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A Shock-Tube Study
on the Combustion Process of Hydrocarbon Fuels*
(2nd Report; Systematic Measurements of Ignition Delays
and Presentation of a Reaction Scheme)

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Measurements were made, with shock-tubes, on the ignition delays of three kinds of representative saturated higher-hydrocarbon fuels over the temperature range of 900-1700K, varying systematically the equivalence ratio, the inert gas concentration and the overall pressure of the mixture. A simplified model of the reaction mechanism for the ignition of general higher-hydrocarbon fuels was proposed, on which the ignition delays under various conditions were calculated with use of available rate constant data. The experimental results, with their dependence on various parameters, were found to be well correlated with the calculations above a boundary temperature where a sharp change in the apparent activation energy takes place.

1. Introduction

The reaction processes of post-shocked gas mixtures of hydrocarbon fuels, especially their ignition processes and cracking reactions, have been studied in shock-tubes to clarify the combustion processes of higher hydrocarbon fuels. In these serial studies, it was found that the ignition lag of n-butane-oxygen mixtures was approximately accounted for by the calculation based on a "hydrogen-like" reaction model and the change in the apparent activation energy with the equivalence ratio was qualitatively explained by it and that the greater part of products of high temperature cracking reaction of n-butane was ethylene(1). Moreover, the half life of n-butane was obtained from the density measurement utilizing a Michelson interferometer and was compared with the ignition delay, and it was found that the latter was shorter at high temperatures and longer at low temperatures. It was also found from high speed streak Schlieren photographs that the ignition in the stagnant region produced by reflected shock waves started from plural sites distributed around the reflection plane(2).

In this work, ignition lags of n-butane, n-hexane and n-octane were measured in the temperature range of 900-1700K under the systematically arranged conditions of the equivalence ratio, the diluent concentration and the total pressure of the mixtures. A simplified model of the reaction mechanism for the ignition of general higher-hydrocarbon fuels was proposed, on which the ignition delays

were calculated with use of available rate constant data and the experimental results, with their dependence on various parameters, were found to be well correlated with the calculations at high temperatures.

2. Measurements of ignition delays

2.1. Experimental apparatus

A conventional shock-tube was employed. The inner diameter and the length of its driven section were 42mm and 5m and those of the driver section were 53mm and 2m respectively. A collision shock-tube(2) was also employed. These had sufficient durabilities for pressure and vacuum. Measurements were made in the region behind reflected shock waves as well as in the region behind incident shock waves depending on the experimental conditions. Temperatures and densities of post-shocked mixtures had to be determined precisely to obtain precise data of ignition delays. Therefore the initial pressure was measured by using a MacLeod gauge and the speed of incident shock wave was measured by means of a digital time-interval counter. The temperature, pressure and density behind shock wave were obtained from these shock speed and initial conditions. Thermo-chemical data required in this calculation were obtained from bibliographies (3)(4).

Ignition delay was determined from the time interval between the signals of pressure and emission which were measured on the same cross sectional plane. The shape of the emission signal changed with every run. Therefore it had to be recorded on a Brauntube or by a digital memory and had to be examined every time to obtain the ignition delay. The signals of emission were compared between the case when all the emission from a quartz window was measured and the case when an inter-

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ference filter (center wave length 305 nm, half-width 10 nm) was inserted in the path which would allow the near ultraviolet emission from OH (306.3 nm). The sensitivity of the photomultiplier tube falls to one half of its maximum at 290 and 630 nm. Measurements were made in the temperature range of 900–1700K. The ignition lag was defined as the time required until the emission became 5% of its maximum intensity. The intensity of the emission increased rapidly and monotonously from its origin to maximum and its shapes were similar whether a filter was used or not at high temperatures. On the other hand, although ignition delays were same, the shapes of emission signals were dissimilar between the cases with and without the filter and the signals were not monotonous at the temperatures lower than 1000K. Examples of these signals are shown in Fig.1. Moreover, the ratio of maximum intensities of emission between the cases with and without the filter at low tem-

Fig.1. Signals for emission
n-C₄H₁₀+O₂ (Equivalence ratio 1.0)

Fig.2. Ignition delay (1)
n-Butane (Equivalence ratio 0.1)

peratures was about 1/5 of the value at high temperatures. This evidence suggests that the concentration of species which emits in the band of the filter (most of them are considered to be OH) is smaller at low temperatures than at high temperatures and that its effects on ignition delays are smaller at low temperatures.

