Combustion and Flame 156 (2009) 1181–1201

Contents lists available at ScienceDirect

Combustion and Flame

www.elsevier.com/locate/combustflame

Combustion chemistry of the propanol isomers — investigated by electron ionization and VUV-photoionization molecular-beam mass spectrometry

T. Kasper [a,b,*], P. Oßwald [a], U. Struckmeier [a], K. Kohse-Höinghaus [a], C.A. Taatjes [b], J. Wang [c], T.A. Cool [c], M.E. Law [d], A. Morel [d], P.R. Westmoreland [d]

[a] *Bielefeld University, Universitätsstr. 25, 33615 Bielefeld, Germany*
[b] *Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*
[c] *School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, USA*
[d] *Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA*

ARTICLE INFO

Article history:
Received 1 October 2008
Received in revised form 19 December 2008
Accepted 22 January 2009
Available online 2 March 2009

Keywords:
Propanol
Laminar flame
Molecular-beam mass spectrometry

ABSTRACT

The combustion of 1-propanol and 2-propanol was studied in low-pressure, premixed flat flames using two independent molecular-beam mass spectrometry (MBMS) techniques. For each alcohol, a set of three flames with different stoichiometries was measured, providing an extensive data base with in total twelve conditions. Profiles of stable and intermediate species, including several radicals, were measured as a function of height above the burner. The major-species mole fraction profiles in the 1-propanol flames and the 2-propanol flames of corresponding stoichiometry are nearly identical, and only small quantitative variations in the intermediate species pool could be detected. Differences between flames of the isomeric fuels are most pronounced for oxygenated intermediates that can be formed directly from the fuel during the oxidation process. The analysis of the species pool in the set of flames was greatly facilitated by using two complementary MBMS techniques. One apparatus employs electron ionization (EI) and the other uses VUV light for single-photon ionization (VUV-PI). The photoionization technique offers a much higher energy resolution than electron ionization and as a consequence, near-threshold photoionization-efficiency measurements provide selective detection of individual isomers. The EI data are recorded with a higher mass resolution than the PI spectra, thus enabling separation of mass overlaps of species with similar ionization energies that may be difficult to distinguish in the photoionization data. The quantitative agreement between the EI- and PI-datasets is good. In addition, the information in the EI- and PI-datasets is complementary, aiding in the assessment of the quality of individual burner profiles. The species profiles are supplemented by flame temperature profiles. The considerable experimental efforts to unambiguously assign intermediate species and to provide reliable quantitative concentrations are thought to be valuable for improving the mechanisms for higher alcohol combustion.

1. Introduction

The needs to control emissions from internal combustion engines, industrial manufacturing or power generation, and to address aspects of climate change have stimulated a growing interest in oxygenated fuels. Ethers, esters and alcohols are promising alternative fuels and fuel additives because they can reduce the formation of PAH and soot and improve ignition and combustion performance. In addition, the production of these oxygenated fuels from renewable sources like biomass can help to balance the emission of carbon dioxide, a major greenhouse gas, from combustion.

Owing to their practical relevance, investigations of the combustion characteristics of alcohols have focused mainly on methanol (e.g. [1–3]) and ethanol (e.g. [4–11]). Ethanol can serve as a fuel extender for petroleum-derived fuels, oxygenate, octane enhancer, and as a pure fuel [12], and it has been shown that the addition of ethanol to gasoline and diesel fuels leads to a reduction of NO_x and particulate emissions from practical engines. However, these studies also suggest an increase in aldehyde emissions [13–16].

Similarly, high concentrations of acetone are found in the exhaust gas of a spark ignition engine upon addition of 2-propanol to a synthetic fuel [17]. This observation emphasizes the fact that the production of oxygenated pollutants is a common feature of alcohol combustion that demands the characterization of the chemical processes involved in the oxidation of higher alcohols. To date, only few studies have addressed the combustion chemistry of propanol, butanol or other higher alcohols. This study is aimed at the investigation of the combustion chemistry of 1-propanol and 2-propanol.

---

* Corresponding author at: Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA.
E-mail address: tkasper@sandia.gov (T. Kasper).

0010-2180/$ – see front matter Published by Elsevier Inc. on behalf of The Combustion Institute.
doi:10.1016/j.combustflame.2009.01.023

Some experimental data on propanol oxidation are available from previous studies. Smith et al. report the flame structures of 1-propanol and 2-propanol diffusion flames [18]. In addition, oxidation and pyrolysis characteristics were investigated in non-flame conditions for 1-propanol [19,20] and 2-propanol [19,21–23]. More recently, Norton and Dryer studied the oxidation of 1-propanol and 2-propanol in a flow reactor [24], while Sinha et al. report the flame structure of opposed flow diffusion flames of 2-propanol [25]. In addition, Wang et al. investigated the PAH and soot production from spray combustion of 1-propanol behind reflected shock waves [26], and Bui et al. present a theoretical treatment of the unimolecular decomposition pathways of 2-propanol [27]. In a parallel study to the work presented here, isomer-selective mole fraction profiles were measured at the National Synchrotron Radiation Laboratory in Hefei, China, with PI-MBMS in lean and fuel-rich 1-propanol and 2-propanol flat flames as well as acetone flat flames [28]. No detailed chemical kinetic model for the combustion of either 1-propanol or 2-propanol has yet been published.

