Exploring the negative temperature coefficient behavior of acetaldehyde based on detailed intermediate measurements in a jet-stirred reactor

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ABSTRACT

Acetaldehyde is an observed emission species and a key intermediate produced during the combustion and low-temperature oxidation of fossil and bio-derived fuels. Investigations into the low-temperature oxidation chemistry of acetaldehyde are essential to develop a better core mechanism and to better understand auto-ignition and cool flame phenomena. Here, the oxidation of acetaldehyde was studied at low-temperatures (528–946 K) in a jet-stirred reactor (JSR) with the corrected residence time of 2.7 s at 700 Torr. This work describes a detailed set of experimental results that capture the negative temperature coefficient (NTC) behavior in the low-temperature oxidation of acetaldehyde. The mole fractions of 28 species were measured as functions of the temperature by employing a vacuum ultra-violet photoionization molecular-beam mass spectrometer. To explain the observed NTC behavior, an updated mechanism was proposed, which well reproduces the concentration profiles of many observed peroxide intermediates. The kinetic analysis based on the updated mechanism reveals that the NTC behavior of acetaldehyde oxidation is caused by the competition between the O_2-addition to and the decomposition of the CH_3CO radical.

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1. Introduction

In recent decades, there has been an increasing interest in biofuels, which are considered to be CO_2 neutral in the long-term. With higher oxygen content than fossil fuels, the increased use of biofuels could reduce the amount of some pollutants like soot, while increasing emissions of other toxic species, like acids and aldehydes [1]. For example, acetaldehyde has been observed as an emission species produced during the combustion of biofuels, particularly for ethanol [2,3], and is a key intermediate in the low-temperature oxidation pathways of transportation fuels. An im-

proved kinetic understanding of acetaldehyde oxidation is therefore essential for developing comprehensive combustion mechanisms for practical fossil fuels and biofuels.

Low-temperature oxidation typically occurs from 500 to 900 K depending on the pressure and plays a vital role in the hot auto-ignition processes responsible for knock in spark ignition engines [4]. The low-temperature oxidation of acetaldehyde exhibits negative temperature coefficient (NTC) behavior leading to interesting phenomena like oscillatory combustion and cool flames [5,6]. Fundamental research characterizing the low-temperature oxidation of acetaldehyde will help validate the low-temperature performance of core chemical mechanisms, which are utilized to understand and prevent knock in compression ignition (CI) engines.

Relatively few experimental studies of the oxidation of acetaldehyde have been published. Flames fueled by acetaldehyde were investigated by three groups [7–9]. Oxidation and pyrolysis experiments of acetaldehyde were conducted in shock tubes (ST) by Kern et al. [10], Won et al. [11] and Yasunaga et al. [12]. The

concentrations of intermediates produced in the oxidation of acetaldehyde in a jet-stirred reactor (JSR) were measured by Dagaut et al. [13] using off-line gas chromatography (GC) in an intermediate temperature range from 950 K to 1250 K.

The above experiments were mainly conducted at temperatures near or above 1000 K, and experimental data regarding the low-temperature oxidation of acetaldehyde remains limited. To the best of our knowledge, there has been no detailed experimental investigation published yet with three experimental studies [14–16] describing the general character of the cool flame. Light emission and concentrations of several species were measured by Gray et al. [14] in a well-stirred reactor at low pressures (5–25 kPa) from 400 K to 620 K. A pressure-temperature ignition diagram delineating five different regimes was developed using the experimental results with three major phenomena described: oscillatory, cool flame, and steady oxidation with light emission. Kaiser et al. [15] carried out acetaldehyde oxidation experiments in a static and closed 1 L Pyrex reactor at two temperatures (553 K and 713 K). A nearly equal rate of fuel consumption at both temperatures was observed indicating the existence of a region of negative temperature dependence in the overall rate of acetaldehyde oxidation. More recently, low-temperature oxidation experiments were performed in a flow reactor by Barari et al. [16] at 550 and 700 K at a low pressure of 8 Torr. They focused on the identification of some intermediates, while quantitative information was not provided.

Generally, NTC behavior results from a balance between low-temperature oxidation pathways and competing alternative pathways. The details of this chemistry for alkane fuels are well understood. The high reactivity at low temperature can be explained by the formation and the decomposition of ketohydroperoxides [17,18]. After two O_2-addition steps and subsequent internal H-abstractions, the initial fuel radical (R) becomes an unstable radical OOQOOH which decomposes to an OH radical and a ketohydroperoxides (HOOQ$_{-H}$O) intermediate. The decomposition of the ketohydroperoxide (HOOQ$_{-H}$O) gives another OH radical and an OQ$_{-H}$O radical, as shown in Ref. [18]. In this scheme, one OH radical reacts with one fuel molecule and leads to the formation of three free radicals: two OH radicals and one OQ$_{-H}$O radical. This chain branching results in the acceleration of low-temperature oxidation. As the temperature increases, the equilibrium of the $R + O_2 = ROO$ reaction shifts to the left and the formation of ROO becomes disfavored. Under these conditions, HO_2 and alkenes are the major products of the $R + O_2$ reaction. The decomposition of QOOH, formed after one O_2 addition and one isomerization, also becomes more important compared to the second O_2-addition. Due to the formation of relatively stable intermediates like HO_2 and alkenes and the decrease in the production of ketohydroperoxides, the global rate of the oxidation decreases with increasing temperature.

