High temperature rate constants of anisole decomposition and ignition delay time measurements of anisole

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Abstract

Tracer-LIF imaging is an important technique for non-intrusive measurements of fuel concentration, temperature, and equivalence ratio in practical combustion systems, in particular in IC engines [1]. Several fluorescence tracers have been suggested, among which ketones and aromatics have become the most popular. In compression-heated environments, such as IC engines, tracers can be used even under conditions where the lifetime of the tracer is only on the order of a few milliseconds. For these conditions, the optical properties of some tracers have been studied in shock tubes [2] where with further increasing temperature the gradual loss of signal was observed due to the decomposition of the tracers. Under high temperature conditions, tracers can partially decompose together with the base fuel in the pre-ignition phase. Thus, the addition of the tracers to fuels for LIF experiments has two important implications. On one hand, the measured fluorescence signals could be misinterpreted in case of the decomposition of the tracer because of either disappearing of the fluorescing species or formation of fragments with different fluorescence properties. On the other hand, the tracer and its fragments can potentially influence the ignition and combustion characteristics of the base fuel.

This means, when used as a tracer, the kinetics of the thermal decomposition of LIF-tracers should be known to derive reliable quantities. An aromatic tracer, suggested because of its increased signal intensity is anisole ($C_6H_5OCH_3$) [3]. It has a relatively low boiling point which makes it compatible to gasolinetype fuels. It is necessary to assess the temperature/time range where it can be used without decomposition. Anisole decomposition has been previously investigated. It is assumed that the first step (R1) occurs via homolytic cleavage of the O-CH_3 bond. This is consistent with anisole bond strengths of 405.4 and 264.4 kJ/mol for (CH_2-H) and C_6H_5O-CH_3, respectively.

$$C_6H_5OCH_3 \rightarrow CH_3 + C_6H_5O \qquad\qquad (R1)$$

Phenoxy radicals from reaction (R1) can then undergo two types of reactions. They can either decompose to cyclopentadienyl (C_5H_5) and CO, where C_5H_5 is assumed to be a main precursor of benzene, naphthalene, and heavier PAHs or they can react with H atoms or CH_3 radicals to yield phenol (C_6H_5OH) or ortho- and para-cresol ($C_6H_4CH_3OH$), respectively.

$$C_6H_5O \rightarrow CO + C_5H_5 \qquad\qquad (R2)$$
$$C_6H_5O + H \rightarrow C_6H_5OH \qquad\qquad (R3)$$
$$C_6H_5O + CH_3 \rightarrow C_6H_4CH_3OH \qquad\qquad (R4)$$
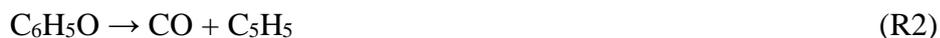
There are only three experimental investigations of reaction (R2). Colussi et al. [4] performed the first study of phenoxy decomposition using a low-pressure Knudsen flow

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setup (very low-pressure pyrolysis, VLPP). Shock-tube experiments were performed by Lin and Lin [5] as well as Frank et al. [6]. While Lin and Lin used large anisole concentrations (0.108−0.758%), Frank et al. were able to carry out their experiments with highly diluted gas mixtures using the sensitive MRAS-technique (molecular resonance absorption spectrometry). The measured rate constants obtained from Frank et al. were around three times larger than those of Lin and Lin. Various theoretical studies have also been conducted to investigate the thermal decomposition of phenoxy radicals [7] - [9]. Colussi et al. [4] proposed a bicyclic intermediate for reaction (R2) that ring-opens to the 2,4-cyclopentadienyl carbonyl radical and subsequently decomposes to CO and cyclopentadienyl (Figure 1).
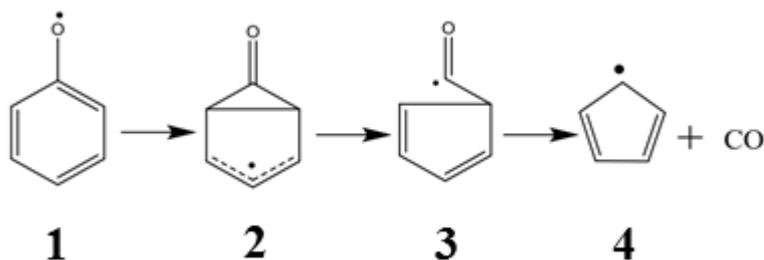

Fig. 1. Schematic pathway of unimolecular decomposition (R2) of phenoxy radical.

Further theory studies supported this pathway. Most recently, Carstensen and Dean performed electronic structure calculations at CBS-QB3 and CBS-QB3//QCISD/6-31G(d) levels of theory to construct the relevant portion of the C_6H_5O potential energy surface (PES).

In the present work, anisole pyrolysis was studied behind reflected shock waves at 1000–1270 K and 1.3–1.6 bar. Absorption measurements with a continuous-wave (cw) quantum cascade (QC) laser near 4.7 μm was applied to monitor time-resolved CO concentration using the P(8) rotational transition in the fundamental vibrational band within 2 ms test time with few microseconds time resolution. Additional experiments with allyl phenyl ether ($C_6H_5OC_3H_5$) as a source of pure phenoxy were performed to determine k_2 without the influence of bimolecular phenoxy reactions. The rate coefficients of unimolecular phenoxy decomposition with allyl phenyl ether as precursor were determined at 970–1170 K and ~1.4 bar. Experimental data of anisole and allyl phenyl ether pyrolysis were then compared to simulations based on the recent kinetics model of Nowakowska et al. [10]. The simulations were conducted using Chemical Workbench assuming a homogeneous constant-volume reactor.

