Knocking Phenomena in Hydrogen-Enriched Gasoline Engines – A Theoretical Study

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ABSTRACT

The effect of hydrogen addition on the time delay of iso-octane/air mixture has been studied by using a fairly detailed reaction scheme for the oxidation of iso-octane, hydrogen and air mixture. Using the time-dependent kinetic flow charts technique, the intricate paths and mechanism, by which autoignition is developed, have been investigated. It was concluded that the autoignition process of iso-octane/air as well as of iso-octane/hydrogen/air mixture may be divided into three main periods. In the first (50 μs), the fuel molecule is attacked by HO_2 radicals to produce H_2O_2 molecules which, in turn, decomposes into OH radicals. In the second (a few microseconds before ignition occurs), the hydrocarbon molecules are broken down mainly by being attacked by the OH radicals, and in the third, the CH_2O is converted into HCO and an avalanche of a series of exothermic reactions take place and accelerate the whole process. It was also concluded that the hydrogen enrichment has a retarding effect on the autoignition process. This is attributed to the reduction of the OH population in the second stage due to the reaction $H_2 + OH \rightarrow H + H_2O$.

INTRODUCTION

The use of hydrogen as a supplemental automotive fuel appears to promise a significant improvement in the performance of a spark ignition engine (1-6) for the following main reasons:

1. A small amount of hydrogen addition produces a combustible mixture which can be burned at an equivalence ratio below the lean flammability limit of gasoline/air mixture (6,7). Therefore, lower temperatures prevail, which means lower NO_x emission and lower heat transfer to the walls. In addition, at partial loads lower throttling is needed and pumping work is lowered.

2. The burning velocity of a hydrogen-enriched gasoline is higher than that of a gasoline/air mixturee (8-10) and, therefore, the actual indicator diagram approaches closer to the ideal diagram and a higher thermodynamic efficiency is achieved (11).

3. The high molecular diffusivity of the hydrogen into the air improves the mixture homogenity and hence the combustion efficiency and the cycle-to-cycle variation (6,12).

4. Using a gaseous rather than a liquid fuel, for short periods, avoids such problems as fuel atomization and evaporation during cold starts and acceleration, and uneven distribution of the fuel among the cylinders.

However, the tendency of a hydrogen-enriched gasoline to knock, as compared to gasoline/air mixture is not very clear. At low temperatures (<1000 °K), the time delay for spontaneous ignition of a hydrogen/air mixture is longer than that of a gasoline/air mixture, while at high temperatures it is shorter.

The theory of the gasoline oxidation chemistry (which is an oxidation process of a mixture of several hydrocarbone fuels) has not been fully developed yet, and since the iso-octane is the main component in the mixture, it is interesting to study the effect of hydrogen addition on the time delay of iso-octane/air mixture and to investigate the mechanism by which autoignition is developed under these special conditions. A fairly detailed and comprehensive theoretical model has been employed. Since our predictions for the time delay, burning velocity and concentration profiles for simple mixtures of H_2/Air, CH_4/Air, C_3H_8/Air and nC_4H_{10}/Air (which are an integral part of our scheme) were found in good agreement with experiments of other investigators (13), we assume that our model (using the same scheme of chemical kinetic and species) is a reliable tool to extrapolate the available experimental data to otherprescribed mixture of iso-octane, hydrogen and air.

NUMERICAL MODEL AND CHEMICAL KINETIC MECHANISM

The governing equations for the time-dependent profiles of the temperature and species concentrations were calculated by solving numerically the coupled zero-dimensional conservation equations of mass, energy and chemical species. The numerical calculations were carried out using our own computer code which is described elsewhere (9,10). The chemical kinetics oxidation mechanism has been adopted from Burcat, Pitz and Westbrook (14). However, since during the actual engine cycle, the end gas in the cylinder is subjected also to low temperatures environment (400-1000 °K) for a considerable length of time, it is possible that during this period some of the chemical kinetic steps, which pertain primarily to cool flames, proceed to a certain extent to produce peroxides that act as proknock agents. In the present scheme, an additional kinetics submechanism was added to the high temperature mechanism to take this possibility (15). The chemical kinetics oxidation mechanism, therefore, considers 653 elementary reaction steps and 111 species. The fall-off region of four "unimolecular" reactions was considered as conforming to the Lindemann form. These are the decomposition of CH_4, C_2H_6, C_2H_5 and C_2H_3.

