



# Toward a better understanding of 2-butanone oxidation: Detailed species measurements and kinetic modeling



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## ABSTRACT

In view of a desired transition from fossil fuels to sustainably produced biofuels that should contribute to a net reduction of CO<sub>2</sub> emissions, promising fuel candidates have been identified including 2-butanone (methyl ethyl ketone, MEK) that is qualified for use in spark-ignition (SI) engines. To support a potential, rapid integration of such biofuels into the existing infrastructure, fundamental studies of their combustion and emission behavior are highly important. In the case of 2-butanone specifically, only very few fundamental combustion experiments have been performed to date, with a notable shortage of detailed speciation data. For predictive model development, accurate and reliable species measurements are needed to describe the oxidation and combustion of 2-butanone and to elucidate the kinetic mechanism.

The present study relies on three different experiments: a laminar flow reactor coupled with molecular-beam mass spectrometry (MBMS, Bielefeld), a rapid compression machine (RCM, Aachen), and a shock tube using advanced laser absorption techniques (Stanford). This combination ensured coverage of a wide regime in temperature, pressure, and mixture composition while providing numerous species profiles. The species measurements in the flow reactor were performed at stoichiometric ( $\Phi = 1.0$ ) and fuel-rich ( $\Phi = 2.0$ ) equivalence ratios at temperatures between about 800–1100 K with an argon dilution of 95%. Ignition delay times in the RCM were measured in air for equivalence ratios of 0.5, 2.0 in the temperature range of 840–945 K to reflect application-relevant conditions. Shock tube measurements were performed at stoichiometric conditions at 1303–1509 K in argon.

To provide insight into the oxidation mechanism of 2-butanone, the newly measured experimental data was used to develop and validate a detailed chemical kinetic model. To this end, the reactions for the low-temperature regime, especially concerning early fuel consumption, radical formation, and subsequent low-temperature oxidation, were examined in detail, and used to extend and adapt an existing reaction mechanism (Burke et al., 2016 [23]) to more accurately predict the new low-temperature conditions studied. The resulting model that incorporates the latest theoretical kinetic calculations available in the literature was compared to the measurements presented here as well as validated using literature data. To the authors' knowledge, the present model represents the most robustly validated mechanism available for the prediction of 2-butanone combustion targets to date.

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## 1. Introduction

One aspect that is thought to contribute to an increasing sustainability of the global energy consumption is a transition in the transportation system from the combustion of fossil fuels to that of second-generation biofuels, eventually reducing net car-

bon emissions. The combustion of some commonly discussed biofuel classes including alcohols, esters, and cyclic ethers has been investigated in detail [1–4] with the conclusion that typically, soot and unburnt hydrocarbon emissions may be reduced, while the formation of oxygenated compounds, including harmful or toxic components, is often increased [2,5–7]. The production of advanced biofuels focuses on the catalytic conversion of cellulosic biomass to reduce competition with food production [4,8,9]. In an interdisciplinary approach, 2-butanone (methyl ethyl ketone, MEK) has recently been identified, among numerous lead structures and investigations on appropriate pathways for their

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production, as a potential next-generation biofuel for spark-ignition (SI) engines [4,10]. Among its advantageous properties is its impressive knock resistance (RON = 117) [10]. Methyl ketones can be produced from biomass and specifically, glucose can be microbiologically fermented by the bacteria *klebsiella oxytoca* to 2,3-butanediol and subsequently catalytically converted with a yield of up to 90% to 2-butanone [11].

In addition to its use as a neat fuel [10] or fuel additive, 2-butanone, similar to other ketones, also serves as a tracer molecule in laser diagnostic measurements in engines [12]. For all combustion applications, it is desirable to understand its combustion kinetics, including possible effects that 2-butanone could have on the combustion characteristics of the main fuel when used as an additive or fuel tracer. To this end, comprehensive fundamental reaction models must be developed that can be reduced with the dual purpose to predict the fuel's behavior under usual operation conditions and to validate those models against experimental data. Regarding modern engine development, it is no longer sufficient for a reaction model to describe the usual high-temperature combustion reactions appropriately, but increasing interest is devoted to low-temperature oxidation, with demands that a realistic model should represent the entire low- to high-temperature regime continuously.

