

High Temperature Oxidation of Aromatic Hydrocarbons

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Motivation

Aromatics have desirable properties such as a high energy rating [1] and a high knock rating [2]. It is well known that the addition of aromatics to gasoline increases the fuel octane number. Owing to these advantages, aromatics such as toluene and xylene have become important components of commercial gasoline and aviation fuels.

Even though several models for toluene oxidation have been developed [3-7], the high temperature combustion of this aromatic is not fully understood. Most high temperature studies of toluene carried out to date have involved monitoring the concentration profiles of reactants, stable intermediates, and final products in flow reactors using GC analyses. However, the ignition process of hydrocarbons is, to a large extent, controlled by the transient radical pool (H, OH, C₆H₅, C₆H₅CH₂, CH₃ etc.) and very little information concerning radical concentration profiles during the ignition process is available in the literature. Detailed measurements of radical time histories would provide additional, important targets for chemical kinetic models, leading to improved model predictions of global kinetic parameters, which is important from an engineering perspective.

Overview

In this work, ignition delay times and OH radical concentration profiles were measured in toluene/O₂/Ar mixtures behind reflected shock waves. Initial reflected shock conditions spanned 1400-2000 K and 1.5-5.0 atm, with equivalence ratios of 0.5-1.875 and C₆H₅CH₃ concentrations of 0.025 - 0.5%. OH time histories were monitored using narrow-linewidth ring dye laser absorption of the well-characterized R1 (5) line of the OH A-X (0, 0) band at 306.7 nm. Ignition time data was extracted from the OH traces and was found to compare very well with measurements using sidewall pressure. Ignition time was defined as the time to 50% of the peak OH concentration [see Figure 1], with zero time defined as the arrival of the reflected shock front at the sidewall measurement location.

This new data was correlated globally with an earlier ignition time study by Burcat et al. [9] and a correlation for ignition delay time applicable over a wide range of conditions has been developed. A typical OH concentration profile is presented in Figure 1. The trace may be divided into three distinct regions: region 1 - OH concentration increases rapidly due to toluene decomposition and at moderate to low temperatures, evens out to form an intermediate plateau; region 2 - OH concentration rises due to chain branching and propagation; and region 3 - rate of production of OH is close to zero. At high fuel concentrations (say 0.5% toluene), the plateau in region 1 is not as well developed as the one shown in Figure 1; instead, the profile slopes gently in the upward direction before showing the steep rise characteristic of region 2.