RESULTS

Model Evaluation

The predictions of the present model for time delay vs. initial pressure, temperature and equivalent ratio were examined against experimental observations and predictions of other investigators as available. These were performed for a fairly wide range of initial conditions. For the iso-octane/air, at T=1100÷1600 °K and ϕ=0.33÷4.0 (14). For the n-butane/air, at P=24 KPa and T=1250÷1700 °K (16), and P=30 KPa and T=600÷1200 °K (18), both for a stoichiometric mixture. For the hydrogen/air, at P=200 KPa and T=980÷1200 °K (17), and P=500 KPa and T=900÷1300 °K (18), for a stoichiometric and a rich mixture (ϕ=2), respectively.

In order to validate the chemistry details of the model, some concentration profiles of the intermediate species were compared with experimental results of Burcat et al. (14) for iso-octane, and with calculated results of Slack and Grillo (19) for a hydrogen-air mixture. A fairly good agreement was obtained for both the time delay and the predicted concentration profiles tests. Based on this series of comparison, we assume that the model is fairly capable of predicting realistic time delay of an iso-octane/hydrogen/air system, and thus, to serve as a reliable tool to extrapolate the
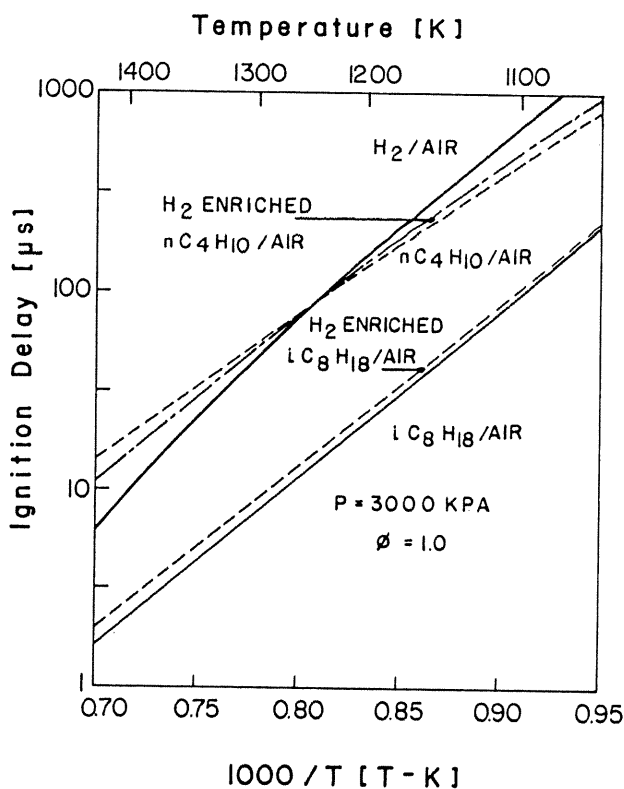

Fig. 1 Predicted time delay vs. initial temperature for several stoichiometric mixtures at 3000 KPA. The hydrogen enrichement is 6%.

available experimental data to other prescribed mixture ratio of iso-octtane, hydrogen and air.

Time Delay

Fig. 1 presents some predictions for the time delay of stoichiometric mixtures of iC_8H_{18}/air, nC_4H_{10}/air, H_2/air and nC_4H_{10}/H_2/air. The calculated time was defined by the steep temperature rise which occurs at autoignition. It seems that while at high temperatures the time delay for hydrogen is shorter than for n-butane, it appears to be rather longer at low temperatures. For the iso-octane, the time delay appears to be much shorter than that of the hydrogen over the entire range of the relevant temperatures. Enrichment of the iso-octane with a small amount of hydrogen (6% on mass base = 342% on molar base) results in an increase in the time delay of the mixture.

