$ path as in the case of $CH_3 + O_2 \longrightarrow CH_2O + OH$ reaction (see Fig.2 of ref.3). At the present stage we can not give the geometry and relative energy for TS2. The $^2A''$ path proceeds beneath the $^2A'$ path until it comes to the crossing region. The energy of the $^2A''$ state obtained in the single-point calculation at the geometry associated with the point C along the $^2A'$ path is higher than the energy of the $^2A'$ state, which indicates that the crossing of the $^2A''$ and $^2A'$ surfaces occurs in a region between

IM2 and TS2 along the $^2A'$ path (before the point C). At the crossing region the coupling of the two states leads to a hopping of the reaction system.

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CH 自由基与 O₂ 反应的从头算研究

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摘要　采用量子化学从头算法（UMP2/6-31G** 水平), 从理论上研究了 CH + O₂ 反应的两个主要通道. 根据计算所得的反应诸途径（连接反应物 CH + O₂ ($X^3\textstyle\sum_g^-$) 及两个通道的最终产物）讨论了复杂的反应机理. 发现反应过程涉及 O₂ 的第一激发态 $^1\Delta_g$, 且沿反应途径有势能面相交, 反应途径中包括多个中间体及过渡态.

关键词：从头算,　　CH 自由基,　　反应机理