Predictive models should be capable of assessing the emission potential of a fuel or fuel blend. Competitive performance of 2-butanone in an SI engine when compared to a RON95 fuel blend, ethanol, and 2-methylfuran was demonstrated in a recent publication by Hoppe et al. [10], outlining 2-butanone's low emission of soot, unburnt hydrocarbons, and  $\text{NO}_x$ . Overall, there are only a few studies regarding the oxidation chemistry of 2-butanone. A first species measurement and quantification coupled to kinetic modeling was presented by Decottignies et al. [13] who studied a methane/air flame doped with 2-butanone by gas chromatography. A reduction of  $\text{NO}_x$  production upon 2-butanone addition to a methane/air flame was reported by Lamoureux et al. [14]. Ignition delay times in shock tubes and laminar burning velocities with a detailed high-temperature chemical kinetic model were provided by Serinyel et al. [15,16]. These ignition delay times were recorded at atmospheric pressure with fuel concentrations of 1.0–2.0%, equivalence ratios of 0.5–2.0, and temperatures of 1250–1850 K. Badra et al. [17] enhanced the previously developed model with new ignition delay times in the temperature range of 1100–1400 K at elevated pressures of 3 and 6.5 atm. Their study includes rate coefficients for the reaction of 2-butanone with  $\text{OH}$ . This reaction has also been studied theoretically by Zhou et al. [18] who considered individual abstraction site selectivities.  $\text{H}$ -abstraction reaction rate coefficients by  $\text{HO}_2$  were calculated by Mendes et al. [19]. Also, species time-histories for the high-temperature pyrolysis of 2-butanone were analyzed and reported by Lam et al. [20].

While these investigations primarily represent high-temperature kinetics, there is one study by Sebbar et al. [21] with calculations of the thermochemistry and kinetics of the reactions of 3-butanoyl with  $\text{O}_2$ , representing an isolated part of the low-temperature oxidation kinetics. Tranter and Walker [22] investigated slowly reacting  $\text{H}_2/\text{O}_2$  mixtures with 2-butanone at 753 K with gas chromatography and elucidated some elementary reactions. Burke et al. [23] presented a first detailed kinetic model including low-temperature reactions of 2-butanone; it is based upon measurements in a rapid compression machine (RCM) and in a shock tube for stoichiometric mixtures at elevated pressures of 20 and 40 bar, covering a temperature range of 850–1280 K. This recent kinetic model also incorporates thermodynamic calculations for 2-butanone's oxidation species and results of laminar burning velocity measurements. A recent publication by Thion et al. [24] studied 2-butanone oxidation at pressures of 1 and 10 atm in a jet-stirred reactor (JSR) and presented a model with newly

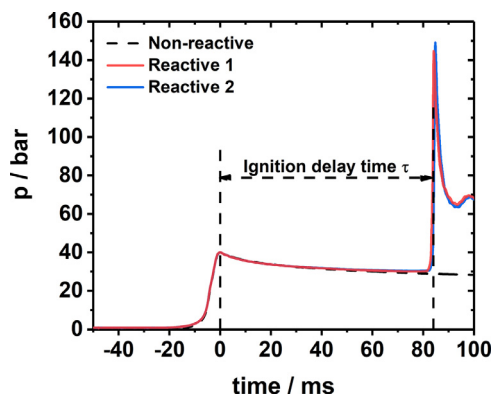


Fig. 1. Pressure trace of the RCM and definition of the ignition delay time for  $\Phi = 2.0$ ,  $T_c = 826$  K and  $p_c = 40$  bar.

calculated reaction rate coefficients. In a previous study [25], some of the co-authors of the present study reported quantitative experiments in a laminar premixed low-pressure fuel-rich flame using electron ionization (EI) as well as photoionization (PI) molecular-beam mass spectrometry (MBMS). This data was compared to kinetic simulations with the model by Burke et al. [23], leading to some modifications of fuel radical reactions, and the conclusion that further work was required to better understand the kinetics of 2-butanone combustion. Since this flame study did not address the low-temperature regime, further model improvement and validation will need a respective extension of quantitative species measurements.

The present work addresses this need by reporting species measurements in a flow reactor at atmospheric pressure and temperatures of 750–1173 K with two equivalence ratios ( $\Phi = 1.0$  and 2.0), as well as  $\text{OH}$  time-history measurements in a shock tube at stoichiometric conditions and various temperatures between 1303–1509 K. Additionally, new ignition delay time measurements at 40 bar for two different stoichiometries ( $\Phi = 0.5$  and 2.0) were performed in an RCM. This body of experimental data is used here to provide insight into the kinetic mechanism of 2-butanone combustion. To this end, a new detailed chemical kinetic model is developed, based on existing experimental results and the newly acquired data presented here. This new model benefits from recently available elementary rate coefficient calculations and previous efforts surrounding the development of an accurate chemical kinetic model for 2-butanone combustion. The present model is also validated against the available experimental data in the literature in order to provide the most accurate and robustly validated model to date for 2-butanone combustion.

## 2. Experimental work

### 2.1. Rapid compression machine

The rapid compression machine used in this study has been described previously in detail in [23,26]. This facility consists of a single horizontal piston set-up that is pneumatically driven and is brought to a steady stop using a hydraulic stopping section. The in-cylinder pressure is monitored using a coated PCB113B24 pressure transducer. The pressure is then used as the diagnostic for the determination of the ignition delay time, see Fig. 1. An externally mounted heating system ensures a homogeneous reactor temperature, and the interchange of end walls allows for the variation of the compression ratio. The RCM can operate up to 1000 bar peak pressure for reactive experiments.

The compressed temperature conditions are calculated using the initial temperature and pressure conditions and the measured

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