



Acetaldehyde oxidation at low and intermediate temperatures: An experimental and kinetic modeling investigation

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ABSTRACT

Acetaldehyde oxidation was investigated in a jet-stirred reactor at temperatures from 460 to 900 K, equivalence ratios from 0.5 to 4.0 and pressures of 710–720 Torr. Reactive intermediates under low-temperature conditions, such as methylperoxy, methylhydroperoxide and ketohydroperoxide were detected using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). A kinetic model for acetaldehyde oxidation was constructed by incorporating recent theoretical and modeling progress of acetaldehyde kinetics, as well as the calculated results of H-atom abstraction reactions of acetaldehyde by acetylperoxy, methylperoxy and methoxy in this work. The present model was then comprehensively validated against the measurements in this work and the experimental data from literature. Modeling analysis reveals that the main chain-branching pathways of acetaldehyde under low-temperature oxidation conditions are the decomposition of acetylhydroperoxide and methylhydroperoxide. The second O₂-addition process was verified to exist in the low-temperature oxidation of acetaldehyde as ketohydroperoxide was observed, while its contribution to the overall reactivity was found to be minor under present investigated conditions. On the other hand, the sub-mechanism of acetylperoxy is crucial in the low-temperature regime while the methyl oxidation mechanism dominates in the negative temperature coefficient (NTC) region at all equivalence ratios investigated in this work.

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1. Introduction

Acetaldehyde (CH₃CHO) is one of the toxic pollutants that can cause allergies, liver diseases and carcinogen risks [1]. It can be produced from combustion process [2,3] since it is a typical combustion intermediate/product of fossil fuels and biofuels (especially alcohols). Understanding the combustion chemistry of acetaldehyde is not only needed for emission reduction, but also critical in the development of kinetic models for hydrocarbon fuels and biofuels. Besides, the extraordinarily weak C–C bond in acetyl (CH₃CO) (~10 kcal/mol [4]) makes it readily decompose to methyl (CH₃) and CO, implying a strong relationship between the acetaldehyde chemistry and the methyl chemistry.

The previous studies of the high-temperature chemistry of acetaldehyde before 2015 were reviewed in detail by Christensen et al. [5], and thus only recent progress is briefly summarized herein. Sivaramakrishnan et al. [6] performed theoretical calculations of the C₂H₄O and C₂H₅O potential energy surfaces (PES) and updated the pyrolysis model of acetaldehyde. Mével et al. [7] measured ignition delay times of acetaldehyde in a shock tube at 1295–1580 K and 306–404 kPa. Tao et al. [8] investigated the laminar premixed flames of acetaldehyde and identified about 40 flame species. Christensen et al. [5] measured the laminar burning velocities of acetaldehyde/air mixture at atmospheric pressure and various initial temperatures. Furthermore, Christensen and Konnov [9] recently measured the laminar burning velocities of diacetyl and updated the sub-mechanisms of acetaldehyde and CH₃CO in their model.

The low-temperature combustion studies of acetaldehyde can date back to 1882 when its beautiful bluish flame (so-called cool flame) was observed by Perkin [10]. However, there are still few experimental investigations on the low-temperature oxidation of acetaldehyde [11] to date. Gray et al. [12] investigated the

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ignition and cool flame behaviors of acetaldehyde using a continuous well stirred flow reactor. However, large uncertainties existed in the determination of the heat exchange coefficient, which caused a big influence on the simulation results [11,13]. Later, Kaiser et al. [14] investigated the acetaldehyde oxidation in a low-pressure static reactor at 553 and 713 K using molecular-beam mass spectrometry and gas chromatography. Besides the major species like CH_3CHO , CO and CO_2 , they observed the mass peaks of $m/z=48$ and 34 and directly attributed them to methyl hydroperoxide (CH_3OOH) and hydroperoxide (H_2O_2). It is recognized that mass spectrometric signals are susceptible to the isomeric structures, the ^{13}C and ^{18}O isotopomers of smaller species and the fragments of larger species. Therefore, more experimental evidences are needed to confirm the existence of these peroxides. Besides, because of the very rapid initial reaction rate, the concentrations of the products could not be reliably measured until approximately 50% of acetaldehyde was consumed and the initial consumption rate of acetaldehyde was uncertain. Recently, Barari et al. [15,16] qualitatively measured the intermediates in the acetaldehyde oxidation at 500–700 K using multiplexed photoionization mass spectrometry with synchrotron radiation. The chlorine atom produced by laser-pulsed photolysis can react with acetaldehyde to form the parent radicals. They observed ketene (CH_2CO) and methylperoxy (CH_3OO), but could not quantify all the measured species.

