High-temperature rate constant measurements for OH + xylenes

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ABSTRACT

The overall rate constants for the reactions of hydroxyl (OH) radicals with *o*-xylene (k_1), *m*-xylene (k_2), and *p*-xylene (k_3) were measured behind reflected shock waves over 890–1406 K at pressures of 1.3–1.8 atm using OH laser absorption near 306.7 nm. Measurements were performed under pseudo-first-order conditions. The measured rate constants, inferred using a mechanism-fitting approach, can be expressed in Arrhenius form as:

$k_1 = 2.93 \times 10^{13} \exp(-1350.3/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ (890−1406 K)
$k_2 = 3.49 \times 10^{13} \exp(-1449.3/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ (906−1391 K)
$k_3 = 3.5 \times 10^{13} \exp(-1407.5/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ (908−1383 K)

This paper presents, to our knowledge, first high-temperature measurements of the rate constants of the reactions of xylene isomers with OH radicals. Low-temperature rate-constant measurements by Nicovich et al. (1981) were combined with the measurements in this study to obtain the following Arrhenius expressions, which are applicable over a wider temperature range:

$k_1 = 2.64 \times 10^{13} \exp(-1181.5/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ (508−1406 K)
$k_2 = 3.05 \times 10^{9} \exp(-400/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ (508−1391 K)
$k_3 = 3.0 \times 10^{9} \exp(-440/T) \, \text{cm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ (526−1383 K)

1. Introduction

Traditional transportation fuels are complex mixtures of different hydrocarbons including n-/iso-/cyclo-alkanes, olefins, and aromatics [1]. Approximately 30% and 20% of gasoline and diesel fuels, respectively, are composed of aromatics [1,2]. Some aromatic molecules, such as toluene, tri-methyl benzene, and xylene, are considered necessary constituents of surrogate fuel formulations [3–5]. Aromatics are found in the initial fuel composition and produced during the oxidation of large aliphatic fuels [2]. Because of their lower reactivity in comparison to n-/iso-alkanes, aromatics are also used as antiknock additives to enhance gasoline octane rating [6]. Hence, studying the kinetic targets (e.g., ignition delay times, species time histories, and reaction rate constants) of aromatics has attracted attention from several researchers [1,3,6–15].
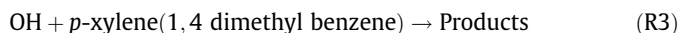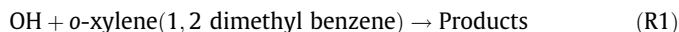
The reaction of hydroxyl (OH) radicals with alkanes, alkenes, and aromatics is one of the primary oxidation pathways for these molecules under atmospheric and combustion conditions. A few studies have investigated the reaction between OH and aromatics, but these studies either targeted lower temperatures or focused on the first two smallest aromatics, benzene and toluene. Perry et al. [13] measured the rate constant of the reaction between OH radicals and benzene, toluene, xylene isomers, and trimethyl benzene isomers at temperatures of 296–473 K using flash photolysis and the resonance fluorescence technique. Tully et al. [14] also used flash photolysis and the resonance fluorescence technique to measure the rate constants for the reaction of OH radicals with benzene and toluene over a wider temperature range of 213–1150 K. Recently, Vasudevan et al. [15] measured the rate constant for OH + toluene behind reflected shock waves using OH laser absorption near 306.7 nm for temperatures ranging between 911 and 1389 K. A recent experimental study on the rate constants for reactions of benzene and toluene with OH radicals was conducted by

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Seta el al. [2] using a shock tube and pulsed laser-induced fluorescence for temperatures in the range of 908–1736 K.

