



A comprehensive experimental and kinetic modeling study of tert-butanol combustion



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ABSTRACT

The combustion of tert-butanol was studied experimentally in this work, including flow reactor pyrolysis at 30–760 Torr, laminar flat premixed flame at 30 Torr, coflow methane/tert-butanol diffusion flame at atmospheric pressure, and laminar flame speed at 1–10 atm. Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) was applied in the investigation of pyrolysis and flame, and the schlieren technique was used in the measurement of laminar flame speed. A detailed kinetic model consisting of 209 species and 1486 reactions was developed in this work, which can predict the decomposition of tert-butanol and the formation of aromatics over wide temperature and pressure ranges. Kinetic analysis illustrates that the unimolecular decomposition of tert-butanol is the most important and sensitive reaction class in different combustion modes, which readily produce the most important aromatic precursors: tert-butanol → iso-butene → 2-methylallyl → allene → propargyl. As a result, the production of benzene, phenyl radical, and benzyl radical are all enhanced in the combustion of tert-butanol compared to those of other butanol isomers. The self-combination of propargyl and the combination of propargyl with other resonantly stabilized radicals are the key steps of aromatics formation in the combustion of tert-butanol.

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1. Introduction

Biofuels such as alcohols are promising future fuels, which can offset CO₂ and soot emission to reduce greenhouse effect and air pollution, etc. [1]. Butanols have several remarkable advantages over ethanol as alternatives to petroleum-based transportation fuels, such as higher energy density, better miscibility with practical fuels, and lower water affinity. Therefore increasing attention has been paid to the investigations of their combustion properties, including flame propagating speed [2–4], ignition delay time [5–8], pollutants emission [9–12], etc. The butanol isomers behave very differently due to the significant influence of isomeric structures. Among the butanol isomers, tert-butanol (tC₄H₉OH) has the most branched molecular structure. It has a high octane number

(RON = 107 [13]), thus has been used for decades as an octane booster to prevent knock in spark-ignition engines [14,15].

A few studies were performed previously on the combustion chemistry of tert-butanol [3,5,7,16–23]. Yasunaga et al. [7] studied the pyrolysis and oxidation of tert-butanol using shock tubes, in the pressure range of 1.2–2.2 atm and temperature range of 1000–1800 K. Gas chromatography was applied to measure the stable products. Cai et al. [18] studied the pyrolysis of tert-butanol in a flow reactor at low pressure using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Both free radicals and stable intermediates were observed. Recently, Lefkowitz et al. [19] also studied the oxidation of tert-butanol in a flow reactor at the pressure of 12.5 atm and in the temperature range of 675–950 K. They found that tert-butanol does not exhibit low temperature oxidation behavior under their experimental conditions, because no negative temperature coefficient region was observed. Welz et al. [24] studied the low-temperature oxidation of tert-butanol at a very low pressure (4–5.1 Torr). The reaction of iso-butyl-2-ol radical (tC₄H₈OH) and O₂ forming OH radical was concluded as the dominant chain-propagating channel in their work. Yang et al. [16] focused on the qualitative identification of

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Table 1
Experimental conditions of laminar flames.

Laminar flame speed								
Name	P^a	T^b	ϕ	$X_{\text{tC}_4\text{H}_9\text{OH}}$	X_{O_2}	X_{N_2}	X_{He}	
FS1	1.0	423	0.7–1.5	1.00	0.21	0.79	–	
FS2	2.0	423	0.7–1.5	1.00	0.21	0.79	–	
FS3	5.0	423	0.7–1.3	1.00	0.21	0.79	–	
FS4	10.0	423	0.7–1.0	1.00	0.21	0.79	–	
FS5	10.0	423	0.8–1.4	1.00	0.14	–	0.86	
FS6	20.0	423	0.7–1.4	1.00	0.14	–	0.86	
Burner stabilized premixed flames ^c								
Name	P^a	\dot{m}^d	ϕ	X_{Ar}	X_{O_2}	$X_{\text{tC}_4\text{H}_9\text{OH}}$		
PF1	0.0395	0.003187	1.30	0.5000	0.4108	0.0892		
PF2	0.0395	0.003520	1.80	0.5000	0.3846	0.1154		
Coflow diffusion flames ^e								
Name	P^a	Q_{air}^f	Q_{Ar}^f	$Q_{\text{N}_2}^f$	$Q_{\text{CH}_4}^f$	$Q_{\text{tC}_4\text{H}_9\text{OH}}^f$	v_{air}^g	v_{fuel}^g
CF1	1.0	80,000	5.87	438	160	24.50	16.48	13.33
CF2	1.0	80,000	5.87	401	209	12.25	16.48	13.33

^a P , initial pressure of premixed gases for flame speed measurements, environment pressure for burner stabilize flames and coflow diffusion flames, unit: atm.

