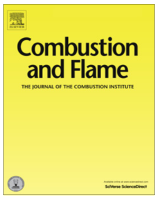
Combustion and Flame 161 (2014) 885–897

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame



Reaction of ketenyl radical with hydroxyl radical over $C_2H_2O_2$ potential energy surface: A theoretical study

Shao-Zhuan Xiong [a], Qian Yao [b], Ze-Rong Li [b,*], Xiang-Yuan Li [a,*]

[a] College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China
[b] College of Chemistry, Sichuan University, Chengdu 610064, PR China

ARTICLE INFO

Article history:
Received 21 June 2013
Received in revised form 22 September 2013
Accepted 15 October 2013
Available online 7 November 2013

Keywords:
Hydroxyketene
Master equation
Rate constant
Product branching ratio

ABSTRACT

The potential energy surface of $C_2H_2O_2$ for HCCO + OH bimolecular reactions and the unimolecular decomposition of hydroxyketene (HOCH=C=O) are investigated employing high-level quantum chemical methods. Variable reaction coordinate transition state theory is used for the high-pressure limit rate constant calculation of the main reaction channels and RRKM-based multiwell master equation is used to calculate the pressure dependent rate constants and product branching ratios of these channels. The predicted rate constants are in good agreement with the limited experimental data available in the literature. The product distribution analysis shows that the association/decomposition of HCCO + OH to the formation of CO + ^{1}HCOH and CO + ^{3}HCOH channels are dominant in the whole temperature range of 500–2000 K below 1 atm, whereas at higher pressure and low temperature, the association reaction producing ^{3}CHCOOH becomes competitive. For the unimolecular decomposition of hydroxyketene, the formation of CO + ^{1}HCOH channel is found to be predominant over a wide range of temperatures and pressures. Rate constants of these reactions and thermodynamic parameters for species involved in these reactions are also provided.

1. Introduction

HCCO is a critical intermediate in the oxidation of all C2 hydrocarbons [1–4] and combustion of several commonly used hydrocarbons involves the HCCO radical. In practical combustion process, reaction $C_2H_2 + O \rightarrow HCCO + H$ is the most important reaction for removal of acetylene in the combustion cycle [3] and in hydrocarbon flames, the majority (nearly 80%) of C_2H_2 molecule is oxidized via the HCCO intermediate [4–6]. Because of its importance in hydrocarbon combustion, there is a strong incentive for kinetic studying of HCCO related reactions. Numerous kinetic studies of HCCO with H [7,8], H_2 [9], O [10,11], O_2 [12–14], NO [15–20], NO_2 [9,14,21,22], SO_2 [23], CH [24], C_2H_2 [14,25], have been reported experimentally or theoretically.

Hydroxyl radical (OH) is one of the most important radical and is the most reactive oxidizing species in the combustion of hydrocarbons [26], hence its reaction with HCCO may be important and Konnov and De Ruyck [27] identified that the HCCO + OH reaction is one important reaction requiring further study. However, this reaction has received little attention in theoretical or experimental study in the literature. The relative significance of these channels for HCCO radical consumption has several important consequences, as the reactions associated with HCCO radical play an important role not only in the combustion of acetylene itself [28], but also for many other fuels since acetylene is an important intermediate in the combustion of methane, larger aliphatic hydrocarbons, and aromatics [29,30]. Accurate measurements or high-level quantum chemistry calculations of these rate constants are urgently needed to develop and refine core mechanisms of combustion chemistry.

In the recombination reaction of two radicals, chemical energy is released and a highly vibrationally excited (HVE) product may be formed and this HVE molecule is capable of further decomposition, isomerization, or collisional stabilization [31,32]. In this study, the recombination reaction of HCCO radical with OH radical is studied and the reaction channels considered are as follows:

$$HCCO + OH \rightarrow HOCH{=}C{=}O^{*}(+M) \xrightarrow{k_{1a}} HOCH{=}C{=}O \qquad (1a)$$

$$\rightarrow HOCH{=}C{=}O^{*} \xrightarrow{k_{2a}} CO + {}^{1}HCOH \qquad (2a)$$

$$\rightarrow HOCH{=}C{=}O^{*} \xrightarrow{k_{3a}} CO + H_2CO \qquad (3a)$$

$$\rightarrow HOCH{=}C{=}O^{*} \xrightarrow{k_{4a}} H + OCHCO \qquad (4a)$$

$$\rightarrow HOCH{=}C{=}O^{*} \xrightarrow{k_{5a}} H + HOCCO \qquad (5a)$$

---

* Corresponding authors. Fax: +86 028 85407797.
E-mail addresses: lizerong@scu.edu.cn (Z.-R. Li), xyli@scu.edu.cn (X.-Y. Li).