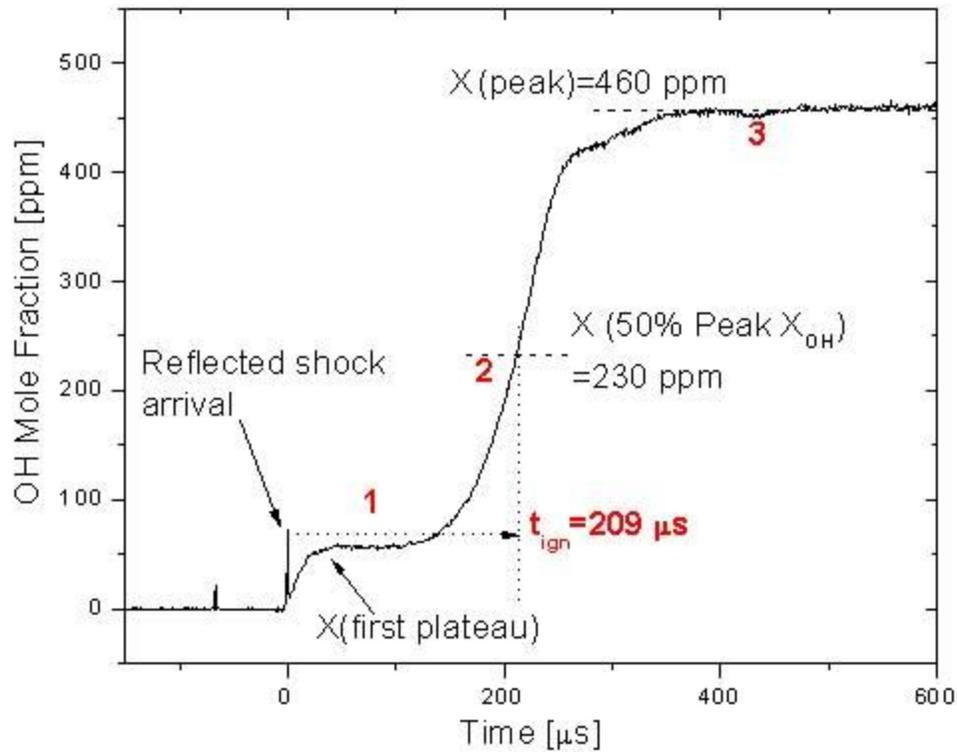


Figure 1: Quantitative OH absorption trace. Reflected shock conditions: 0.1% C₆H₅CH₃, 0.9% O₂, 1689 K, 1.796 atm. Zero time defined as arrival of reflected shock. $t_{ign} = 209 \mu s$.

Ignition times from various shock tube studies, normalized to 1% C₆H₅CH₃, 9% O₂ and 1 atm is shown in Figure 2. Data from this study and Burcat et al. [9] correlate very well, while the ignition time data of Pitz et al. [6] and the older Burcat et al. [8] data are shorter and show greater scatter.

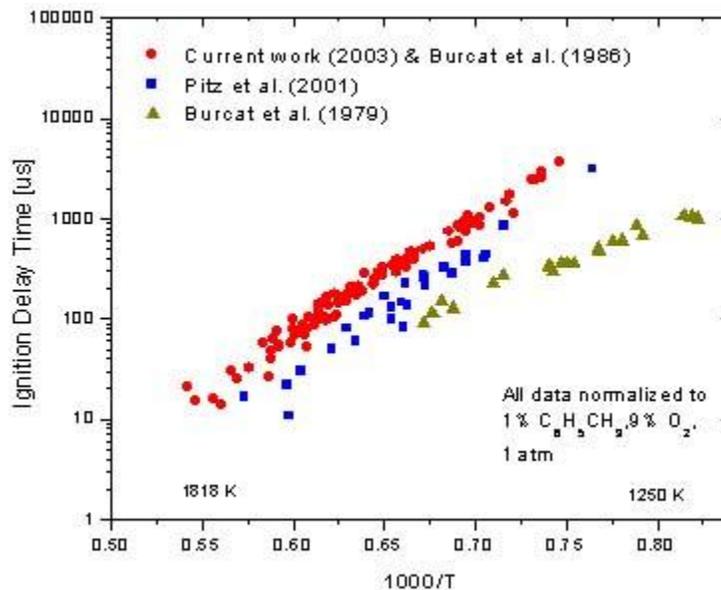


Figure 2: Normalized ignition times: all data normalized to 1% C₆H₅CH₃, 9% O₂, 1 atm.

The ability of three toluene oxidation mechanisms [5-7] to predict the measured ignition time and OH concentration data was analyzed. Sensitivity analysis using the Pitz et al. and Dagaut et al. models reveal that the OH concentration is most sensitive to the chain branching reaction: $H + O_2 \rightarrow O + OH$. We elected to update the Pitz et al. mechanism with the rate coefficient for this reaction in GRI Mech 3.0. Agreement between model and experiment was much better with GRI rate for the $H + O_2$ chain branching reaction (modified Pitz et al. mechanism), although the modified model under predicts both OH plateau concentrations slightly, see Figure 3. Figure 4 presents a comparison of measured OH time histories, with traces modeled using the modified Pitz et al. mechanism, for a series of four shocks spanning the temperature range 1600-1800 K. Agreement is excellent at moderate to high temperatures, while at low temperatures, modeled OH concentrations lag the measured time histories.

