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An Experimental and Kinetic Study of Acetone Oxidation in a Flow Reactor

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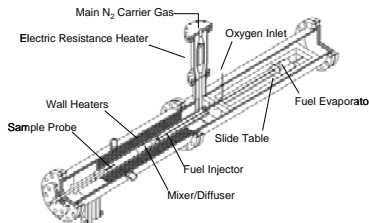


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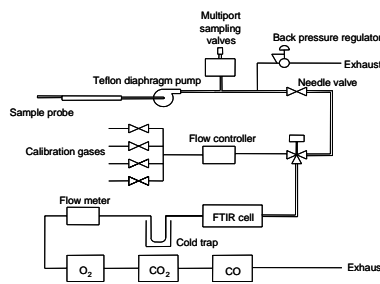
Introduction

- Acetone (CH_3COCH_3) is an important species formed during the free radical oxidation of hydrocarbons (e.g. propane, isobutene, neo-pentane) as well as some proposed oxygenated fuels (aldehydes, alcohols, ethers).
- Acetone is widely used as a marker species in two-phase vaporization/combustion studies (using PLIF), it is an important tracer species in the atmosphere, and its oxidation/pyrolysis generates reactive intermediates, such as ketene (CH_2CO).
- Understanding of acetone kinetics as well as an expanded validation database are, therefore, important. To date, however, kinetic modeling and experimental studies of this molecule under combustion-relevant conditions are scarce.
- Here, we present data obtained in a Variable Pressure Flow Reactor (VPFR) for the oxidation of acetone under high pressure (12.5 atm), and intermediate to high temperatures for a range of stoichiometries.
- It is shown how available acetone kinetic models fail to reproduce the data collected in this study.
- As a first attempt, a model based on the hierarchical nature of reacting systems has been assembled based on previous models developed in our laboratory. The model includes acetone decomposition and abstraction reactions obtained from an exhaustive literature review.
- The model is shown to adequately reproduce the present flow reactor data as well as ignition delay. Further work is warranted to optimize the model which is presently the subject of further work.

Princeton Variable Pressure Flow Reactor (VPFR)



VPFR Sampling System



Experiments and Kinetic Modeling

- New acetone oxidation experiments were performed in a flow reactor at 12.5 atm pressure to measure time histories of stable species concentrations
- The experimental apparatus and flow sampling system are shown in the figure on the left. Uncertainties in measured species are as follows: CH_3COCH_3 - $\pm 4\%$; O_2 - $\pm 2\%$; CO - $\pm 2\%$; CO_2 - $\pm 2\%$; CH_2O - $\pm 6\%$; CH_4 - $\pm 2\%$; C_2H_2 - $\pm 3\%$; C_2H_4 - $\pm 3\%$; C_2H_6 - $\pm 4\%$.
- Experiments were performed at 960 K for equivalence ratios of 0.6, 1.0, and 1.6 at an initial fuel concentration of 1,800 ppm.
- A reactivity experiment was also performed for $\phi = 1.0$ scanning a temperature range from 530 to 950 K.
- The initial model developed, presented here, consists of 46 species undergoing 248 reversible reactions.
- The model was assembled in a hierarchical manner and is built upon a $\text{H}_2/\text{C}_1\text{-C}_2$ submodel recently developed in our laboratory based on reaction schemes for H_2 [1], $\text{H}_2/\text{CO}/\text{CH}_3\text{O}/\text{CH}_3\text{OH}$ [2], and $\text{C}_2\text{H}_5\text{OH}$ [3]. These baseline models have recently been used to generate a comprehensive dimethyl ether model [4].
- Acetone-specific kinetic steps include reaction with O_2 as well as thermal decomposition as initiation processes. Interactions with the radical pool include abstractions by H , O , OH , HO_2 , CH_3 , CH_3O , and C_2H_5 . Rates were obtained from a wide literature survey (see table). The rate expression of abstraction by OH was fitted to available experimental data using least-squares analysis.
- Only acetylonyl (CH_3COCH_2) decomposition is considered

Reaction: (cm ³ /mol·sec/cal): (°) - This study	A	n	E _a	Ref.
$\text{CH}_3\text{COCH}_3 = \text{CH}_3 + \text{CH}_3\text{CO}$	6.310E-16	0.00	8.145E+04	[5]
$\text{CH}_3\text{COCH}_3 + \text{H} = \text{CH}_3\text{COCH}_2 + \text{H}_2$	5.630E+07	2.00	7.700E+03	[6]
$\text{CH}_3\text{COCH}_3 + \text{O} = \text{CH}_3\text{COCH}_2 + \text{OH}$	1.000E+13	0.00	5.961E+03	[7]
$\text{CH}_3\text{COCH}_3 + \text{OH} = \text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}$	1.783E+00	3.96	1.369E+03	(*)
$\text{CH}_3\text{COCH}_3 + \text{O}_2 = \text{CH}_3\text{COCH}_2 + \text{HO}_2$	1.200E+14	0.00	4.600E+04	[6]
$\text{CH}_3\text{COCH}_3 + \text{HO}_2 = \text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}_2$	1.700E+13	0.00	2.046E+04	[6]
$\text{CH}_3\text{COCH}_3 + \text{CH}_3 = \text{CH}_3\text{COCH}_2 + \text{CH}_4$	3.162E+13	0.00	1.648E+04	[5]
$\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{O} = \text{CH}_3\text{COCH}_2 + \text{CH}_3\text{OH}$	1.000E+11	0.00	7.000E+03	[6]
$\text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5 = \text{CH}_3\text{COCH}_2 + \text{C}_2\text{H}_6$	1.229E+11	0.00	4.270E+03	[8]
$\text{CH}_3\text{COCH}_3 = \text{CH}_3\text{CO} + \text{CH}_3$	1.000E+14	0.00	3.100E+04	[6]