0010-2180/$ - see front matter © 2013 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.combustflame.2013.10.013

$$\rightarrow \mathrm{HOCH{=}C{=}O^*} \xrightarrow{k_{6a}} \mathrm{H_2O} + {}^1\mathrm{C_2O} \tag{6a}$$

$$\rightarrow \mathrm{HOCH{=}C{=}O^*} \xrightarrow{k_{7a}} \mathrm{CHO} + \mathrm{CHO} \tag{7a}$$

$$\rightarrow \mathrm{HOCH{=}C{=}O^*} \xrightarrow{k_{8a}} \mathrm{H_2} + 2\mathrm{CO} \tag{8a}$$

where $HOCH{=}C{=}O^*$ represents a highly vibrationally excited state of $HOCH{=}C{=}O$ intermediate, which can be stabilized by collisions with a third body M, as well as isomerization of the intermediate to trans-glyoxal and $HC{\equiv}COOH$ and subsequent decomposition to the bimolecular products.

On the singlet potential energy surface (PES), the reaction may also take place by OH attacking on the CO group at the carbon atom giving ^1CHCOOH which can produce $CO + CH_2O$.

$$\mathrm{HCCO} + \mathrm{OH} \rightarrow {}^1\mathrm{CHCOOH^*}(+\mathrm{M}) \xrightarrow{k_{9a}} {}^1\mathrm{CHCOOH} \tag{9a}$$

$$\rightarrow {}^1\mathrm{CHCOOH^*} \xrightarrow{k_{10a}} \mathrm{CO} + \mathrm{H_2CO} \tag{10a}$$

On the triplet PES, electrophilic addition of OH to HCCO producing $CO_2 + {}^3CH_2$ and $CO + {}^3HCOH$ via ^3CHCOOH and HOHCCO-T, respectively, are also explored.

$$\mathrm{HCCO} + \mathrm{OH} \rightarrow {}^3\mathrm{CHCOOH^*}(+\mathrm{M}) \xrightarrow{k_{11a}} {}^3\mathrm{CHCOOH} \tag{11a}$$

$$\rightarrow {}^3\mathrm{CHCOOH^*} \xrightarrow{k_{12a}} \mathrm{CO_2} + {}^3\mathrm{CH_2} \tag{12a}$$

$$\rightarrow {}^3\mathrm{CHCOOH^*} \xrightarrow{k_{13a}} {}^3\mathrm{C_2O} + \mathrm{H_2O} \tag{13a}$$

$$\rightarrow {}^3\mathrm{CHCOOH^*} \xrightarrow{k_{14a}} \mathrm{CH_2CO} + {}^3\mathrm{O} \tag{14a}$$

$$\mathrm{HCCO} + \mathrm{OH} \rightarrow \mathrm{HOHCCO\text{-}T^*}(+\mathrm{M}) \xrightarrow{k_{15a}} \mathrm{HOHCCO\text{-}T} \tag{15a}$$

$$\rightarrow \mathrm{HOHCCO\text{-}T^*} \xrightarrow{k_{16a}} \mathrm{CO} + {}^3\mathrm{HCOH} \tag{16a}$$