For the model development, Halstead et al. [17] proposed a 14-step mathematical model for acetaldehyde to interpret its cool-flame phenomenon. They considered acetyl played an exclusive role in the chain-branching process through $\text{CH}_3\text{CO} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{O} + \text{OH}$, which was supported by the theoretical work of Felton et al. [18] and the detailed kinetic modeling work of Cavanagh et al. [19]. However, Gibson et al. [20] concluded the cool flame phenomena of acetaldehyde originated from methyl oxidation and the degenerate branching via CH_3OOH ($\text{CH}_3 \rightarrow \text{CH}_3\text{OO} \rightarrow \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O} + \text{OH}$). In the studies of Kaiser et al. [14], they concluded the competition between the radical decomposition reaction ($\text{CH}_3\text{CO} = \text{CH}_3 + \text{CO}$) and the addition of O_2 to acetyl ($\text{CH}_3\text{CO} + \text{O}_2 = \text{CH}_3\text{C}(\text{O})\text{OO}$), is the key factor determining the dominant chain-branching pathway. Very recently, Pelucchi et al. [11,13] developed the low-temperature oxidation model for acetaldehyde as well as C3–C4 aldehydes and considered both aforementioned chain-branching pathways and validated their model against the previous experiment in a continuous well stirred flow reactor [12]. In summary, there are still inadequate investigations on the chemical structure measurements for the low-temperature oxidation of acetaldehyde, especially the unambiguous identification and quantification of some reactive key species. Besides, the chain-branching reactions which determine the low-temperature oxidation rate of acetaldehyde are still in debate.

This work has three main targets. Firstly, the species concentration information was provided for the acetaldehyde oxidation in a jet-stirred reactor (JSR) at temperatures from 460 to 900 K, equivalence ratios from 0.5 to 4.0 and 710–720 Torr. A variety of intermediates, especially reactive species, were identified and quantified by the synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Secondly, critical reactions in the low-temperature acetaldehyde oxidation were investigated, combining with the quantum chemical calculations for the H-atom abstraction reactions of acetaldehyde by $\text{CH}_3\text{C}(\text{O})\text{OO}$, CH_3OO and CH_3O due to the limited investigations in literature. Thirdly, a kinetic model of acetaldehyde was developed and validated against the present experimental data and those from literature over the temperatures of 400–2100 K, pressures of 0.02–10 atm and equivalence ratios between 0.09 and pyrolysis. Particularly, the chain-branching reactions of acetaldehyde under low-temperature conditions were discussed.

Table 1

Experimental conditions in the present work.

No.	ϕ	P (Torr)	Fuel%	$\text{O}_2\%$	Ar%
1	0.5	710	2	10	88
2	1.0	720	2	5	93
3	4.0	720	2	1.25	96.75

2. Experimental method

The experiments were conducted at the BL03U beamline of the National Synchrotron Radiation Laboratory. Introduction of this VUV undulator beamline can be found elsewhere [21]. The JSR used in this work has a similar design to our previous reactor [22] complying with the rules established by Matras and Villermaux [23]. The volume of the JSR is 100 cm^3 and a quartz sampling nozzle with a $\sim 70 \mu\text{m}$ orifice is welded into the sphere. Quartz wall effects are considered as negligible based on previous research [24]. A short annular preheating zone is attached to the reactor for preheating the inlet mixtures in a very short period of time (a few percent of the residence time) to achieve more reliable temperature homogeneity in the reactor [25]. Both the reactor and the preheating zone were heated by the heating jackets and controlled by the temperature-controlling units. The reaction temperature was measured by a K-type thermocouple located in the center of the reactor, which had a fluctuation within 2 K for each setting temperature during the experiments. The schematic diagram of the JSR can be found in the *Supplementary Materials*. No complex patterns, like oscillatory cool flames or multi-stage ignitions [20], were observed in this work.

Liquid acetaldehyde (purity 99.5% from Aladdin) was prepared in a stainless-steel vessel cooled by liquid N_2 . After pumping the vessel until there was no N_2 signal detected by the mass spectrometer, pure acetaldehyde vapor was generated by keeping the vessel at a constant temperature of 310 K using heated oil bath. The gas flow rates of acetaldehyde, O_2 and Ar were regulated by mass flow controllers. A three-meter-long stainless-steel pipe was used to connect the mass flow controllers and the reactor to ensure sufficient mixing of inlet gases. The total flow rate of the mixture was 0.5 SLM under all temperature conditions, thus the residence time varied from 3 to 6 seconds. The experimental conditions are summarized in Table 1 for three investigated mixtures with different equivalence ratios (0.5, 1.0 and 4.0).

In this work, the temperature scan was performed at the photon energies of 16.64, 11.7, 11.0 and 10.0 eV. Particularly, at 16.64 eV, cold gas experiments were performed for CO , CO_2 , H_2 and CH_4 . Methyl hydroperoxide and ethane were measured at 10 and 11.7 eV, respectively. Other species were measured at 11 eV. The identification and mole fraction evaluation of intermediates were based on previously reported methods [26]. The photoionization cross sections (PICSSs) were referred to our online database [27]. For major products (H_2 , CH_4 , CO , H_2O and CO_2), the uncertainties of measured mole fractions are estimated within $\pm 20\%$. For minor species, the uncertainties was $\pm 50\%$ for species with known PICSSs and a factor of 2 for CH_3OOH based on the calculated PICS from Moshhammer et al. [28] and for CH_3OO based on estimation.

3. Theoretical calculations

Rate constants of H-atom abstraction reactions of acetaldehyde by $\text{CH}_3\text{C}(\text{O})\text{OO}$, CH_3OO and CH_3O were calculated theoretically in this work (R15–R20). Note that the order of reactions in the main text is shown in Table S1 of the *Supplementary Materials* which lists the key reactions discussed in this work. R15–R18 can produce $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and CH_3OOH which are degenerate chain-branching triggers under low-temperature conditions

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