The shock-tube was evacuated sufficiently prior to a run and test gas and driver gas were introduced into each section of it up to the appointed pressures. The diaphragm was then ruptured by a manual or an electromagnetic cutter. Helium or air was employed as the driver gas. Initial pressures were determined such that the densities behind shock waves attained the appointed values which were 2, 4, 40×10^{-3} mol/l. These densities correspond to 0.25–4.9 atm at 1500K.

2.2. Ignition delays

Ignition delays of n-butane, n-hexane and n-octane were measured under systematically arranged conditions of the equiva-

Fig.3. Ignition delay (2)
n-Hexane (Equivalence ratio 0.1)

Fig.4. Ignition delay (3)
n-Octane (Equivalence ratio 0.1)

lence ratio, the concentration of diluent, the density and the temperature. Representative results, which were obtained for equivalence ratio 0.1, are shown in Figs. 2 to 4. Open circles, triangles and filled circles correspond to the appointed densities of $2, 4, 40 \times 10^{-3} \text{ mol/l}$ respectively. The errors from appointed densities were less than 10%. The temperature dependencies of ignition delays change their values appreciably at around 1200K and are linear on both sides. This rule holds true for other equivalence ratios. Therefore, the data for high temperatures and low temperatures were represented individually by an empirical formula

$$\log \tau = 0.4343E/RT + A \quad (1)$$

by using the method of least squares and these formulae were used in farther dis-

Fig. 5. Empirical formulae for ignition delays (1), n-Butane (Equivalence ratios 1.0, 0.1, 0.05)

Fig. 6. Empirical formulae for ignition delays (2), n-Hexane (Equivalence ratios 0.1, 0.05, 0.02)

cussions. $\tau(\text{s})$ is the ignition delay, E (kcal/mol) is the apparent activation energy, R (kcal/mol·K) is the gas constant, T (K) is the temperature and A is a constant which has the dimension of $\log(\text{s})$. Results are shown in Figs. 5 to 7 in which solid lines, broken lines and chain lines correspond to the densities of $2, 4, 40 \times 10^{-3} \text{ mol/l}$ respectively. The figures denote the equivalence ratios and the figures in parentheses denote the concentrations of argon. Ignition delays were too long at low temperatures under the conditions of data being available only at high temperature and were too short at high temperatures under the condition of data being available only at low temperatures, to be measured by our apparatus.

2.3. Discussions on the measured ignition delays

Figs. 5 to 7 show nearly the same ignition delays without distinction of equivalence ratio at high temperatures when their densities are equal except the results for the mixtures which contain argon. Higher hydrocarbon fuels need, in general, large amount of oxygen. Even n-butane, which consumes the least amount of it in the fuels used here, needs 6.5 mol of oxygen per one mol of the fuel. Therefore, most part of the mixture of higher hydrocarbons consists of oxygen when its equivalence ratio is smaller than unity. Ignition delays for density $2 \times 10^{-3} \text{ mol/l}$ are 1.5–3.0 times longer than those for $4 \times 10^{-3} \text{ mol/l}$. These evidences suggest that ignition delays are in inverse proportion to the concentration of oxygen but are independent of that of fuel at high temperatures. Fig. 8 shows this clearly in which the ignition delays for n-butane are represented by using the product $\tau(\text{O}_2)_0$. Moreover it shows that ignition delays are not affected by argon concentrations. On the other hand, ignition delays depend also on the concentrations of fuel and argon to some extent when the temperature is lower than that of boundary

Fig. 7. Empirical formulae for ignition delays (3), n-Octane (Equivalence ratios 0.1, 0.05, 0.02)

where the apparent activation energy changes its value appreciably. However, data are too few and too scattered to get a quantitative result. Reflecting the characteristics obtained at high temperatures, measured ignition delays for each fuel were fitted to the formula,

$$\log \{\tau(O_2)_0\} = 0.4343E/RT + B \quad (2)$$

where $(O_2)_0$ (mol/l) is the concentration of oxygen just behind the shock wave and B is a constant which has the unit of $\log(\text{mol} \cdot \text{s}/\text{l})$. Although the difference in apparent activation energies between the results at low temperatures and at high temperatures suggests that the rate controlling mechanisms are also different between them, ignition delays depend most on the concentration of oxygen. Therefore, the data were also fitted to the formula at low temperatures. The results are shown in Table 1 and Fig. 9. They show slight difference between fuels, but this difference is considered to depend on where the test plots around the boundary are attributed, i.e. to low or high temperature region. Therefore, the ignition delays of these fuels were concluded to be essentially same and the mean value was also included in the table and the figure.