Kinetic Flow Chart (KFC)

In order to identify the major reaction channels in the system of interest, it is convenient to construct a time-dependent kinetic flow diagram (9,10). The diagram consists of a set of flow charts. The kinetic flow chart (KFC) illustrates the mechanism and the rate by which each of the species is formed and consumed at a particular time. Figs. 2
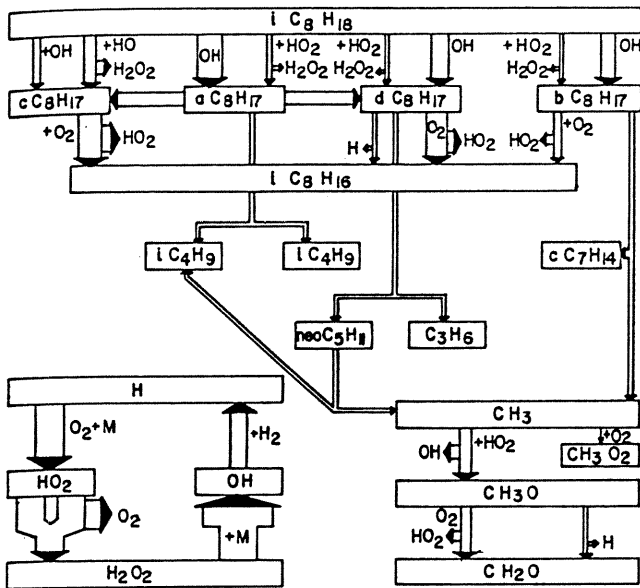
i C8H18/H2/Air Ti = 1000 K Pi = 30 at
0.0139/0.0472/0.9389 ϕ = 1
at T = 1008 K time = 0.450 ms

Fig. 2 Kinetic flow chart (KFC) for a stoichiometric iso-octane-air mixture enriched with 6% (on mass basis) of hydrogen, at time = 0.450 ms. The initial conditions are P=3000 KPa and T=1000 K. The widths of the arrows represent the relative net reaction rate on a molar basis. Slow reaction rates (smaller than 2% of the maximum rate on the chart) have been omitted. When compared to Fig. 3, the arrows' width should be reduced by 2000. The H_2O formation has been omitted.

and 3 present two KFCs for a stoichiometric iso-octane/air mixture enriched with 6% of hydrogen (hydrogen to fuel mass ratio) at a constant pressure ignition process. This amount of hydrogen enrichment was found previously (5,6) to minimize the brake specific fuel consumption of a conventional SI engine. The initial conditions for this case are P=3000 KPa and T=1000 °K, while the KFCs were plotted at 0.450 ms (T=1008 °K) and 0.774 ms (T=1403 °K). The widths of the arrows represent the relative net reaction rate on a molar basis (the rate of consumption of the particular species). For the sake of simplicity, slow reaction rates (smaller than 2% of the maximum rate on the chart) have been omitted. In fact, a close examination of the KFC diagrams for iso-C_8H_{18}/air and iso-C_8H_{18}/H_2/air showed no noticeable difference between the mechanism of oxidation. A similar trend was also found for n-butane/hydrogen/air mixtures (13). However, small variations were noticed and will be discussed. Fig. 2 shows the important role of both the OH and HO_2 radicals during the early stage of the

autoignition process of an iso-octane/hydrogen/air system. It seems that the fuel is broken down into its derivatives mainly by the attack of the OH radical via the following four reactions:

$$iC_8H_{18} + OH \rightarrow (a,b,c \text{ and } d)C_8H_{17} + H_2O. \tag{1}$$
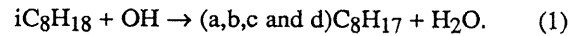
This mechanism is the dominant path for the fuel consumption during most of the induction period. However, during the very early stages, the first 50 μs, the fuel is consumed solely by the reactions:

