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CONF-850767--5

UCRL--91677

DE87 008137

[illegible] 1987

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This paper was prepared for submittal to
15th International Symposium on Shock Waves
and Shock Tubes, University of California,
Berkeley, CA July 29-August 1, 1985

July, 1985

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Abstract

The current capabilities of kinetic modeling of hydrocarbon oxidation in shock waves are discussed. The influence of molecular size and structure on ignition delay times are stressed. The n-paraffin fuels from CH_4 to n-C_5H_{12} are examined under shock tube conditions, as well as the branched chain fuel isobutane, and the computed results are compared with available experimental data. The modeling results show that it is important in the reaction mechanism to distinguish between abstraction of primary, secondary and tertiary H atom sites from the fuel molecule. This is due to the fact that both the rates and the product distributions of the subsequent alkyl radical decomposition reactions depend on which H atoms were abstracted. Applications of the reaction mechanisms to shock tube problems and to other practical problems such as engine knock are discussed.

INTRODUCTION

The analysis of shock tube experiments often involves the use of detailed chemical kinetic reaction mechanisms. Shock tube ignition delay time measurements and their variation with temperature, density, and composition provide essential tests of reaction mechanisms for hydrocarbon and other fuels. Numerical modeling studies are now using these reaction mechanisms, tested against shock tube experiments, to examine the structure and other properties of gaseous detonation waves, engine knock in internal combustion engines, and other practical combustion systems.

In a particularly well formulated study, Burcat et al.[1] examined the shock tube ignition delay of a series of n-alkanes from methane to n-pentane, in oxygen-argon mixtures which were chosen to approximate fuel-air mixtures. The general conclusions of this work were that methane had a much longer ignition delay than the other fuels, ethane had a slightly shorter delay period than the other fuels, and the other n-alkanes all had very similar ignition delay times. The present numerical modeling study was intended to simulate the experimental study of Burcat et al. and interpret the results in terms of the elementary chemical kinetic steps which control the overall rates of reaction.

NUMERICAL MODEL AND REACTION MECHANISM

The detailed reaction mechanism used in these computations was based on the previous mechanism for n-butane[2], which has been tested extensively against experimental results for a variety of conditions. The mechanism was extended to include n-pentane, assuming that the rates of primary and secondary H atom abstraction in n-pentane are the same as in propane and n-butane. The decomposition reactions of the pentyl radicals were assumed to follow the "one bond removed" rule of Dryer and Glassman[3], leading immediately to C_3 and C_2 radicals and olefins.

Subsequent reactions of these C_2 and C_3 species have been tested extensively in the mechanism. An additional fuel, not considered in the experimental study of Burcat et al., is the branched chain species iso-butane (methyl propane), an isomeric form of butane. The interest in branched chain hydrocarbon fuels was motivated by the experimental fact that straight chain hydrocarbons tend to ignite more rapidly than branched chain fuels with the same overall composition. No shock tube ignition delay data were available to test the model predictions for iso-butane, but the mechanism for iso-butane oxidation has been tested against experimental data in the turbulent flow reactor[4] and should be reasonably accurate under shock tube conditions. It is also well known that branched chain hydrocarbon fuels tend to be more resistant to engine knock in internal combustion engines, so the applications of these reaction mechanisms to practical situations also tend to validate the model predictions.

The ignition delay calculations were carried out using the HCT program[5], assuming constant volume in the gaseous mixtures under reflected shock wave conditions. The variations in shock tube ignition delay times for methane, ethane, and propane have been examined in previous numerical studies[6,7], and the present mechanism reproduced the past results for these fuels. Results of modeling studies of the oxidation of n-butane[2] were incorporated into the present reaction mechanism, and further extensions to n-pentane and iso-butane were also included into the reaction mechanism[8].

RESULTS

The detailed chemical kinetic reaction mechanism was able to reproduce the observed ignition delay times for all of the fuels which were studied experimentally. The post-shock density was 3.54×10^{-3} gm/cm^3 for each mixture, and the initial temperatures were varied from 1150 K to 1700 K, except for methane, where the initial temperature ranged from 1500 K to about 1900 K. Computed results for methane and ethane (and for mixtures of methane and ethane) agree very well with experimental results[6]. Results for the methane mixtures are shown in Fig. 1, and results for ethane and mixtures of methane and ethane are reported in Reference 6. Computations presented previously[9] showed that the ignition of natural gas, which contains small but not negligible amounts of propane together with methane and ethane, could also be simulated well with the present reaction mechanism. Computed results for propane ignition were presented in earlier work[7], and the predictions are compared with experimental results of Burcat et al. in Fig. 1. Finally, comparisons between experimental and computed results for n-butane and n-pentane are summarized in Fig. 2. Also shown are the computed results for ignition of iso-butane, showing that the ignition of iso-butane is distinctly slower than the ignition of n-butane or n-pentane.