Figure 2 shows measured CO concentration–time histories during the pyrolysis of a 400 ppm $C_6H_5OC_3H_5$/Ar mixture at 1045–1154 K and ~1.4 bar. Rate constants k_2 were inferred through the mass balance $1 − ([CO]_t/[C_6H_5OC_3H_5]_0)$ versus time assuming first-order kinetics.

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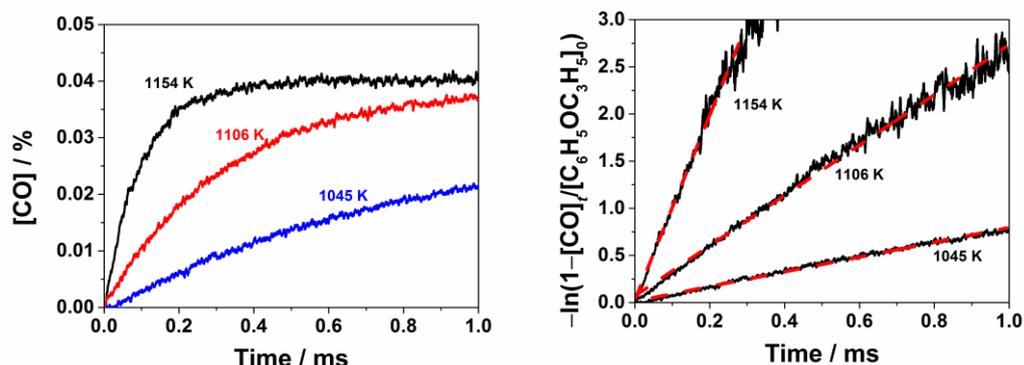
Fig. 2. Left: CO mole fraction time histories of pyrolysis of allyl phenyl ether mixture (400 ppm $C_6H_5OC_3H_5$/Ar). Right: Rate constants determination under first-order assumption at temperatures 1045–1154 K and ~1.4 bar, black line: measurements, red dashed lines: linear fits.

In order to rationalize the experimental findings reported in this work, we have re-evaluated the potential-energy surface (PES) for the phenoxy radical decomposition presented by Carstensen and Dean by conducting electronic structure calculations at the G4 level of theory. Like CBS-QB3, G4 is another composite method in which a sequence of ab initio calculations is performed to get the total energy of a molecular compound. The electronic structure calculations were conducted using the Gaussian09 program package. Master equation calculations were carried out with Unimol using the ab initio-based rovibrational properties and energetics of the minima and transition states to obtain theoretical rate constants.

The results of the first-order evaluations are plotted in Figure 3. Experimental data from Lin and Lin [5] and Frank et al. [6], as well as theoretical predictions from Carstensen and Dean and theoretical results of the present study are also included.
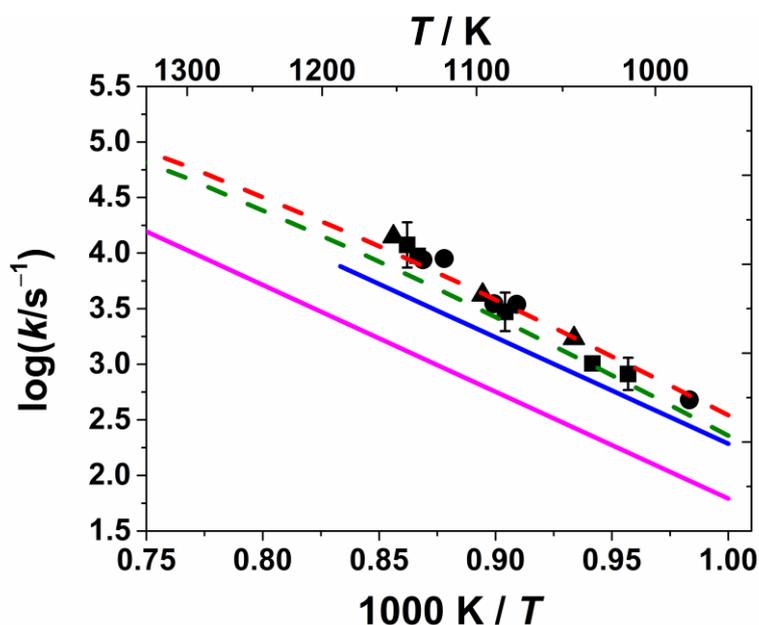

Fig. 3. Rate constants for (R2). squares: 400 ppm $C_6H_5OC_3H_5$ in Ar, circles: 250 ppm $C_6H_5OC_3H_5$ in Ar, triangles: 200 ppm $C_6H_5OC_3H_5$ in Ar; red dashed line: Theoretical calculation, this work, G4 level of theory (1.4 bar); pink full line: Lin and Lin [5]., blue full line: Frank et al.[6];green dashed line: Carstensen and Dean [9], CBS-QB3 (1.4 bar).

Due to the lack of ignition data of anisole at engine relevant conditions, also ignition delay times of this species were measured at 10, 20, and 40 bar at lean ($\Phi = 0.5$) and stoichiometric conditions in the 770–1600 K range in a high-pressure shock tube. The measured ignition delay times were compared with simulations with the mechanism from Nowakowska et al. [10].

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