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Preliminary Results from the Modeling of the Role of Cyclopentadienyl in the Combustion of Cyclopentadiene

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Introduction

Soot formed by hydrocarbon combustion are a significant source of particulate matter emissions in the US and vehicular emissions are the major source of nanoparticles that penetrate deeply into the lungs and even into the bloodstream. There is an urgent need to reduce particulate matter emissions because local airborne particulate concentrations correlate directly with increased mortality due to cancer, cardiac and pulmonary diseases. The combustion of aromatic compounds in transportation fuels is a major source of Polycyclic Aromatic Hydrocarbons (PAHs), which are the precursors to soot. Aromatic compounds as octave enhancers make up 25% by volume of Aromatic Hydrocarbons (PAHs), which are the precursors to soot.

The combustion of aromatic pollutants formed during its combustion.

The partial flux map below shows how a significant fraction of the cyclopentadienyl ring is oxidized to n-butenyl, which isomerizes to i-butenyl and then can either gain or lose a hydrogen atom, producing 1,3-butenediene and vinyl acetylene respectively.

We improved the ability of the present model to predict the emissions of the carcinogenic 1,3-butenediene by tuning the i-butenyl + CPD reaction rate. The original rate constant, 4.5x10^19 cm^3 mol^-1 s^-1, was decreased to 2.1x10^18 cm^3 mol^-1 s^-1. Other reactions, such as n-butenyl + CPD, were also tested but the results were most sensitive to the i-butenyl + CPD reaction rate.

The prediction of the overall reaction is highly sensitive to the choice of the thermodynamic parameters for cyclopentadienyl. We examined six literature values for the pair \( \Delta H_{298}^\circ, S^\circ \) for cyclopentadienyl. The present work supports a value of \( S^\circ \) near the mean of the literature values but recommends a value of \( S^\circ \) at the high end. The figure below shows the results when \( S^\circ \) = 261, 285 & 308 J/mol/K, and \( \Delta H_{298}^\circ \) = 243 kJ/mol.

We also report on the results of our ongoing investigation into the thermodynamics of the cyclopentadienyl radical and show how its entropy value can be tuned with the data. We chose to tune the entropy since the literature knowledge of \( \Delta H_{298}^\circ \) greatly exceeds that of \( \Delta S_{298}^\circ \). The entropy is significant because at the temperatures of this study, \( S^\circ \) is just as important as \( \Delta H_{298}^\circ \) in the calculation of \( \Delta G^{\circ} \) and the reverse rate constants.

The mechanism below shows how decreasing the rate of hydrogen abstraction from CPD reduces the production of 1,3-butenediene and increases the production of vinyl acetylene.

Results and Discussion

Chemical kinetic samples were obtained using the Princeton Flow Reactor (shown below) in the form of detailed concentration versus time data in order to elucidate the importance of specific elementary reactions. The reactor operates at atmospheric pressure and in the temperature regime at which pollutants form and are destroyed in internal combustion and jet engines.

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Modeling

The role of cyclopentadienyl is a weak link in current aromatic oxidation models. To correct this situation, a detailed, quantitative, zero-dimensional kinetic C12 sub-model, with new thermodynamic parameters for 16 species and 137 new and modified reactions, was integrated with literature models for 1-methyl napthalene, tolane, and C5 oxidation. The combined model, with 137 species and 720 reactions, was compared with the experimental results and flux analyses. The model includes detailed oxidation and pyrolysis chemistry of methyl naphthalene, naphthalene, indene and allyl aromatics that are important intermediates in the combustion scheme. A number of species and isomers have been included which have not been dealt with in less comprehensive literature models. Previously reactants, products and rate constants for five combination reactions of two C9 species had been determined and eleven reaction rate constants had been derived using the model from the experimental data. The present results represent further refinement of the model by tuning an additional reaction rate to the data to improve the prediction of important intermediates.

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Conclusions

Refinement of the rate constant for i-butenyl + CPD enables a more accurate calculation of the emissions of 1,3-butenediene. Modeling the overall oxidation rate of cyclopentadienyl by honing its entropy represents an advance in predicting the pollutants formed during its combustion. The model will be a building block for improvements in pollution predictions of aromatic fuels.

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