This reaction scheme cannot necessarily explain the observed NTC behavior in acetaldehyde oxidation, as it is much harder to produce ketohydroperoxides from acetaldehyde than from alkanes. In a theoretical study of the $CH_3CO + O_2$ reaction, Maranzana et al. [19] concluded that only the first O_2-addition and internal H-abstraction readily occurred to form ROO (CH_3CO_3) and QOOH (CH_2CO_3H) radicals. The subsequent second O_2-addition was difficult to accomplish due to a high energy barrier and fast collisional deactivation, suggesting the production of negligible amounts of ketohydroperoxides.

Kaiser et al. [15] found experimentally that the NTC behavior of acetaldehyde was sensitive to the competition between the decomposition of and the O_2-addition to acetyl radical. Pelucchi et al. [20] agreed with this conclusion in their mechanism, which could reproduce the pressure-temperature ignition diagrams of Gray et al. [14]. Despite these successful characterizations, the detailed

chemistry of acetaldehyde remains untested, mainly due to the lack of detailed experimental information

The primary aim of this paper is to characterize the NTC behavior of acetaldehyde oxidation at a kinetic level by quantifying several important intermediates produced during the low-temperature oxidation in a jet-stirred reactor. To explain the NTC behavior, a mechanism was developed and validated against the present experimental results.

2. Experimental approach

2.1. Experimental details

The experiments were performed at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. Acetaldehyde was oxidized in a JSR connected via a molecular beam (MB) sampling system to a reflectron time-of-flight mass spectrometer (TOF-MS) which used the tunable synchrotron vacuum ultra-violet (SVUV) radiation as the source for photoionization (PI). Details of this setup can be found in Refs. [21,22], thus only a brief description is given here. The JSR, with the volume of about 33.5 cm^3, was embedded in an electrically heated oven. The gaseous compositions in the JSR were extracted from the exit of the reactor through a quartz nozzle with a ~50 μm diameter orifice on the tip. The pressure difference between the reactor (700 Torr) and the first stage pumping chamber (<0.001 Torr) forced the sampled gas to form a molecular beam, in which the further reactions among molecules were prevented. The "frozen" molecules were introduced into the ionization area via a skimmer and subsequently ionized and analyzed by the mass spectrometer. The high resolution (m/$\triangle$m ~3500) of the mass spectrometer makes it possible to distinguish those molecules with the same nominal mass but different chemical compositions (for example C_3H_4O and C_4H_8).

Temperatures were measured by a thermocouple (K-type, Thermocoax) which have been successfully employed in many flame experiments before. The uncertainty in the temperature measurement will be discussed in the next section. The experiments were performed at 31 different temperatures varying from 528 K to 946 K with a fixed pressure of 700 Torr. The flow rates of acetaldehyde, oxygen and argon were separately controlled by calibrated mass controllers to get a fixed residence time around 3 s at different temperatures. The equivalence ratio was kept at 0.5 with the dilution ratio of argon fixed at 85%. Detailed experimental conditions are presented in the *Supplemental material*. The mass spectra were collected at each temperature at several selected photoionization energies. In addition, energy-dependent mass spectra, which can be used to obtain mass-specific photoionization efficiency (PIE) curves, were obtained from 9.5 eV to 12.0 eV at 638 K to help with the species identification.

2.2. Data evaluation

Jet-stirred reactors have been used as a powerful apparatus to study low-temperature oxidation for decades [23]. Recently, this power was enhanced by its connection with SVUV-PI-MBMS [22,24,25]. The routines to convert the mass spectral signal into mole fractions are based on the methods described in Ref. [22], which have been slightly modified as described next.

The procdeure is based on the principle that the integrated signal $S_i(T)$ of a species i at a certain temperature T and photon energy E varies linearly with its concentration x_i, i.e., [26]

$$S_i(T) = C \cdot x_i \cdot \sigma_i(E) \cdot D_i \cdot \varphi(E) \cdot F(k, T, P) \tag{1}$$

where, C is a proportionality constant, $\sigma_i(E)$ is the photoionization cross-section (PICS) of species i at photon energy E, D_i is the