Results

- Figures 1-4 show data from the present flow reactor experiments compared against model results. As opposed to model predictions obtained using models available from Lawrence Livermore (see dashed line in Fig. 1), acetone does not exhibit NTC behavior and the present model captures this trend.
- Comparison against species time histories obtained for $\phi = 0.6, 1.0$, and 1.6 (Figs. 2, 3, and 4 respectively) show relatively good agreement although the predictive capability of the model deteriorates as the equivalence ratio increases. Less satisfactory are the comparisons against water (not shown for clarity) which are considerably overpredicted (see Fig. 1).
- Comparison against a recently published acetone model (developed for high temperature applications) [9] shows its inability to predict the present results as evidenced by the slow fuel evolution shown by the dashed line in Fig. 2.
- Figs. 5 and 6 show model predictions against data collected in a shock tube [9]. Ignition delays are relatively well reproduced for both pure acetone as well as hydrogen-doped acetone/ O_2/Ar mixtures (Fig. 5). Stable species measured in the single-pulse shock tube are shown in Fig. 6; good agreement is observed, however, the model overpredicts ketene (CH_2CO) and ethylene while underpredicting methane.
- Results from sensitivity analyses under both flow reactor and shock tube conditions are shown in Figs. 7 and 8. Figure 7 shows the sensitivity of selected species for the fuel-rich case shown in Fig. 4 at 65% fuel consumption. The system is sensitive to reactions involving methyl, formaldehyde, and the formyl radical. In addition, and not surprisingly, ketene plays an important role in acetone oxidation. Figure 8 shows ignition delay sensitivity for the case shown in Fig. 5 (Mixture D, 1500 K). Most of the important reactions are at the small molecular level ($C < 2$) with acetone thermal decomposition and abstractions by H and CH_3 playing an important role.

Summary

- New high pressure acetone oxidation experiments have been performed in a flow reactor.
- A preliminary kinetic model has been developed based on the hierarchical nature of reacting systems and shown to reasonably reproduce the present flow reactor data as well as data obtained in other experimental systems.
- Additional refinement is needed at the small molecular level. Sensitivity analyses suggest that ketene kinetics are important for acetone oxidation which is the subject of further studies currently underway.

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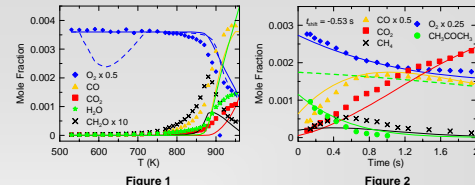


Figure 1

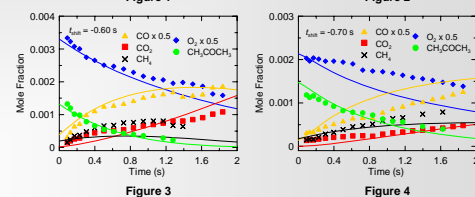


Figure 2

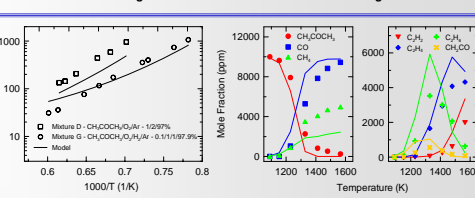


Figure 3

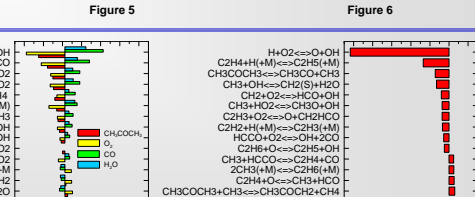


Figure 4

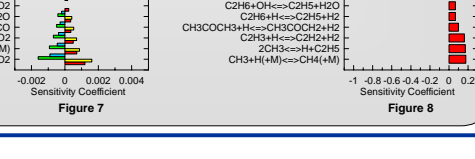


Figure 5

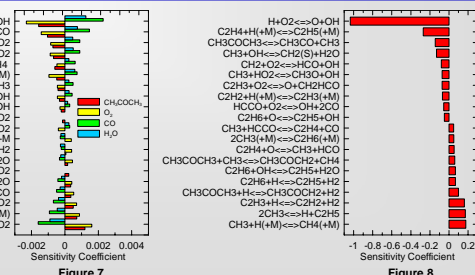


Figure 6

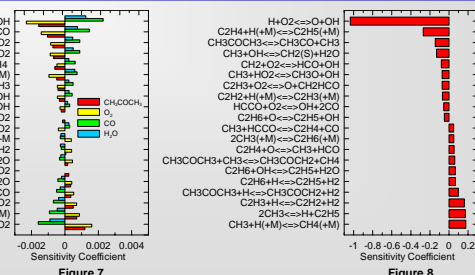


Figure 7

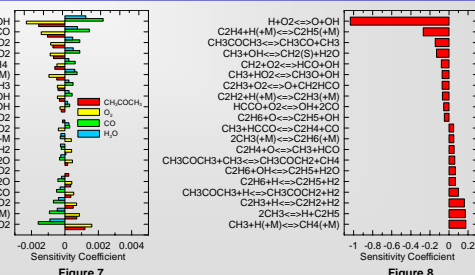


Figure 8