The overall conclusion of these comparisons between experimental and computed results is that the numerical model is accurately reproducing the experimental data for all of the fuels studied. Furthermore, the model is also indicating that iso-butane has a significantly longer ignition delay period than either n-butane or n-pentane. Although there are no comparable experimental data for comparison, the conclusion is that the numerical model and detailed reaction mechanism adequately reproduce the available experimental data.

For each fuel, the variation in ignition delay period can be traced directly to the details in the reaction mechanism. The case of methane has been studied extensively and can be summarized here very briefly. Every methane molecule eventually produces a methyl radical; these radicals are very difficult to oxidize further, particularly since recombination of methyl radicals to produce ethane

$$CH_3 + CH_3 = C_2H_6$$

is very important. Because of this recombination, methane oxidation and ignition is not really typical of the ignition of most simple hydrocarbon fuels. In the case of ethane, all H atom abstraction reactions produce ethyl radicals, which subsequently decompose under shock tube conditions

$$C_2H_5 + M = C_2H_4 + H + M$$

to produce H atoms. These H atoms then can react with molecular oxygen to provide chain branching through the reaction

$$H + O_2 = O + OH \quad .$$

Therefore, all H abstractions from ethane lead to chain branching, explaining why ethane ignition is faster than all other n-alkanes.

For all of the higher hydrocarbon fuels, distinction must be made between different H atom sites in the fuel molecule. For propane, the two types of propyl radicals which can be produced are the n-propyl radical, which leads primarily to methyl radicals and ethene

$$n\text{-}C_3H_7 = CH_3 + C_2H_4$$

while isopropyl radicals lead to propene and H atoms

$$i\text{-}C_3H_7 = C_3H_6 + H \quad .$$

Since the methyl radicals lead to ethane formation through the reaction

$$CH_3 + CH_3 = C_2H_6$$

while H atoms lead to chain branching, it is clear that production of n-propyl radicals leads to retarding of the rate of ignition while production of iso-propyl radicals provides overall acceleration of the rate of ignition. Therefore, the key to describing propane ignition is the description of the relative rates of primary to secondary H atom abstraction reactions.

In similar terms, the ignition of n-butane and n-pentane can also be shown to depend on the relative rates of primary and secondary H atom abstractions. In the case of n-butane, abstraction of a primary H atom leads to the production of H atoms and chain branching through

$$\begin{aligned} p\text{-}C_4H_9 &= C_2H_4 + C_2H_5 \\ C_2H_5 &= C_2H_4 + H \end{aligned}$$

while the abstraction of a secondary H atom leads to chain termination

$$s\text{-}C_4H_9 = CH_3 + C_3H_6 \quad .$$

In the case of n-pentane, a new element appears. All of the secondary H atoms are not the same. The abstraction of a primary H atom leads to

$$\begin{aligned} p\text{-}C_5H_{11} &= C_2H_4 + n\text{-}C_3H_7 \\ n\text{-}C_3H_7 &= C_2H_4 + CH_3 \end{aligned}$$

and chain termination. However, the abstraction of an H atom attached to a secondary C atom leads to

$$\begin{aligned} 2\text{-}C_5H_{11} &= C_3H_6 + C_2H_5 \\ C_2H_5 &= C_2H_4 + H \end{aligned}$$

and chain branching, while the abstraction of a symmetric H atom leads to

$$3\text{-}C_5H_{11} = {}_1C_4H_8 + CH_3$$

and chain termination. Therefore, the rate of chain branching depends very sensitively on the relative rates of H atom abstraction from the parent fuel molecule at each H atom site.

The same trend applies in the case of iso-butane. There are nine identical primary H atoms in iso-butane. At the elevated temperatures of shock tube conditions, the dominant reaction is the abstraction of a primary H atom, although at lower temperatures the abstraction of a tertiary H atom is most important. After abstraction of a primary H atom, the alkyl radical decomposition is primarily

$$i\text{-}C_4H_9 \;=\; C_3H_6 + CH_3$$

which results in chain termination. Only the t-butyl radical leads to chain branching through

$$t\text{-}C_4H_9 \;=\; i\text{-}C_4H_8 + H \qquad .$$

However, at the temperatures encountered in shock tubes, the production of isobutyl radicals is strongly preferred. The strong degree of chain termination which is the result of production of isobutyl radicals explains the slower rate of ignition for iso-butane.