Table 1. Mean values for measured ignition delay

Fuel	High Temperature		Low Temperature	
	E	B	E	B
$n\text{-C}_4\text{H}_{10}$	39.6	-13.35	8.1	-7.13
$n\text{-C}_6\text{H}_{14}$	30.8	-11.55	15.5	-8.73
$n\text{-C}_8\text{H}_{18}$	38.5	-12.71	24.4	-10.30
Mean	34.0	-12.20	13.4	-8.29

$$\log \{\tau(O_2)_0\} = 0.4343E/RT + B$$

E (kcal/mol), B ($\log(\text{mol} \cdot \text{s}/\text{l})$)

Fig. 8. Products of ignition delay and concentration of oxygen, n -Butane (Equivalence ratios 1.0, 0.1, 0.05)

Many works have been done on the high temperature ignition delays, among which the results of White(5), Burcat et al.(6) and Oppenheim et al.(7) can be compared with ours. White followed the density behind incident shock waves in the mixtures of fuel, oxygen and inert gas (helium or argon) by means of an interferometer and measured ignition delays for hydrogen, acetylene and ethylene. Burcat et al. used the mixtures of methane, ethane and propane which contained 90 to 99% argon and their equivalence ratios were around unity. They measured ignition delays in the region behind reflected shock waves by following the emission. Their experimental condition of pressure was 2 to 9 atms. Oppenheim et al. measured ignition delays for the stoichiometric mixtures of n -

Fig. 9. Mean values of measured ignition delays

From Literatures		This Work
H_2 (5)	C_2H_6 (6)	$n\text{-C}_4\text{H}_{10}$
CH_4 (6)	C_3H_8 (6)	$n\text{-C}_6\text{H}_{14}$
C_2H_2 (5)	$n\text{-C}_7H_{16}$ (7)	$n\text{-C}_8H_{18}$
C_2H_4 (5)	$iso\text{-C}_8H_{18}$ (7)	

Fig. 10. Comparison of ignition delays with other fuels

pentane and iso-octane under the pressure of 1 to 4 atms. Considering the knocking in spark ignition engines they took high speed framing photographs of interferograms behind reflected shock waves to clarify the conditions of ignition spots and flame propagations. The experimental condition of temperature of these works corresponds to the high temperature region of ours, but, sufficient data are not available from the low temperature region. Therefore, their results were extrapolated to our experimental conditions and were compared with ours at high temperatures. The results are shown in Fig.10, which shows that ignition delays of saturated hydrocarbons are nearly same value except those of methane and ethane and that their apparent activation energies are larger than those for hydrogen and unsaturated hydrocarbons. Methane shows longer ignition delay than other fuels. It is considered to be due to methane being more stable than other fuels. Ethane also shows longer ignition delay. But it is not clear whether the difference is inherent or is attributable to the extrapolation.

3. Reaction scheme for ignition process

3.1. Selection of the reaction scheme

Generally speaking, all the reactions between all the species in a system have to be taken into account to get a reaction scheme. However some reactions can be ignored, in many cases, without serious errors when only macroscopic results are considered. It is desirable, in these cases, to select only important reactions and to clarify the leading reactions in the system.

Based on the experimental results for ignition delays of higher hydrocarbons mentioned above, a simplified reaction model for ignition process has been proposed and is compared with the experimental results in which it is shown that the apparent activation energy changes its value appreciably at 1100-1200K. This evidence suggests that different reactions are rate controlling in both temperature ranges. However, there is not sufficient information in low temperature range. Therefore, the reaction model is based only on the natures of ignition delays at high temperatures. The low temperature ignition processes of hydrocarbon fuels are known to have special natures such as cool flame. These phenomena are known to be caused by intermediate species such as aldehydes and peroxides and to disappear at high temperatures. It is surmised from these features that these intermediate species lose their importance at high temperatures. Therefore they were ignored in the selection of reaction scheme and we got hydrocarbon fuels(RH), oxygen(O₂), hydrocarbon radicals(R), hydrogen atom(H), oxygen atom(O), and hydroxyl radical(OH) as important reactant and intermediate species. These selections were also based on the results of measurements of emission with and