In this work, 1-propanol and 2-propanol are chosen as a simple pair of isomeric fuels to test the capabilities of isomer-specific detection for tracking changes in reaction pathways associated with the fuel structure. The comparable thermodynamic properties of the isomeric propanols lead to nearly identical flame conditions (stoichiometry, mass flow, C/O ratio). For this reason, differences in the species pool of flames with a similar stoichiometry are linked directly to differences in the combustion chemistry that are caused by the position of the hydroxyl group at the central carbon atom (2-propanol) or the terminal carbon atom (1-propanol). Mole fraction profiles measured in 1-propanol and 2-propanol flames of similar stoichiometry can be compared directly to identify differences in the fuel consumption pathways.

Three pairs of 1-propanol and 2-propanol flames of nearly identical flame conditions are each investigated by EI- and PI-MBMS. The photoionization experiments have proven well suited for isomer-selective detection; e.g., individual mole fraction profiles for allene/propyne and ethenol/acetaldehyde have been reported in flames fueled by propane [29], cyclohexane [30], and ethanol [9]. Because the higher mass resolution in the EI experiments allows resolution of species of near-identical mass (e.g., ketene and propene) that would appear in a single mass channel in the photoionization mass spectrometer, it offers an additional means of discriminating between some species of similar ionization energies that would be difficult to separate in the photoionization experiments.

The measurements in different MBMS systems establish the reproducibility of the flame conditions and help to identify instrument-dependent parameters, including the influence of background gas, control over pressure and gas flow, and mass discrimination effects encountered in the mass spectrometric analysis. In addition, experimentally measured ionization cross sections, a key parameter in the data analysis, may be available for only one of the two ionization techniques. In these cases, the combination of the EI and PI data sets can help to avoid estimation procedures for the cross sections. The comparison of the resulting mole fraction profiles provides some guidance on their accuracy. Especially for a complex species composition as expected here, results from a single technique may cause misleading interpretations.

The data generated in the EI and PI measurements are in reasonably good general agreement. In addition, they compare favorably to the quantitative flame data presented by Li et al. [28]. However, the species assignment in this work, which is based on the determination of the exact mass of a species and its ionization energy, differs in several cases from the assignments suggested by Li et al. based on the ionization energies alone. It is thus thought useful to comment on some specific features of measurement and analysis for both techniques for an improvement of the quality of quantitative species data for flame model development and validation; this latter task is, however, a project by itself and far beyond the scope of this paper.

Table 1
Flame conditions for all flames.

	ϕ	Fuel [slm]	O_2 [slm]	Ar [slm]	v [cm/s]	$m \times 10^{-3}$ [g/cm s]	p [Pa]
2-Propanol							
EI	1.00	0.33	1.50	1.02	47	2.2	3333
	1.51	0.50	1.50	1.02	50	2.3	3333
	1.90	0.63	1.50	1.02	37	2.4	4666
PI	1.00	0.33	1.50	1.02	51	2.4	3333
	1.51	0.50	1.50	1.02	54	2.5	3333
	1.90	0.63	1.50	1.02	40	2.7	4666
1-Propanol							
EI	1.03	0.33	1.50	1.02	47	2.6	3333
	1.55	0.50	1.50	1.02	50	2.9	3333
	1.94	0.63	1.50	1.02	37	3.1	4666
PI	1.03	0.34	1.50	1.02	51	2.9	3333
	1.55	0.52	1.50	1.02	54	3.1	3333
	1.94	0.65	1.50	1.02	41	3.4	4666

2. Experimental

2.1. MBMS measurements

The data of twelve flame conditions presented here are recorded with two different MBMS systems. One instrument combines electron ionization with high-resolution mass detection. The other employs photoionization using vacuum ultraviolet radiation with a high energy resolution, produced by the Lawrence Berkeley National Laboratory's Advanced Light Source (ALS) at the Chemical Dynamics Beamline 9.0.2. The mass resolution of this instrument is about a factor of ten smaller than for the EI setup. Detailed individual descriptions of each instrumental setup can be found in [31] for the EI system and in [29,32] for the PI system. A short side-by-side presentation of both instruments is included in [9]. To appreciate the relevance of some intrinsic features of both techniques and procedures, the key factors of influence for species assignment and quantitative calibration need some more detailed discussion that is not completely available from previous publications.

2.1.1. Flame conditions

All flames are stabilized on the water-cooled, sintered plate of a flat-flame burner. In the PI experiments a stainless-steel McKenna burner (Holthuis) with a diameter of 6.0 cm is used. The diameter of the bronze matrix of the home-made brass burner in the EI experiments is 6.3 cm. Calibrated mass flow controllers (MKS) adjust the gas flows. The flow of the fuel is set in both experiments by metering the liquid via a syringe pump (ISCO) and ensuring its complete evaporation in a heated vaporizer (125 °C). The flame chamber of the EI-MBMS setup has a smaller diameter and is pumped from behind the burner head, which leads to recirculation of burnt gases. In this case, a quartz tube is mounted to the burner head; it shields and thus stabilizes the flame. The same setup has been used in prior experiments [31].

Very similar gas and liquid flows are used for the 1-propanol and 2-propanol flames, leading to small differences in stoichiometry and C/O ratio for the two fuels. The flame conditions in both setups are summarized in Table 1.

2.1.2. Sampling systems

The following brief description of the sampling procedure applies to both devices. Due to practical considerations, e.g. pumping