$$iC_8H_{18} + HO_2 \rightarrow (a,b,c \text{ and } d)C_8H_{17} + H_2O_2. \tag{2}$$
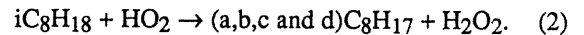
The importance of this set of reactions is not only to break the fuel molecule at the very early stage, but mainly to produce H_2O_2 molecules which, in turn, decompose to OH radicals through

$$H_2O_2 + M \rightarrow OH + OH + M, \tag{3}$$
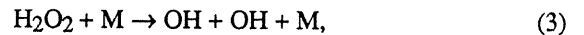
to build the so important concentration of OH (fig. 5). Although the role of reactions 2 is virtually minor during the induction period, its role in initiating the autoignition process is clear.

The aC_8H_{17} radicals are then partially decompose to iC_4H_9 and iC_4H_8 and partially are transformed into cC_8H_{17} and dC_8H_{17}, which in turn are oxidized (as well as the bC_8H_{17} radicals) to yield iC_8H_{16} and HO_2. The iC_8H_{16} is then decomposes thermally throught:
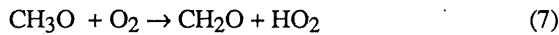
$$iC_8H_{16} \rightarrow iC_4H_7 + tC_4H_9 \tag{4}$$
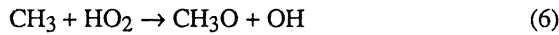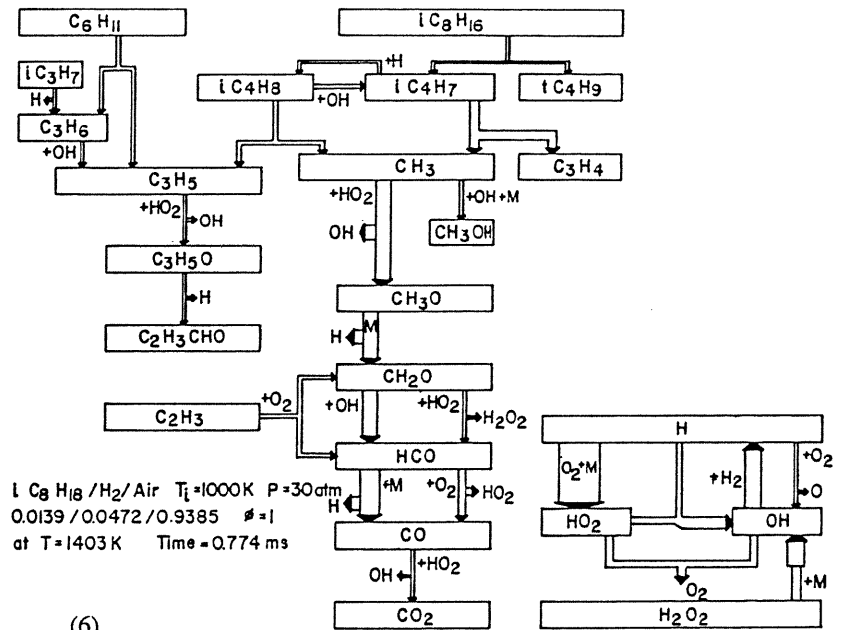
and then,
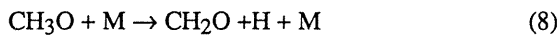
$$iC_4H_7 \rightarrow C_3H_4 + CH_3. \tag{5}$$
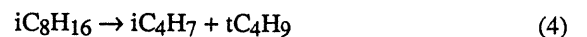
and a decomposition of the tC_4H_9 molecules n a later stage. From this KFC it is also clear that only a small fraction, although not negligible, of the butyl radicals are consumed by O_2 to produce butane. The reason for the high butene concentration observed experimentally in the end gas of an engine is mainly a result of its rather slow decomposition by H and OH radicals, which are available only in small quantities (fig. 5) for most of the induction time.