without the filter in which OH was supposed to play an important role in high temperature ignition processes of hydrocarbon fuels as well as in the combustion processes of hydrogen. Many hydrocarbons and hydrocarbon radicals are probably produced from a higher hydrocarbon fuel. However, most of them are considered to be the mother fuel and the primary products within the ignition delay. Moreover, reaction rates for these species have nearly the same value, which will be explained later. Therefore, hydrocarbons and hydrocarbon radicals were assumed to react respectively with one reaction rate and are represented by symbols RH and R. The six species, mentioned above, collide with each other in the mixture. These collisions also include energy transfer reaction such as recombination reactions and cracking reactions. Although effects of a third body are in general different for every species, they are assumed here to be identical. The third body is denoted by M, which corresponds to the sum of all species. Therefore, seven species, RH, O₂, R, H, O, OH and M, react with each other in two- and three-body collisions, whose combinations are shown in Table 2. The upper right half and the lower left half correspond to bimolecular reactions and termolecular reactions respectively. For example, the reaction between the second row and the third column(2,3) represents H+O₂ and the reaction (3,2) corresponds to H+O₂+M. Unimolecular cracking reactions are included in the bimolecular reactions with M. In the table, T denotes the reaction which is not considered to play an important role in the ignition processes of hydrocarbons and A denotes the reaction which is disregarded under the assumption ignoring peroxides, alcohols and aldehydes. Moreover, the concentrations of intermediate species are considered to be small during the ignition delay. Therefore, the reactions between these species denoted by S in the table are ignored. Under these considerations we have selected the reactions shown in Table 3 which are denoted by * in Table 2. The decomposition reaction of O₂, which corresponds to the re-

Table 2. Combination of reactants

A \ B	RH	O ₂	H	O	OH	R	M	Bimolecular Reaction A + B
RH	T	T	*	*	*	T	*	
O ₂	A	T	*	T	T	A	T	
H	T	A	S				T	
O	A	T	S				T	
OH	T	T					T	
R	T	A					*	
Termolecular Reaction A + B + M								

* Included in the reaction model

T Not important in the ignition process

A Ignored by the assumption of high temperature

S Reactions between intermediate species

action O_2+M in Table 2, may be considered an initiation reaction as well as the reaction (O) in Table 3. However, the initiation reactions are considered to play an important role only in a short duration just after the heating of mixture and we have selected only the most probable reaction (O). The reaction (1) is considered to play an important role in the ignition processes of hydrocarbon fuels as well as in the mixtures of hydrogen and oxygen. Although the products of the reactions (2) to (4) have not yet been fully understood, they are assumed to be the species shown in Table 3.

3.2. Calculations of the ignition delay

If the rate constants are available for the reactions in Table 3, one can calculate the ignition delays for higher hydrocarbons. However they have not been reported so much, especially for higher hydrocarbons and for high temperatures. Table 4 shows the reported values for the rate constants for the reactions in Table 3 with their measured temperatures and Fig.11 shows their values or the extrapolation to the temperature range considered here. The rate constant for the reaction (4) in the table corresponds to that for the unimolecular reaction in

Table 3. Chain reaction model for ignition process

Kind	No.	Reaction Rate Constant Reaction Equation
Initiation	(O)	$RH + M \xrightarrow{k_0} 2R + M$
Branching	(1)	$H + O_2 \xrightarrow{k_1} OH + O$
Branching	(2)	$O + RH \xrightarrow{k_2} OH + R$
Propergating	(3)	$OH + RH \xrightarrow{k_3} R + H_2O$
Propergating	(4)	$R + M \xrightarrow{k_4} RH + H + M$
Propergating	(5)	$H + RH \xrightarrow{k_5} RH + R$

Fig.11. Reaction rate constants

high pressure limit. However the experimental condition of pressure is not considered to be sufficiently high. Therefore, the reaction was assumed to be second order when the effect of pressure was examined. It is shown in Table 4 and Fig.11 that reaction rates do not change their value so much with the kinds of hydrocarbons. The values, which corresponded to the highest saturated hydrocarbons in the table, were used in the following calculations and it was assumed that intermediate species reacted with the same reaction rates.

