Uncertainties in rate constants of important reactions for propene oxidation

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Abstract—A detailed chemical kinetic mechanism has been developed to describe the oxidation of propene over a wide range of experimental conditions in experimental devices including a flow reactor, shock tubes, jet-stirred reactors and in flame studies. The mechanism contains uncertainties in the choice of critical rate constants for certain key reactions, which are discussed, particularly at high pressure.

I. INTRODUCTION

Propene is a key intermediate in the combustion of higher alkanes, and thus understanding the kinetics of propene is vital in the hierarchical development of the kinetic mechanisms. Propene oxidation can also contribute to soot production (and other pollutant formation). Therefore strategies for mitigating pollutant formation in advanced combustion systems depend on a complete understanding of the oxidation of alkenes such as propene.

Several studies have investigated propene pyrolysis and oxidation at high temperatures experimentally. Burcat and Radhakrishnan [1] and Qin et al. [2] separately used a shock tube to measure ignition delay times for propene oxidation in shock tubes over a temperature range of 1270–1840 K and at post-shock pressures in the range of 0.95–7.04 atm. Hidaka et al. [3] studied the thermal decomposition of propene behind reflected shocks with a temperature range of 1200–1800 K and measured the product distribution.

Davis et al. [4] studied the pyrolysis and oxidation of propene in a flow reactor at atmospheric pressure and at temperatures of 1181–1210 K and also measured laminar flame speeds of propene/air mixtures. Other flame speed studies include the study of Jomaas et al. [5] at pressures of 1, 2 and 5 atm. Saad and Stone [6] studied burning velocities of propene-air mixtures at varying temperatures (293 and 425 K) and pressures (0.5, 1.0, 2.0 and 3.5 bar).

There are several speciation studies in a jet-stirred reactor (JSR) by Dagaut and co-workers [7–9]. The most recent work by Le Cong et al. [9] investigated the oxidation of pure propene and its oxidation in the presence of CO2 and H2O at atmospheric pressure over a temperature range of 950–1450 K. The older studies [7], [8] investigated propene oxidation as a function of residence time over the temperature range 900–1200 K in the pressure range of 1–8 atm.

A. Model

AramcoMech1.4 contains 315 species and 1804 reactions. It is based on a previously published mechanism which described the oxidation of C1–C2 hydrocarbon and oxygenated hydrocarbon species [10]. A brute force sensitivity analysis was carried out to identify the important reactions for propene oxidation, described below. The recommended rate constants for the important reactions are discussed in the text were carried out using CHEMKIN PRO.

B. Sensitivity analysis

In order to highlight the important chemistry involved in propene oxidation a ‘brute force’ sensitivity analysis was performed. The sensitivity coefficient (σ) is defined as: σ = \log(τ/k) / \log(2.0/0.5) where τ the ignition delay time calculated with a factor of two increase in k, and k" is the ignition delay time calculated with a factor of two decrease in k. A negative σ indicates an overall promoting effect on reactivity, and vice versa.

C. Rate constant discussion

C3H6 + OH ⇌ Products: Fig. 1 shows that the system is sensitive to the branching ratio of the three radicals formed; the production of the resonantly stabilized allyl (3-propenyl) radical inhibits reactivity while the other two channels producing 2-propenyl (C3H5-t) and 1-propenyl (C3H5-s) respectively, lead to an increase in reactivity. We have adopted a rate constant from Vasu et al. [11], where the total rate constant was measured in a shock tube but it was not possible to distinguish the three product channels. However, this measurement was in excellent agreement with an ab-initio study by Zádor et al. [12]. Thus, we utilize the rates recommended by Zádor et al. Fig. 2 shows the difference is branching ratio from the old to the current mechanism. A relatively small change in branching ratio (Fig. 2) has a significant effect on model prediction of JSR data (Fig. 3).
Despite being the subject of several studies [1–9, 11–14], the oxidation of propene is still not well understood especially at higher pressures. There is scope for further studies into the uncertainties associated with some of the important rate constants; for example the abstraction reaction of propene with molecular oxygen and the relative branching ratios for hydrogen atom abstraction from propene by the hydroxyl radical.

D. Summary

REFERENCES