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IGNITION KINETICS IN FUELS OXIDATION

(ARO Grant No. W911NF-04-1-0151)

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SUMMARY/OVERVIEW

This program studies fundamental chemical kinetics as well as its individual and coupled effects with aerodynamics on laminar nonpremixed ignition and flame propagation for hydrocarbons, through experimental, computational, and theoretical approaches. During the reporting period, three projects were undertaken, namely: (1) Experimental determination of high-pressure laminar flame speeds and kinetic modeling of carbon-monoxide / hydrogen combustion; (2) experimental and computational determination of the ignition temperatures and reaction mechanism of 1,3-butadiene at atmospheric and elevated pressures; and (3) experimental and computational studies on the ignition of the butene isomers.

TECHNICAL DISCUSSION

1. Experimental determination of high-pressure laminar flame speeds and kinetic modeling of carbon-monoxide / hydrogen combustion

The objective for the present study is to experimentally determine high-pressure laminar flame speeds and update $CO-H_2$ mechanism for enhanced accuracy and comprehensiveness. The experimental data, obtained in our high-pressure combustion chamber up to 40 atm, are shown in Figs. 1 and 2.

A detailed reaction mechanism was developed based on the latest evaluation of the kinetic data for combustion modeling and recently published literature. The reaction of OH with CO is responsible for the major fraction of energy release in the oxidation of hydrocarbons to CO_2 and H_2O , and the reaction rate is the most sensitive for the prediction of $CO-H_2$ flame speeds. The reaction $H+O_2+M \rightarrow HO_2+M$ provides another route for the conversion of CO to CO_2 through $CO+HO_2 \rightarrow CO_2+OH$ at high pressures or in the initial stages of CO oxidation. However, the rate constant for $CO+HO_2$ at temperatures above 800 K is limited to indirect determinations. To further investigate this reaction rate, we performed high-level *ab initio* calculations and follow the reaction mechanism with the first stage in the reaction being the formation of a free radical intermediate $HO_2+CO \rightarrow HOOC\bullet O$ which then decomposes to yield the products, and with the rate of formation of the intermediate equal to the formation of the products. By using the MP2(full)/6-31G(d,p) optimized geometries and canonical transition state theory, we calculated this rate constant to be $k = 1.15 \times 10^5 T^{2.2785} \exp(-17.55 \text{ kcal/RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 – 2500 K.

The modeling results indicated that our current kinetic model accurately predicts the measured flame speeds and the non-premixed counterflow ignition temperatures determined in our previous study (Fig. 3) as well as homogeneous system data from literature, such as concentration profiles from flow reactor and ignition delay time from shock tube experiments.

This work is reported in Publication No. 1.

2. Experimental and Computational Determination of Counterflow Ignition Temperatures at Atmospheric and Elevated Pressures, and Reaction Mechanism of 1,3-butadiene

1,3-Butadiene is a common product of hydrocarbon combustion and an industrial chemical used to produce polymers such as poly-butadiene and styrene-butadiene rubbers. There have been quite a number of kinetic studies of 1,3-butadiene, although they are mainly for homogeneous systems. Few kinetic studies have been performed for inhomogeneous systems, particularly tailored for low- to intermediate-

temperature chemistry. In the present study, nonpremixed ignition of 1,3-butadiene was investigated experimentally employing the counterflow configuration.

Specifically, the ignition temperature of nitrogen-diluted 1,3-butadiene by heated air in counterflow was experimentally determined for system pressures from 1.0 to 5.1 atmospheres at pressure-weighted strain rates from 100 to 240 s⁻¹. These experimental data were compared to calculations based on the mechanism developed by Laskin *et al.* and the results are shown in Figs. 4 and 5. In general, the Laskin-mechanism over-predicts the ignition temperature by 25-40K, and the differences become slightly larger at higher pressures and lower temperatures. Sensitivity analyses showed that the ignition of 1,3-butadiene is sensitive not only to the H₂/CO chemistry as well as the reaction pathways involving ethylene oxidation, and O addition to and H abstraction of 1,3-butadiene, but is also to the binary diffusion between 1,3-butadiene and nitrogen since it determines the amount of diffusion-constrained fuel available for ignition.