The temporal variations of the concentrations are expressed, according to the reaction scheme in Table 3, as follows;

$$d(RH)/dt = -k_0(RH)(M) - k_2(RH)(O) - k_3(RH)(OH) + k_4(R)(M) \quad \dots (3)$$

$$d(O_2)/dt = -k_1(O_2)(H) \quad \dots (4)$$

$$d(H)/dt = -k_1(O_2)(H) + k_4(R)(M) - k_5(RH)(H) \quad \dots (5)$$

$$d(O)/dt = k_1(O_2)(H) - k_2(RH)(O) \quad \dots (6)$$

$$d(OH)/dt = k_1(O_2)(H) + k_2(RH)(O) - k_3(RH)(OH) \quad \dots (7)$$

$$d(R)/dt = 2k_0(RH)(M) + k_2(RH)(O) + k_3(RH)(OH) - k_4(R)(M) - k_5(RH)(H) \quad \dots (8)$$

where () denotes the concentration of the species in them. These simultaneous equations are solved subject to the following initial conditions.

$$(RH) = (RH)_0, (O_2) = (O_2)_0, (M) = (M)_0, \\ (H) = (O) = (OH) = (R) = 0 \text{ at } t = 0. \quad \dots (9)$$

The ignition delay is defined as the duration in which a combustible mixture suf-

Table 4. Reaction rate constants

No.	Fuel	A	E	Temperature	Literature
(1)		$*2.24 \times 10^{11}$	16.8	whole	8
(2)	C_4H_{10}	$*3.0 \times 10^{10}$	4.2	220-660 K	8
	C_3H_8	1.7×10^{10}	3.0	about 300 K	8
	C_2H_6	8.4×10^{10}	7.5	about 700 K	8
(3)	C_2H_6	$*2.4 \times 10^{11}$	6.0	400-700 K	8
	C_2H_4	4.4×10^{11}	6.5	400-700 K	8
(4) [#]	C_4H_9	1.0×10^{13}	29.0	about 850 K	9
	C_2H_5	$*3.0 \times 10^{14}$	39.5	about 850 K	9
(5)	C_4H_{10}	$*1.0 \times 10^{11}$	7.7	about 800 K	10
	C_3H_8	1.0×10^{10}	5.0	about 800 K	11
	C_2H_6	1.3×10^{11}	9.7	about 800 K	10

$$k = A \exp(-E/RT) \quad \text{l/mol.s} \quad (\# \text{ l/s})$$

$$A \quad \text{l/mol.s} \quad (\# \text{ l/s})$$

$$E \quad \text{kcal/mol}$$

fers a sudden compression and heating, then reactions more and more grow and finally a measurable change appears in some macroscopic feature such as emission, pressure or density. Consequently it depends on the principle and sensitivity of the detector. Therefore it is necessary to define the sensitivity by using the concentration of some species and it is defined here, like the previous work⁽¹⁾, as the duration until the concentration of OH becomes 10^{-6} mol/l. The reactions in the induction period at high temperatures grow exponentially, as was seen in the signals of emission. Therefore ignition delays do not change their values so much with the definition of ignition. Integrating Eqs.(3) to (8), it was also confirmed that the variation of the ignition delay was only within 10% when the sensitivity for the concentration of OH changed one order. It is also possible to obtain the temporal variation of the temperature if one substitutes some species into RH and R and introduces an energy equation. However preliminary calculations showed the deviations of the temperature and the number of molecules to be sufficiently small. Therefore, the following calculations were executed under the conditions of constant temperature and volume.

3.3. Calculated results and discussions

Ignition delays were calculated for several equivalence ratios with fixed concentration of oxygen or fuel to clarify their dependency on the fuel and oxygen. If the cracking reaction of hydrocarbon radicals (4) is assumed to be first order, resultant ignition delays are in inverse proportion to the concentration of oxygen but are independent of pressure. The results are shown, using the product $\tau(O_2)_0$, in Fig.12. It is shown in the figure that the dependency of the ignition delay on the fuel is small except at extremely high temperatures. Therefore, the reactions (2) and (3) are considered to be sufficiently faster than other reactions in this region. On the other hand, the rates for the reactions of large activation energies increase relatively with temperature and the reactions (2) and (3) control the rate to some extent. Consequently they reduce the apparent activation energy and make the ignition delay longer when the concentration of the fuel is small. The stoichiometric mixture shows slightly longer ignition delay at low temperatures, which is considered to be attributable to the reaction (5). The rates of the reactions (2) and (3) are considered to be sufficiently large to adopt the quasisteady assumptions for O and OH in the higher temperature region of the experimental conditions, then the ignition delays are approximately represented by the following equation.