Two practical combustion problems can be related to the rate of ignition of fuel-oxidizer mixtures under shock tube conditions. The first of these concerns the ignition of fuels in detonation waves. Previous modeling analysis[10] has shown how shock tube ignition delay times can be related to detonation properties including detonation limits, critical tube diameters, and minimum energy for initiation of detonation. Overall, these results indicate that branched chain hydrocarbon fuels should be less detonable than their straight chain counterparts. Specifically, methane is predicted to be much less detonable than the other fuel-oxidizer mixtures, which is certainly well established experimentally. In addition, the detonation parameters of the other n-alkane fuels are predicted to be very similar to each other, also in agreement with experimental observations. Although not available for comparison with experimental results, the model predicts that iso-butane mixtures should be less susceptible to detonation than the n-alkane mixtures.

The second application area in which ignition calculations are of particular interest is that of engine knock. In previous modeling studies of engine knock[11,12], it has been shown that the rate of ignition of fuel-air mixtures at elevated pressures can be related to the susceptibility of a mixture to engine knock. It is well known that straight chain fuels are more likely to knock than are branched chain fuels, and the present reaction mechanism indicates that these differences are due to differences in the product channels for the alkyl radicals which are produced. At the elevated pressures encountered in knocking engines, H atoms produced from ethyl radicals do not decompose into H atoms but rather react with O_2 molecules to produce HO_2 radicals. These radicals then react further with the fuel to produce H_2O_2 which then decomposes further to produce two OH radicals

$$H_2O_2 + M \;=\; OH + OH + M \qquad .$$

The result of this sequence is a net production of radical species and an increase in the rate of fuel oxidation. At the high pressures which are typical of engine knock, the production of HO_2 is preferred in comparison to the chain branching reaction producing O + OH, and the rate of fuel oxidation is more sensitive to variations in the abstraction of H atoms by HO_2 than the abstraction of H atoms by other radicals such as OH, H and O.

CONCLUSIONS

The reaction mechanism which has been developed in earlier modeling studies has been shown to be applicable to the shock tube ignition of a family of hydrocarbon-air mixtures. This mechanism correctly reproduces the observed shock tube ignition delay times reported by Burcat et al.[1] for a fairly wide range of hydrocarbon fuels. Since the mechanism has been so extensively tested for hydrocarbon ignition, it can be applied to other studies of shock tube ignition of fuel-air mixtures. Even more important, these reaction mechanisms, validated through comparisons with shock tube experiments, have been shown to be applicable to a variety of important and practical combustion environments. The shock tube data therefore provide an essential means of testing detailed reaction mechanisms under coditions that are impossible to achieve under other conditions. The relationships between shock tube conditions and detonation phenomena and engine knock problems make the study of shock tube phenomena of particular importance, and the present paper outlines the essential elements of these reaction mechanisms. Extension of the present formalism to more complex fuels should be very straightforward, given the fundamental basis provided by the reaction mechanisms for the more simple fuels discussed in this paper.