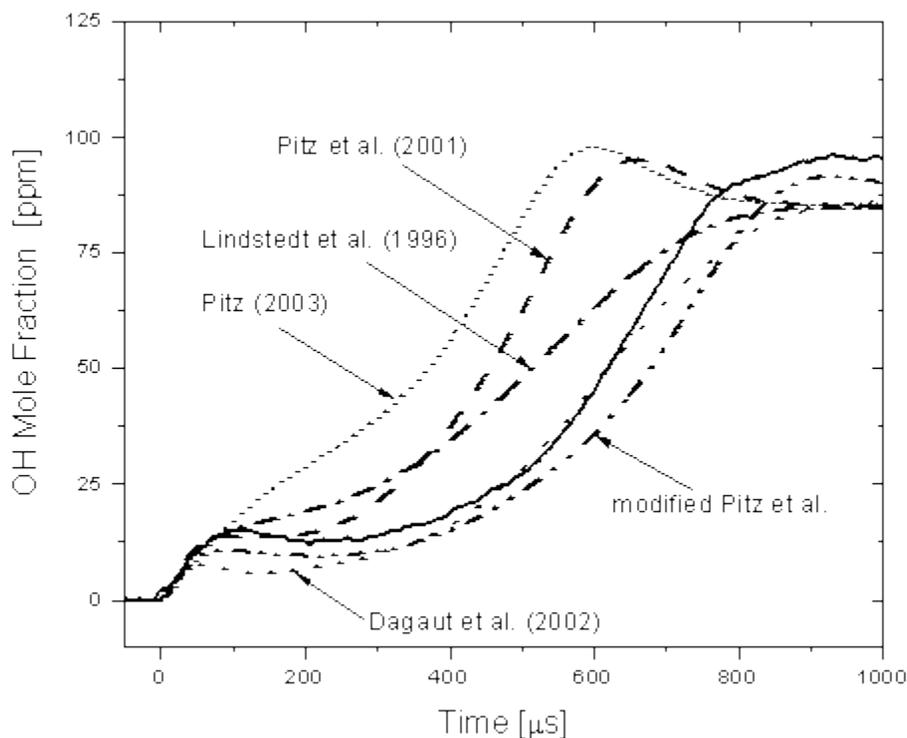


Figure 3: Time vs OH mole fraction

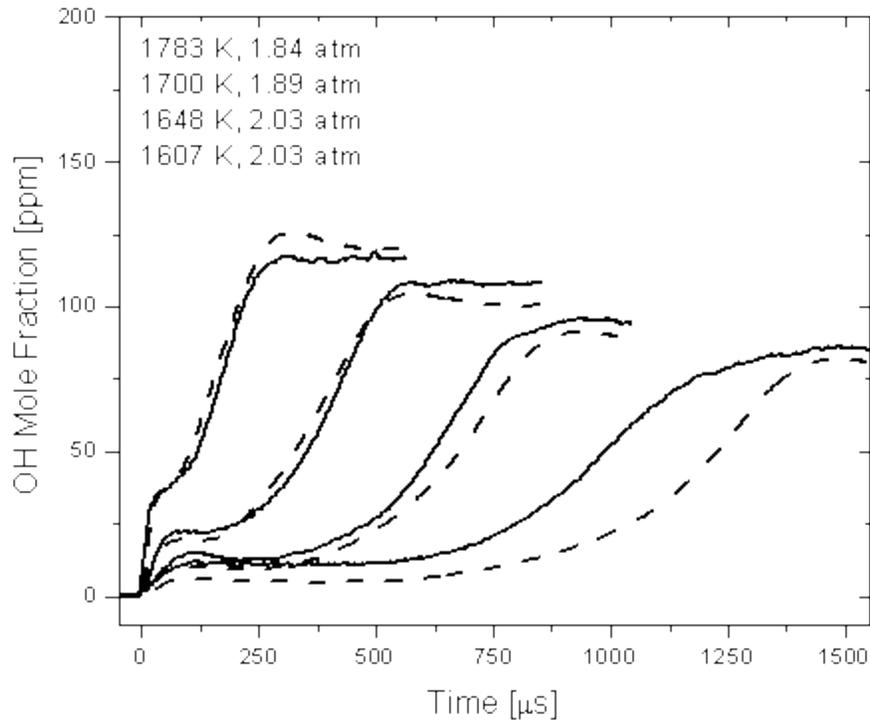


Figure 4: Time vs OH mole fraction

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