^b T , initial temperature of premixed gases, unit: K.

^c PF: abbreviation for burner stabilized premixed flames;

^d \dot{m} , mass flow rate, unit: g/(s cm²).

^e CF: abbreviation for coflow diffusion flame.

^f Q_i , flow rate of species i , unit: SCCM; the gas temperature for fuel mixture and air are 493 and 298 K, separately.

^g v_i , converted into mean velocity of fuel/oxidizer stream at 273 K, unit: cm/s.

intermediates in the rich flames of four butanol isomers ($\phi = 1.7$). Oßwald et al. [17] then measured the mole fractions of major flame species and intermediates in the flames of four butanol isomers at the same equivalence ratio of 1.7. Furthermore, Moss et al. [5], Yasunaga et al. [7] and Stranic et al. [20] measured the ignition delay times of tert-butanol at different temperatures, pressures and equivalence ratios, while Wu et al. [2] and Veloo et al. [3] measured laminar flame speeds of tert-butanol. tert-Butanol, has a much higher sooting tendency than its isomers [25,26]. However, no kinetic model for tert-butanol combustion has been comprehensively validated over wide pressure and temperature ranges. The formation mechanism of the polycyclic aromatic hydrocarbon (PAH) in the combustion of tert-butanol remains unclear. Therefore, refinements on current tert-butanol models are urgently needed to expand their capability to predict the combustion of tert-butanol and the formation of PAH in this process over wide pressure and temperature ranges.

In this work, the pyrolysis of tert-butanol was studied in a flow reactor in the temperature range of 850–1550 K and at pressures of 30, 150 and 760 Torr. The laminar flame speeds of tert-butanol were measured at pressures of 1–20 atm. These experiments focused on the pressure effect upon the combustion of tert-butanol. Two rich laminar premixed tC₄H₉OH/O₂/Ar flames at 30 Torr and two coflow methane/tert-butanol diffusion flames at atmospheric pressure were also studied using SVUV-PIMS. A model consisting of 209 species and 1486 reactions was developed based on our previous butanol and methane models [18,27]. A comprehensive model validation and detailed kinetic analysis on the high temperature combustion of tert-butanol will be presented in the following paragraphs.

2. Experimental methods

Flow reactor pyrolysis, premixed flat flame, coflow diffusion flame, and laminar flame speed were all carried out at National Synchrotron Radiation Laboratory in Hefei, China. All of the experimental conditions are listed in Table 1 (except pyrolysis). The purities of the samples, including CH₄, N₂, O₂, Ar, He and tC₄H₉OH, are

99.995%, 99.999%, 99.999%, 99.99%, 99.99% and 99%, respectively. The gas flow rates were regulated using mass flow controllers, and tert-butanol was injected into a vaporizer with a chromatography pump. The SVUV-PIMS system, including the synchrotron beamline and the experimental apparatuses, were introduced in detail in previous studies [10,28–32]. Here, we will briefly introduce each of them in this section.

The uncertainty in the SVUV-PIMS measurements is related to the sampling process and the photoionization cross sections (PICS) of the combustion species. Generally, it is within $\pm 10\%$ for combustion species quantified via cold gas calibration, $\pm 25\%$ for stable combustion species with known PICSs, and about a factor of 2 for free radicals and combustion species with estimated PICSs [10,33]. The PICSs of combustion species are available online in the database of [34].

2.1. Pyrolysis in a flow reactor

The flow reactor pyrolysis apparatus consists of a pyrolysis chamber with an electrically heated furnace, a differentially pumped chamber with molecular beam sampling system and a photoionization chamber with a home-made reflectron time-of-flight mass spectrometer (RTOF-MS). The flow reactor is equipped in the pyrolysis chamber. It contains a 6.8-mm-ID (inner diameter) α -alumina tube, which is heated by a furnace over a length of 150 mm. α -Alumina is thermally stable, the catalytic effect of which been evaluated to be very weak in pyrolysis experiments [35]. The pyrolysis products are sampled 10 mm downstream of the outlet of the reactor using a quartz conical nozzle. The molecular beam that is formed by the sampled gas is then ionized by the tunable SVUV light, and detected by RTOF-MS.

The pyrolysis of tert-butanol was studied at different pressures (30, 150 and 760 Torr), while the inlet compositions of reactant and diluent gas remained constant (3% tC₄H₉OH and 97% Ar). tert-Butanol was vaporized at 393 K, mixed with the carrier gas (Ar), then injected to the flow reactor. Temperature distributions along the centerline of the flow reactor were measured with a Pt-6%Rh/Pt-30%Rh thermocouple, which are provided as Supplementary material. The measured temperature profiles were used

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