ACKNOWLEDGMENTS

This work was carried out under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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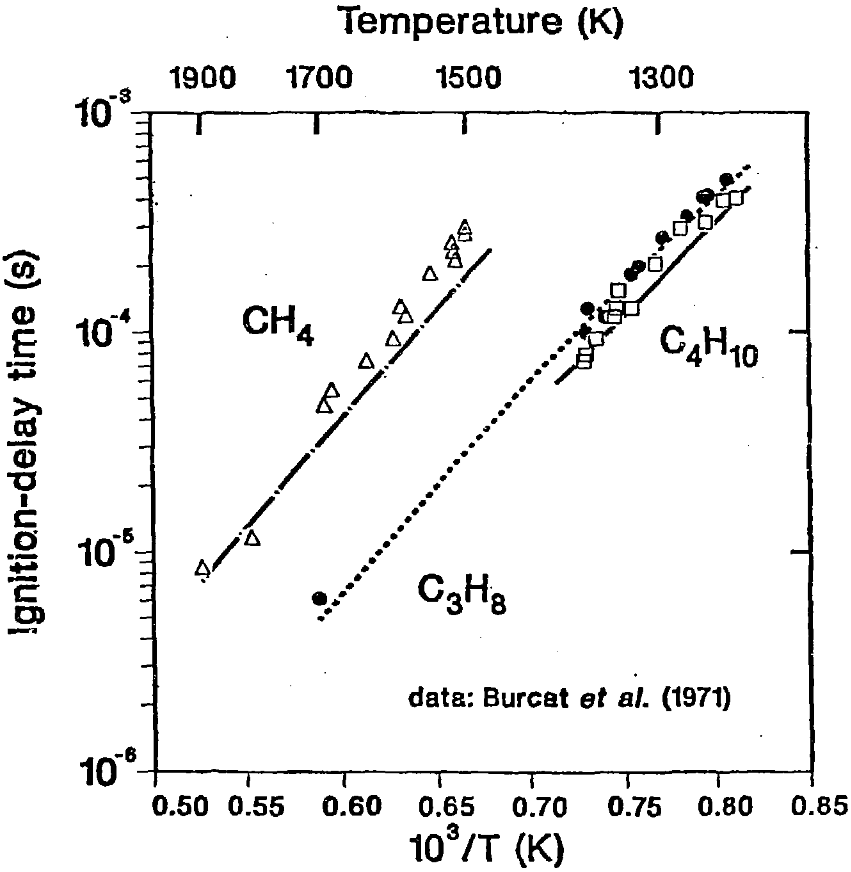
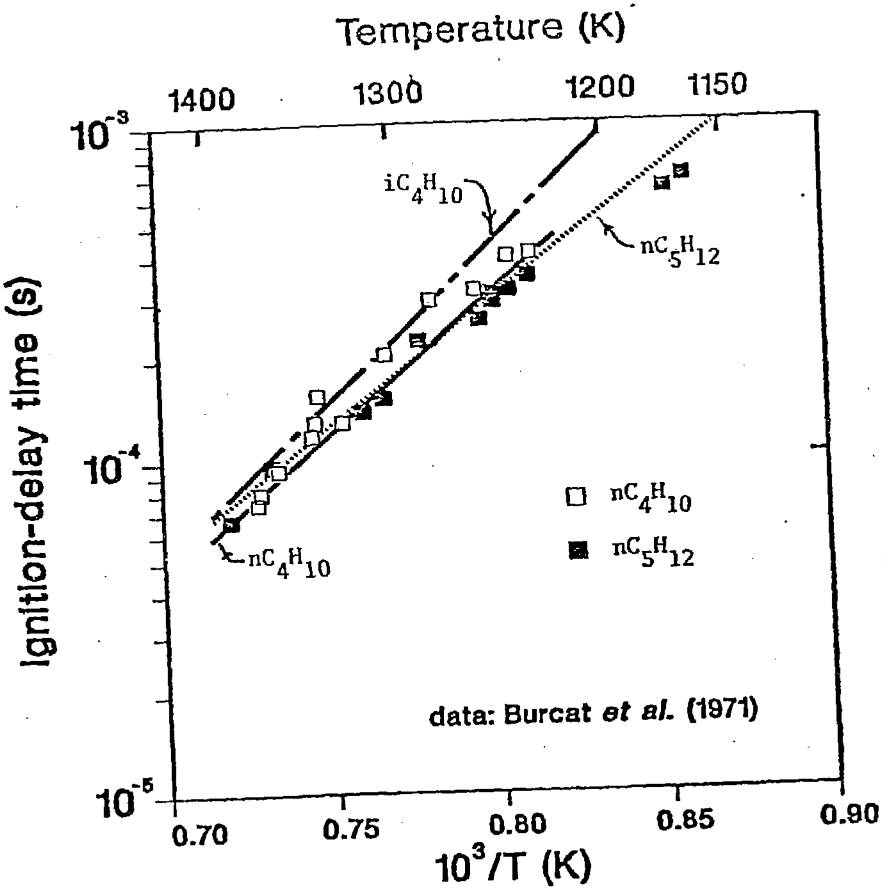
FIGURE CAPTIONS

1. Comparison between computed (lines) and experimental (symbols) ignition delay times for stoichiometric fuel-oxygen-argon mixtures at an initial density of 3.54 x 10^{-3} gm/cm^3. Triangles indicate results for methane, solid circles show propane, and squares show n-butane.

2. Comparison between computed (lines) and experimental (symbols) ignition delay times for stoichiometric fuel-oxygen-argon mixtures at an initial density of 3.54 x 10^{-3} gm/cm^3. Open squares indicate experimental results for n-butane, solid squares for n-pentane. No experimental results were available for iso-butane.




Temperature (K)
1400
1300
1200
1150
10^{-3}
10^{-4}
10^{-5}
Ignition-delay time (s)
iC_4H_{10}
nC_5H_{12}
nC_4H_{10}
□ nC_4H_{10}
■ nC_5H_{12}
data: Burcat *et al.* (1971)
0.70
0.75
0.80
0.85
0.90
$10^3/T$ (K)