At elevated temperatures, the abstraction reactions on the triplet potential energy surface are also possible:

$$\mathrm{HCCO} + \mathrm{OH} \xrightarrow{k_{17a}} \mathrm{HC{\equiv}COH} + {}^3\mathrm{O} \tag{17a}$$

$$\xrightarrow{k_{18a}} \mathrm{CH_2CO} + {}^3\mathrm{O} \tag{18a}$$

$$\xrightarrow{k_{19a}} \mathrm{H_2O} + {}^3\mathrm{C_2O} \tag{19a}$$

Although these reactions may be important in the detailed modeling of the combustion of hydrocarbons, however, only a few of them appeared in popular combustion mechanisms [33–42]. And the rate constants in different mechanisms may have large differences, see Table 1. Miller et al. [33] estimated the reverse rate constant of the reaction (17a), which has been adopted by Glarborg et al. [34] for a modeling study of ethylene oxidation. For the reverse of reaction of the reaction (18a), Miller et al. reported the rate constant as $1.66 \times 10^{-11} \times \exp(-8000\ \mathrm{cal\ mol^{-1}}/RT)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ [35] and adjusted it to $3.32 \times 10^{-17} \times T^{2.00} \times \exp(-10{,}000\ \mathrm{cal\ mol^{-1}}/RT)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ [33]. Several groups either directly adopted these kinetic data [36–38] or derived a new rate constant expression based on these rate constants [39,40] in the construction of combustion mechanism of hydrocarbons. Moreover, Curran et al. [37] obtained the forward rate constant of the reaction (18a) using the reverse rate constant and the equilibrium constant derived from the thermochemical data. Similarly, Miller et al. [35] also reported a rate constant value of $4.98 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ for reaction (19a). This rate constant value was directly used in USC_Mech_II mechanism [41] and was doubled in the combustion mechanism of Miller et al. [33] and was tripled in Zeuch mechanism [42]. Consequently, controversy still exists for the rate constants of these reactions.

The possible thermal decomposition channels of hydroxyketene ($HOCH{=}C{=}O$), the stabilized product of the HVE molecule $HOCH{=}C{=}O^*$ in reaction (1a), are also explored in this study. However, to the best of our knowledge, experimental or theoretical study of the decomposition of $HOCH{=}C{=}O$ is missing. In contrast, much attention has been paid to the decomposition of its isomerization product glyoxal $(CHO)_2$ [43–46]. Saito et al. [43] investigated the unimolecular decomposition of glyoxal in temperatures range 1100–1540 K behind reflected shock waves and the $H_2 + 2CO$ production was found to be the main product channel, and the high-pressure limit rate constant was determined to be $1.07 \times 10^{14} \times \exp(-55{,}100\ \mathrm{cal\ mol^{-1}}/RT)\ \mathrm{s^{-1}}$. Experimentally and theoretically, Friedrichs and co-operators [45] studied the temperature and density dependences of the unimolecular glyoxal decomposition, and gave the sum of the rate constants of multi-channels as well as individual rate constant of the CHO-forming channel. Koch et al. [46] explored the potential energy surface of glyoxal dissociation by means of G3 methodology. They further discussed the decomposition of hydroxymethylene, but did not consider the CHO-forming channel and kinetics for all reaction channels. All these reaction channels are explored in this study.

Recently, there has been considerable progress in the methodology for accurate rate constant calculations for barrierless radical–radical association reactions [47–50] and for complicated

Table 1
Summary of kinetic data ($k(T) = AT^n \exp(-E/RT)$) available for OH + HCCO abstraction reaction in some popular reaction mechanisms.

Source	*A*	*n*	*E*
HCCO + OH → $HC{\equiv}COH + {}^3O$			
Miller et al. [33], Glarborg et al. [34], REV/	3.32×10^{-17}	3.00	1900
HCCO + OH → $CH_2CO + {}^3O$			
Miller et al. [35], GRI3.0 [36], Curran et al. [37] and Daugaut et al. [38], REV/	1.66×10^{-11}	0.00	8000
Miller [33], Glarborg et al. [34], REV/ (estimate)	3.32×10^{-17}	2.00	10,000
Sandiego2011 [39], REV/	1.66×10^{-11}	0.00	2000
Ranzi et al. [40], REV/	2.24×10^{-16}	2.00	8782
Curran et al. [37],	6.18×10^{-15}	0.45	3108
HCCO + OH → ${}^3C_2O + H_2O$			
USC_Mech_II [41], Miller et al. [35]	4.98×10^{-11}	0.00	0
Miller et al. [33]	9.96×10^{-11}	0.00	0
Zeuch et al. [42]	1.50×10^{-10}	0.00	0

Units are molecule, cm^3, s^{-1}, K and cal. REV/ denotes reverse reaction.