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 vitally important 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 Radhakrishan [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. Saaed 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 CO_2 and H_2O 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 pressures 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 C_1–C_2 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 Fig. 1. The sensitivity coefficient (σ) is defined as: $\sigma = \log(\tau'/\tau'') / (\log 2.0/0.5)$ where τ' the ignition delay time calculated with a factor of two increase in k, and τ'' 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.

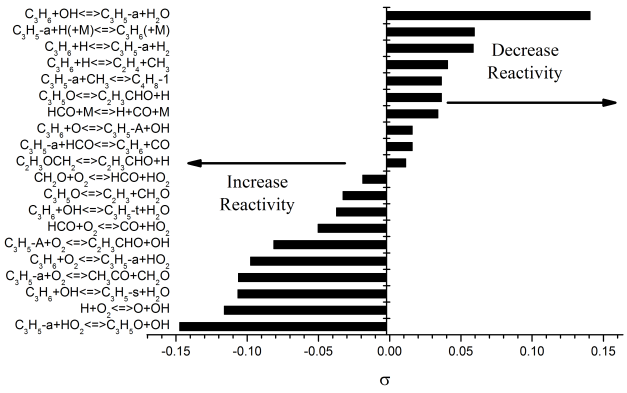

Fig. 1. Brute force sensitivity analysis of C_3H_6/air shock tube ignition delay time, $\phi = 1.0$, $p = 1$atm, $T = 1250$ K.

C. Rate consant discussion

C_3H_6 +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 (C_3H_5-t) and 1-propenyl (C_3H_5-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).

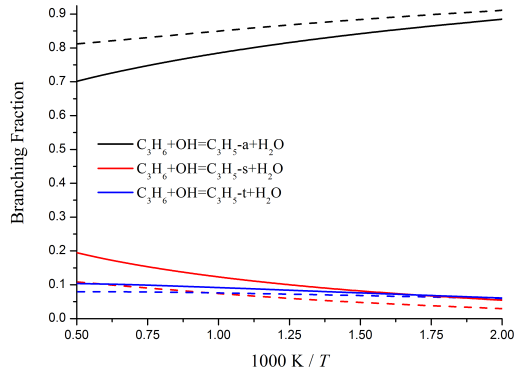

Fig. 2 Branching ratio for the reaction C_3H_6+OH as recommended in a previous version of the mechanism [10] - - - and Zádor *et al.*[12] ——

C_3H_5-a+HO_2⇔Products: The sensitivity analysis emphasizes the importance of the ally radical and hydroperoxyl system. Goldsmith *et al.* [13] theoretically investigated the kinetics of the allyl + HO_2 reaction, the thermal decomposition of C_3H_5OOH, and the uni-molecular reactions of C_3H_5O, and we use these calculated values.

C_3H_5-a+O_2⇔Products: This system has been adopted from the study of Bozzelli and Dean [14]. These reactions promote reactivity as they convert the stable allyl radical to more reactive hydroxyl, vinoxy and hydroperoxyl radicals. We believe these reactions require further investigation.

C_3H_6 +O_2⇔Products: The reaction of propene with molecular oxygen to give allyl and a hydroperoxyl radical is a very sensitive one, Fig 1. The rate constants for all three channels adopted in this work are estimated values. The activation energies are based on the heat of reaction while the pre-exponential factors are estimated. There appears to be a high level of uncertainty associated with this rate constant especially at higher temperatures. The dotted line in Fig. 3 highlights the effect the Baulch *et al.* [15] recommendation for propene has on the model prediction on propene oxidation in a JSR.

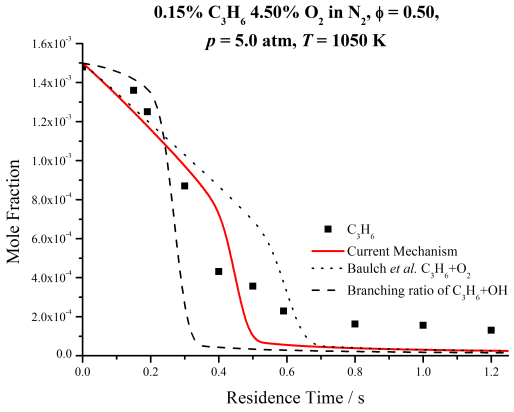

Fig. 3. Propene species profile from a JSR. —— current mechanism, - - - current mechanism plus C_3H_6+O_2 description from Baulch *et al.*, ⋯ current mechanism plus original branching fraction for C_3H_6 +OH.

D. Summary

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.

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