Fuel reactions involving CH_3 and CH_3O radicals make only minor contributions to fuel consumption. However, their role in the evolution of the chemical kinetics, in particular for the formation of CH_2O, is dominant (figs. 2 and 3). This is mainly through the following steps:

Fig. 3   Kinetic flow chart (KFC) for a stoichiometric iso-octane-air mixture enriched with 6% (on mass basis) of hydrogen, at time = 0.774 ms. The initial conditions are P=3000 KPa and T=1000 K. The widths of the arrows represent the relative net reaction rate on a molar basis. Slow reaction rates (smaller than 2% of the maximum rate on the chart) have been omitted. When compared to Fig. 3, the arrows' width should be multiplied by 2000. The H_2O formation has been omitted.


$$CH_3 + HO_2 \rightarrow CH_3O + OH \qquad (6)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (7)$$

and

$$CH_3O + M \rightarrow CH_2O + H + M \qquad (8)$$

During the intermediate period, in which the fuel molecules are broken down and the CH_2O concentration is built up (fig. 4), the role of the OH radical is central. In this

During the intermediate period, in which the fuel molecules are broken down and the CH_2O concentration is built up (fig. 4), the role of the OH radical is central. In this period, the OH radicals are produced mainly through the recombination of HO_2 to H_2O_2:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \qquad (9)$$
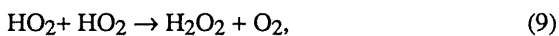
followed by the decomposition of H_2O_2 to OH via
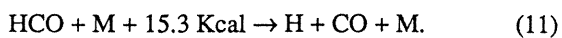
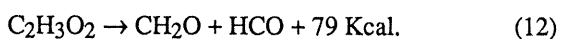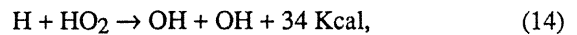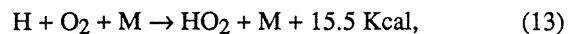$$H_2O_2 + M \rightarrow OH + OH + M \qquad (10)$$
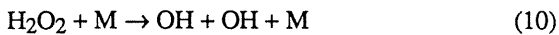
Fig. 6 demonstrates the key role of the CH_2O species in enhancing and accelerating the autoignition process. First is the reaction of CH_2O with OH, H and O_2 to produce HCO (fig. 3), and then the endothermic reaction (the heat of reaction refers to standard conditions):

$$HCO + M + 15.3 \text{ Kcal} \rightarrow H + CO + M. \qquad (11)$$

Simultaneously, CH_2O is produced via the exothermic reaction:

$$C_2H_3O_2 \rightarrow CH_2O + HCO + 79 \text{ Kcal.} \qquad (12)$$

Next are the exothermic reactions:

$$H + O_2 + M \rightarrow HO_2 + M + 15.5 \text{ Kcal}, \qquad (13)$$

$$H + HO_2 \rightarrow OH + OH + 34 \text{ Kcal}, \qquad (14)$$

and

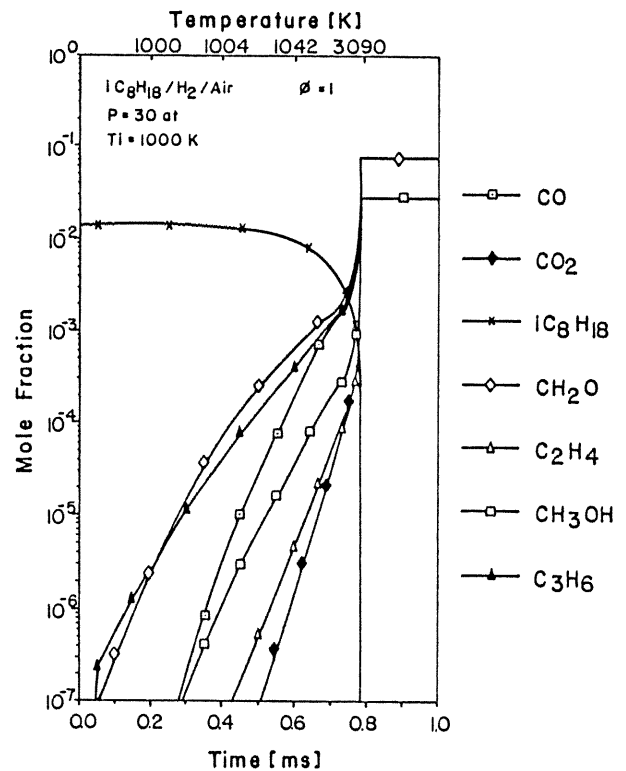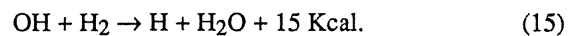$$OH + H_2 \rightarrow H + H_2O + 15 \text{ Kcal.} \qquad (15)$$