The attempt to obtain a reduced mechanism has evolved into a substantial and rewarding effort in that a new algorithm combining DRG and sensitivity analysis was developed that is capable of identifying skeletal mechanisms of minimal size for given accuracy requirements. A 46-species skeletal mechanism was thus developed which was further simplified to a 30-step reduced mechanism based on QSS assumptions. These two mechanisms were then validated against the detailed mechanism for both auto-ignition and PSR under a variety of parameter ranges, and were further validated for heterogeneous systems: counterflow ignition and laminar flame speeds. Excellent agreements between these two mechanisms and the detailed one were found over extensive parametric ranges. The error is less than 4K for counterflow ignition temperatures and 2cm/s for laminar flame speeds, and the reduction error under atmospheric pressure is smaller than the difference in detailed mechanism and experiment data. Both mechanisms conserve all the important reaction pathways and major species constituting the detailed mechanism, and as such, they provide a more efficient platform for the study of the controlling mechanisms and expedited combustion simulations of 1,3-butadiene.

This work is reported in Publication No. 2.

3. Experimental and Kinetics Study of Ignition Temperatures of Butene Isomers at Atmospheric and Elevated Pressures

Previous studies on the effects of molecular structure on ignition have been mainly on alkanes. Similar studies of alkenes, however, have been relatively few, even though they are the major intermediates of alkane oxidation and are important fuels themselves. In view of the need for further information on the effects of molecular structure of alkenes on ignition, we have conducted a systematic study on the ignition of the four isomers of butene, namely 1-butene, cis-2-butene, trans-2-butene, and isobutene. Butene isomers were selected for study because butene is the smallest alkene which has more than one isomer.

Specifically, the ignition temperatures of the four butene isomers were determined in the counterflow. The measured ignition temperatures were found to increase in the order of 1-butene, 2-butenes and isobutene. The ignitability of cis-2-butene and trans-2-butene cannot be compared because the difference between their ignition temperatures is less than 7 K, which is within the $\pm 2\sim 5$ K repeatability range of the experimental data. Nevertheless, cis-2-butene was determined to be slightly easier to ignite than trans-2-butene (Figs. 6 and 7).

A thorough comprehension of the observed trend of butene ignition is however hampered by the lack of adequately validated mechanism for the C₄ hydrocarbons. Alternatively, we performed the kinetic analysis on three important pathways for ignition, namely the initiation by O₂ abstraction, and HO₂ and OH addition, as numerous literatures have illustrated their importance on ignition. While any single pathway or even all three together is not comprehensive enough to predict ignition, it is nevertheless recognized that a study of the present nature does yield useful insights into ignition. For example, the calculated reaction rate constants (*k*) for four abstraction reactions are shown in Fig. 8 as functions of temperature. It is seen that they vary with temperature and increase in the order of isobutene, trans-2-butene, 1-butene and cis-2-butene in the lower-temperature ignition regime. The trend for these calculated rate constants can be understood by the allylic C-H bond energy and the number of equivalent H atoms in the butenes. We first note that since the differences between the allylic C-H bond energies for the four butenes are small, less than 5 kcal/mol, there is no dramatic difference between their rates for the H-abstractions. Secondly, the lower value of the bond dissociation energy generally corresponds to the higher abstraction rates except that cis-2-butene has higher values of *k* than 1-butene. This exception is

due to the different number of equivalent H atoms which affects the Arrhenius factor: 2-butenes and isobutene all have six equivalent allylic H atoms, but 1-butene has only two and therefore has a smaller A factor. Therefore, except for the fact that cis-2-butene is slightly more reactive than 1-butene, the trend for the reaction rate constants of the H-abstraction reactions qualitatively agrees with our experimental results on ignitability. The present study has provided reliable thermochemical and kinetic data, which are essential components in the future development of C_4 hydrocarbon mechanisms.

This work is reported in Publication No. 3.

JOURNAL PUBLICATIONS

- [1] "High-pressure laminar flame speeds and kinetic modeling of carbon-monoxide / hydrogen combustion" by H. Y. Sun, S. I. Yang, and C. K. Law, *Proc. Combust. Inst.* 31, in press.
- [2] "Experimental counterflow ignition temperatures and reaction mechanisms of 1,3-butadiene" by X. L. Zheng, T. F. Lu, and C. K. Law, *Proc. Combust. Inst.* 31, in press.
- [3] "Ignition of the butene Isomers: an experimental and kinetics study" by X. L. Zheng, H. Y. Sun, and C. K. Law, submitted.
- [4] "Thermochemical and kinetic analyses on oxidation of isobutenyl radical and 2-hydroperoxy-methyl-2-propenyl radical" by X. L. Zheng, H. Y. Sun, and C. K. Law, *J. Phys. Chem. A*, 2005; 109, 9044-9053.