The high-temperature H-abstraction reactions of OH radicals with the three xylene isomers can be expressed by the following:

$$OH + o\text{-xylene}(1, 2 \text{ dimethyl benzene}) \rightarrow \text{Products} \qquad (R1)$$

$$OH + m\text{-xylene}(1, 3 \text{ dimethyl benzene}) \rightarrow \text{Products} \qquad (R2)$$

$$OH + p\text{-xylene}(1, 4 \text{ dimethyl benzene}) \rightarrow \text{Products} \qquad (R3)$$

Most previous studies of these reactions have been limited to room temperature conditions [16–20], with the exception of three studies that measured rate constants at higher temperatures (296–970 K). As mentioned earlier, Perry et al. [13] measured the rate constants of R1–R3 for a temperature range of 296–473 K. Mehta et al. [21] used the relative rate and discharge flow mass spectrometry technique with 1,4 dioxane as the reference compound over a range of 240–340 K to measure the rate constants of R1–R3 reactions. Nicovich et al. [12] investigated the kinetics of these reactions using the flash photolysis and resonance fluorescence technique over a temperature range of 250–970 K.

In this work, the rate constants for R1–R3 are measured at combustion relevant temperatures (890–1406 K). Measurements are performed under pseudo-first-order conditions with the help of narrow line-width absorption of OH radicals near 306.7 nm. This study reports the first rate-constant measurements for R1–R3 at temperatures higher than 970 K. Arrhenius expressions are derived for the studied temperature range and then extended to lower temperatures using previously published data.

2. Experimental set up

All experiments were performed behind reflected shockwaves in a high-purity stainless steel shock tube facility. The inner surface of the shock tube is honed and electro-polished to reduce boundary layers and trapped impurities. The driven section is 9 m long, while the driver section length can be varied to a maximum of 9 m; both sections have an inner diameter of 14.2 cm. Further details of the shock tube can be found elsewhere [22]. The incident shock velocity was determined (±0.1%) using five PCB (Model 113B26) piezo-electric pressure transducers (PZT) spaced over the last 1.3 m of the driven section. The shock velocity at the endwall was determined by extrapolating the measured velocity. The preshock pressure and temperature, P_1 and T_1, are measured using a high-accuracy Baratron pressure transducer and a K-type thermocouple, respectively. Reflected shock conditions, P_5 and T_5, were calculated using standard normal-shock relations and thermochemical data taken from the Sandia thermodynamics database [23].

Gas mixtures were prepared manometrically in a uniformly heated (50 °C) stainless steel mixing tank equipped with a magnetic stirrer assembly. *Tert*-butyl hydroperoxide (*t*BHP), a well-known precursor of OH radicals [15], is thermally decomposed to produce OH radicals. Previous work draws a comparison between *t*BHP and gaseous nitric acid as hydroxyl radical precursors [2,15]. High-purity He (99.999%), supplied by Abdullah Hashim Gases (AHG), is used as the driver gas. Test gas mixtures are prepared using research grade argon (99.999%) supplied by AHG, 70% *t*BHP aqueous solution and *o*-, *m*- or, *p*-xylene (≥99%) supplied by Sigma Aldrich. Repeated freeze–pump–thaw cycles were used to further purify the xylenes.