Fig. 4   Predicted profiles of concentration for the $iC_8H_{18}/H_2/air$ system described in Figs. 2 and 3.
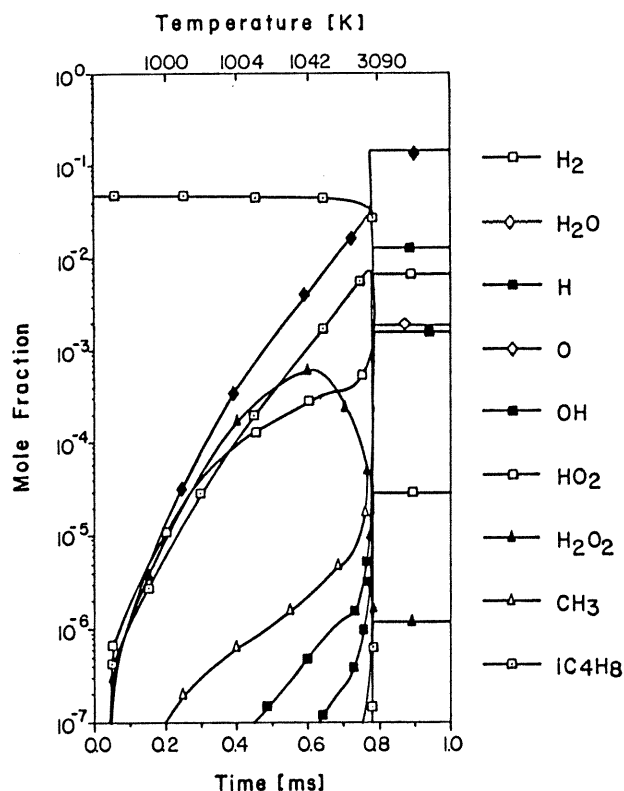
Temperature [K]

Fig. 5 Predicted profiles of concentration for the iC$_8$H$_{18}$/H$_2$/air system described in Figs. 2 and 3.

Reaction 14 is a fast by-pass to the production of OH radicals by the recombination of HO$_2$ to H$_2$O$_2$, followed by the decomposition of H$_2$O$_2$ to OH (reactions 9 and 10). The fast production of OH through this channel accelerates the ignition process and leads to the highly exothermic reaction:

$$H + OH + M \rightarrow H_2O + M + 119 \text{ Kcal.} \qquad (16)$$
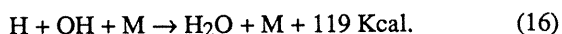
It is not surprising, therefore, that reaction 9 was found by other investigators (17) to play a very important role in determining the aduction time. (It was found that an increase in the rate of reaction 12 by a factor of 2 results in a retarding of the ignition time by 24%.) Since reaction 10 is a relatively slow reaction, an increasing of the rate of reaction 9 would retard the fast production of OH radicals through reaction 14, and will result in an accumulation of H$_2$O$_2$. Such an accumulation will eventually result in a fast production of OH through reaction 10, but in the meantime will retard the autoignition process.