4. Figures

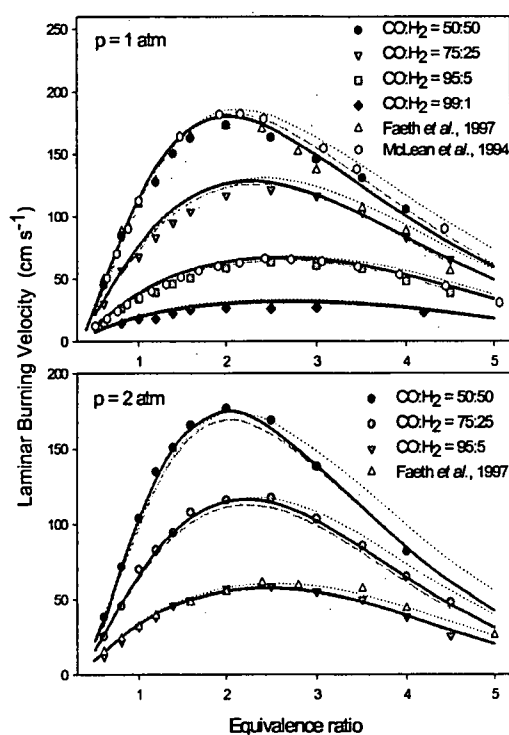


Fig. 1. Measured and calculated laminar flame speeds vs. equivalence ratio for different CO/H₂/air mixtures at 1 and 2 atmospheres.

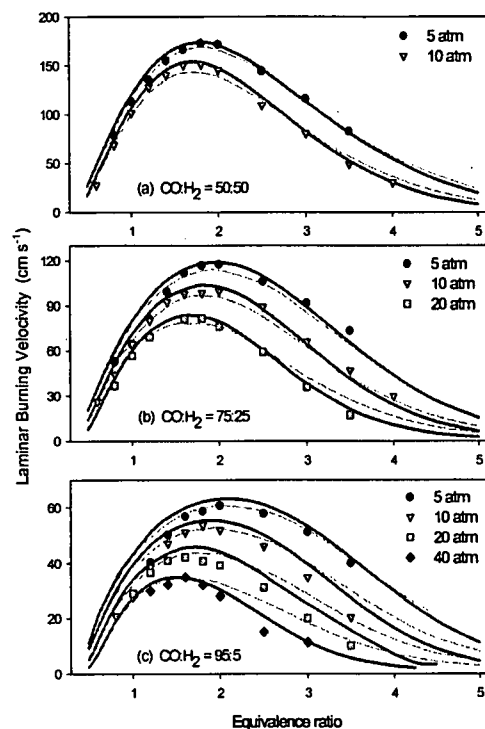


Fig. 2. Measured and calculated laminar flame speeds vs. equivalence ratio for different CO/H₂/He/O₂ mixtures at 5, 10, 20, and 40 atmospheres

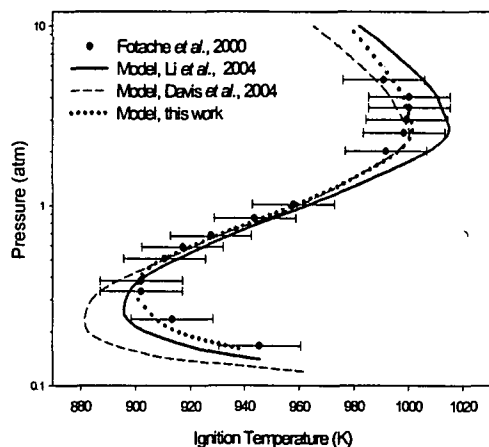


Fig.3. Comparison of calculated ignition temperatures vs. pressure with the experimental data at the strain rate of 100 s^{-1} for 5% H_2 in CO .