$$\tau = \frac{1}{\alpha} \ln \left[\frac{\beta - \alpha}{\beta} \cdot \left\{ \frac{k_3(OH)}{2k_0(M)_0} \tau + 1 \right\} \right] \quad \dots (10)$$

where

$$\alpha = (-\gamma + \sqrt{\gamma^2 + \delta}) k_1(O_2)_0 / 2$$

$$\beta = (-\gamma - \sqrt{\gamma^2 + \delta}) k_1(O_2)_0 / 2$$

$$\gamma = 1 + k_4(M)_0 / k_1(O_2)_0 + k_5(RH)_0 / k_1(O_2)_0$$

$$\delta = 8k_4(M)_0 / k_1(O_2)_0$$

$(OH)_\tau$ denotes the sensitivity that is the concentration of OH at the defined ignition. The relation,

$$|\beta \exp(\alpha \tau)| \gg |\alpha \exp(\beta \tau)|,$$

has been used and the consumption of the fuel and oxygen has been assumed to be small. The result is also shown in Fig.12 in which Eq.(10) reveals itself to be a good approximation.

Ignition delays were also calculated for stoichiometric mixtures which contain 88.6 and 98.8% argon to clarify the effects of the inert gas. These mixtures correspond to the mixtures of equivalence ratios of 0.1 and 0.01 in which excess oxygen has been replaced with argon. The results are shown in Fig.13. The initiation reaction (0) and the reaction (4) are assumed here to be second order and their rates to be directly proportional to the total pressure. The ignition delays reduce their values to 1/5 and 1/10 respectively at 1250K when the total pressures become 10 times and 100 times. This effect is small at higher tempera-

Fig.12. Calculated results for ignition delays

tures, which is attributable to the activation energy of the reaction (4) being larger than others and its effect as the rate controlling reaction being reduced.

The mean value of the measured ignition delays, which is shown in Fig.9, is also included in Fig.12 for comparison. The reaction model in Table 3 approximates the features obtained in the measurements of ignition delays of higher hydrocarbons in higher temperature region. Especially it represents well the apparent activation energy and the features that the ignition delays are independent of the kind and concentration of fuel and are in inverse proportion to the concentration of oxygen. Fig.8, which summarizes the experimental results for n-butane, shows that the ignition delay for mixtures containing argon is nearly the same as that for mixtures without argon at high temperatures but is slightly shorter at low temperatures. This tendency agrees qualitatively with the calculated results shown in Fig.13 but the effect of inert gas is larger in the latter. This evidence suggests that the pressure dependency of the reaction (4) is smaller than second order and is closer to first order.

On the other hand, this model can not predict a small apparent activation energy and the dependency of ignition delays on the fuel concentration which is observed at the temperatures lower than 1200K. Within the calculated results Eq.(10) is a good approximation for the reaction model in Table 3 at these temperatures. Therefore, the reaction (4) is considered to be one of the main rate controlling reactions in the model and to be replaced at low temperatures by the reactions other than those in Table 3, which have very small activation energies. These reactions are supposed to produce active species such as H, O, OH or to oxidize the fuel through peroxides and aldehydes which have been ignored here.

Fig.13. Effects of inert gas

4. Conclusions

The ignition delays were measured in the mixtures of three kinds of representative saturated higher hydrocarbon fuels, n-butane, n-hexane, n-octane and oxygen under the systematically arranged conditions of the equivalence ratio, the diluent concentration and the total pressure, in which the following features were observed. The temperature dependencies of the ignition delays of higher hydrocarbon fuels change their value appreciably at 1100-1200K. Ignition delays are in inverse proportion to the concentration of oxygen but are independent of the concentration of fuels and only slightly depend on argon at the temperatures higher than the boundary. Ignition delays of these fuels are essentially of same value in this region. Moreover it is confirmed, using the values available in literatures, that this rule holds true for other higher hydrocarbon fuels than those used here. The apparent activation energy is 30 to 40 kcal/mol which is fairly larger than those for hydrogen and unsaturated hydrocarbons. On the other hand, the apparent activation energy is smaller at low temperatures than at high temperatures.

The measurements of emission with an interference filter also suggest that the rate controlling reactions are different between these temperature ranges.

Based on these experimental results, a simplified reaction model for high temperature ignition processes was proposed, on which the ignition delays were calculated and compared with the measured values. The results show that this model represents the ignition delays fairly well at high temperatures.

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