The Effect of Hydrogen Enrichment

When the hydrocarbon/air mixture is enriched with a small quantity of hydrogen, the time delay is extended. For a stoichiometric mixture of iso-CH$_8$H$_{18}$/air mixture at an initial

temperature of 1000 K and P=3000 KPa, an enrichment of 6% H$_2$ (H$_2$ to iso-C$_8$H$_{18}$ mass ratio) increased the time delay from 0.721 ms to 0.780 ms. A possible explanation which is based on the theory of shortage of OH radicals is proposed here. The shortage of OH radicals approach stems from the assumption that the OH radicals plays the most important role in breaking down the fuel molecules and the CH$_2$O to HCO. Any type of kinetic perturbation that increases the production of OH radicals will accelerate the overall rate. Conversely, processes that reduce the OH radical population and reactions that compete for OH radicals will lead to retard the autoignition process. A systematic analysis of the KFCs (figs. 2 and 3) revealed that at high pressures the most influencing reaction is:

$$OH + H_2 \rightarrow H + H_2O \qquad (17)$$

A high initial concentration of H$_2$ retard the build-up of OH concentration and thus will retard not only the production of HCO via the reaction:

$$CH_2O + OH \rightarrow HCO + H_2O \qquad (18)$$
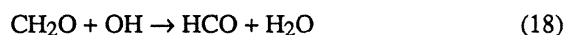
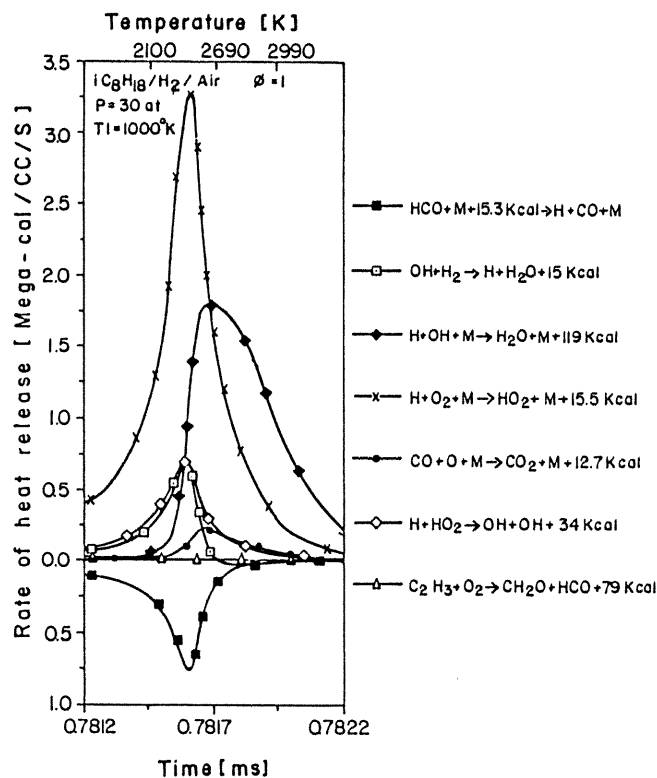but also the consumption of the fuel through reaction 1.

Fig. 6 Predicted rates of heat release for the iC$_8$H$_{18}$/H$_2$/air system described in Figs. 2 and 3, showing the seven most contributing reactions.

CONCLUSIONS

1. The autoignition process of n-butane/air, as well as of n-butane/hydrogen/air, mixture may be divided into three main periods:

    a. In the first (~50 μs) - the early stage - the first molecule is attacked by HO_2 radicals to produce H_2O_2 molecules which, in turn, decompose to OH radicals.

    b. In the second (which ends a few microseconds before ignition occurs) - the intermediate stage - the OH radicals play the most important role in breaking down the hydrocarbon molecules. During this period the OH radicals are produced mainly by the decomposition of the H_2O_2 molecules.

    c. In the third - the final stage - the CH_2O is converted into HCO by an endothermic reaction and then an avalanche of a series of exothermic reactions taking place and accelerate the whole process.

2. The hydrogen enrichment has a retarding effect on the autoignition process. This is attributed to its interruption during the second stage when H_2 reacts with OH, thus reducing the OH population and retarding the formation of CH_2O.

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