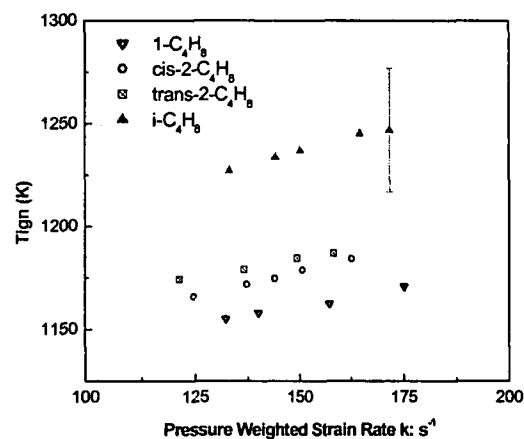


Fig.6. Effect of strain rate on the ignition temperatures for butene isomers. Conditions: 5.9% Fuel in N_2 and 2.4atm.

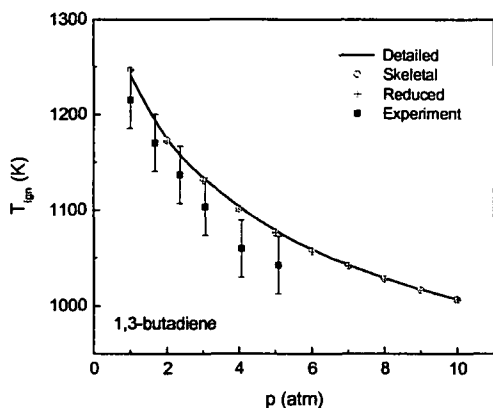


Fig.4. Ignition temperatures of 5.9% 1,3-butadiene in N_2 as a function of pressure. Condition: pressure weighted strain rate of 150 s^{-1} .

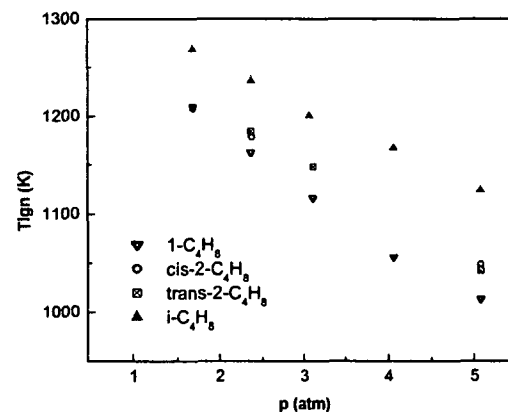


Fig.7. Effect of pressure on the ignition temperatures for butene isomers. Conditions: 5.9% Fuel in N_2 and $k=150 \text{ s}^{-1}$.

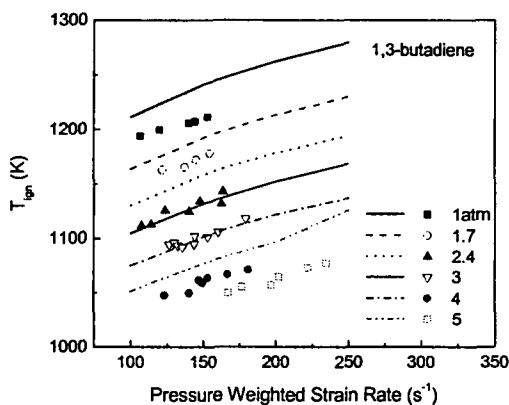


Fig.5. Ignition temperatures of 5.9 % 1,3-butadiene in N_2 as a function of pressure-weighted strain rate under different pressures.

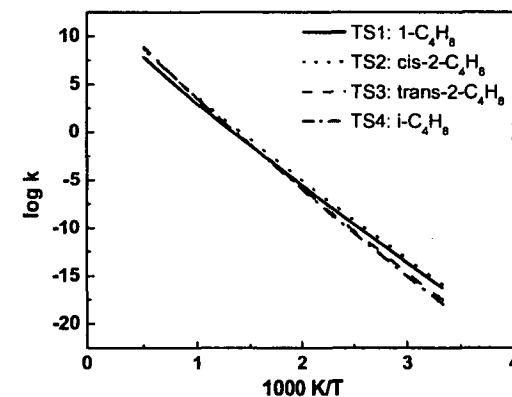


Fig.8. Reaction rate constants as functions of temperature for the H abstraction reaction by oxygen: $\text{C}_4\text{H}_8 + \text{O}_2 = \text{C}_4\text{H}_7 + \text{HO}_2$.