OH radicals were measured using the well-characterized R1 (5) line of the OH A–X (0, 0) band. UV light was tuned to the peak of the absorption line near 306.6868 nm. Visible red light near 613.4 nm (~1 W) was generated in a Matisse ring dye laser from
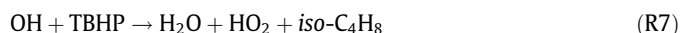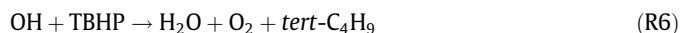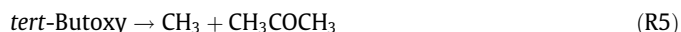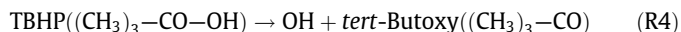
Sirah by pumping a solution of 0.75 g/L Rhodamine B dye in ethylene glycol with a 10 W, 532 nm, cw beam produced by the Millenia Prime laser from Spectra Physics. The visible red beam was then sent to a CW Spectra Physics Wave Train frequency doubler that generates UV light (~100 mW) near 306.7 nm. A beam splitter is used to send a fraction of the UV beam to a reference detector and the remaining fraction to pass through the shock tube at an optical location 2 cm from the endwall (see Fig. 1). Hydroxyl radical mole fractions were determined quantitatively using the Beer–Lambert law, $I/I_0 = \text{Exp}(-k_v X_{OH} P_5 L)$, where I and I_0 are the transmitted and incident laser intensities, respectively; k_v is the absorption coefficient calculated following the work of Herbon [24]; P_5 is the total reflected shock pressure (atm); and L is the optical path length (14.2 cm). The overall estimated uncertainty in the measured OH mole fraction, X_{OH}, is approximately ±3%, mainly due to the uncertainty in reflected shock temperature (±0.7%) and absorption cross section.

3. Results and discussion

3.1. High-temperature rate-constant measurements

The overall rate constants for the reactions of *o*-, *m*-, and *p*-xylene with OH (R1), (R2), (R3) were measured behind reflected shockwave under pseudo-first-order conditions over a temperature range of 890–1406 K and pressures ranging between 1.3 and 1.8 atm. The experiments were performed using varying initial fuel concentrations/*t*BHP: 130 ppm *o*-xylene/10 ppm *t*BHP, 120 ppm *m*-xylene/9 ppm *t*BHP, and 220 ppm *p*-xylene/17 ppm *t*BHP. Argon was used as the diluent bath gas.

Hydroxyl radical decay was simulated using the mechanism by Narayanaswamy et al. [25], which was developed for the oxidation of toluene, styrene, ethylbenzene, 1,3-dimethylbenzene (*m*-xylene), and 1-methylnaphthalene. The *m*-xylene submechanism was validated against ignition delay time and burning velocity measurements of *m*-xylene. The TBHP ((CH3)3–CO–OH) chemistry set (described in [22,26–28]) is included in the base mechanism of Narayanaswamy et al. [25] to simulate OH radical formation.

$$TBHP((CH_3)_3-CO-OH) \rightarrow OH + tert\text{-Butoxy}((CH_3)_3-CO) \qquad (R4)$$

$$tert\text{-Butoxy} \rightarrow CH_3 + CH_3COCH_3 \qquad (R5)$$

$$OH + TBHP \rightarrow H_2O + O_2 + tert\text{-}C_4H_9 \qquad (R6)$$

$$OH + TBHP \rightarrow H_2O + HO_2 + iso\text{-}C_4H_8 \qquad (R7)$$

TBHP decomposes almost instantaneously to form an OH radical and a *tert*-butoxy radical that subsequently decomposes to form acetone and methyl radical. Moreover, the OH radical can attack TBHP to produce water and other products [22,27,28]. Thermodynamic properties of the newly introduced species, including TBHP and a *tert*-butoxy radical, were extracted from the thermodynamic database from Goos et al. [29] and the updated thermodynamic parameters of OH radicals were taken from Herbon et al. [30]. Rate constants for R4, R6, and R7 reactions were obtained from Pang et al. [31], and the rate constant for reaction R5 was taken from Choo and Benson [32].

A representative OH sensitivity analysis for a mixture of 120-ppm *m*-xylene (written in the base mechanism as A1CH₃CH₃) with 9-ppm *t*BHP (and 24-ppm H_2O vapor) and balanced argon is shown in Fig. 2 at 1024 K and 1.54 atm. All simulations were performed using CHEMKIN PRO [33] with constant volume and internal energy (constant UV) constraints. OH sensitivity is calculated as $S = (\partial X_{OH}/\partial k_i) \times (k_i/X_{OH})$, where X_{OH} is the OH radical mole fraction and k_i is the rate constant of the *i*th reaction. Sensitivity