The Addition Effect of CH_3I on the Ignition of CH_4

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Synopsis. Measurements and calculations of ignition delay times were performed in a mixture of CH_4-CH_3I-O_2-Ar in order to understand the characteristics of compouds including iodine during ignition. CH_3I accelerated the ignition of CH_4 more than CH_3Cl did, but less than CH_3Br did. The remarkably small bond-dissociation energies of CH_3I and HI, in comparison to these of other halomethanes, were the major cause of the characteristic behavior.

It is well-known that CH_4 is very difficult to ignite in relatively simple hydrocarbons and that all additives but permanent gases, which act only as diluents, promote the ignition.[1-8] The addition effects of CH_3Br and CH_3Cl[8] on the ignition of CH_4 have already been analyzed in experiments using shock tubes and by simulations based on an assumed reaction mechanism. CH_3Br was more effective as an ignition-promotor than CH_3Cl, although both of them promoted the ignition; the differences were accounted for by chemical kinetic reasons.

In this study, the addition effect of CH_3I on the ignition of CH_4 is investigated by the same method, and the action due to the difference in halogens is discussed.

Experimental

The ignition-delay times were measured in a mixture of CH_4 (2.0 mol%)-O_2 (4.0 mol%)-CH_3I (0.1 mol%)-Ar (93.9 mol%) at temperatures between 1500 and 2000 K and at pressures between 2.3 and 3.3 atm behind the shock wave. Analytical studies were performed by using the mechanism shown in Table 1, in addition to that of the CH_4-oxidation.[8] The details of the experiments and calculation are given in Ref.8. The measurements included an error of only a few %; the error due to the procedure of estimating the ignition-delay times was below 1 μs at 1800 K.

Results and Discussion

The measured ignition-delay times agree well with the calculated values (Fig. 1). The promotion effect of CH_3I is larger than that of CH_3Cl, but somewhat smaller than that of CH_3Br. Table 1 includes ignition-delay times which calculated by simultaneously decreasing both forward and reverse rate constants concerning halogen species, one by one, to zero or to one-tenth of their both values at 1800 K. The time calculated by means of normal rate constants was 124 μs. The results indicate that the reactions which have large effects on the ignition are $R1_I$, $R4_I$, $R5_I$, and $R8_I$ (hereafter, a subscript will express the kind of halogen

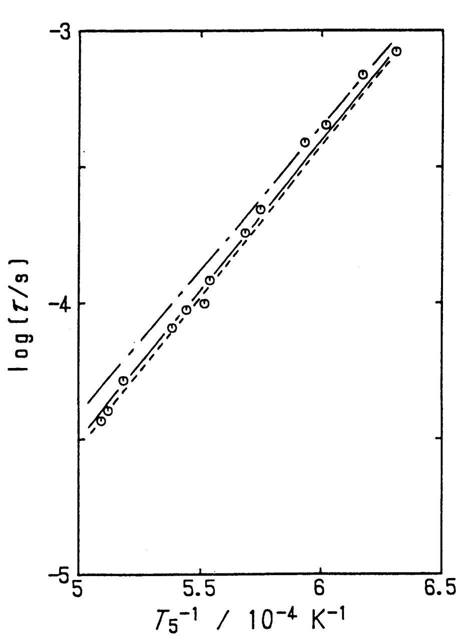

Fig. 1. Measured and calculated ignition delay times in CH_4-CH_3I-O_2-Ar. T_5 is temperature behind shock wave.
○: measured in CH_3I, ——: calculated in CH_3I, ----: calculated in CH_3Br,[8] —-—: calculated in CH_3Cl.[8]

Table 1. Reaction Mechanism, Rate Constants, and Calculated Ignition-Delay Times at 1800 K

	Reaction[a)]	Ignition-delay time/10^{-6} s		k[b)]			
		k×0	k×0.1	log A	n	E	Ref.
R1	$CH_3I=CH_3+I$	213	126	13.40	0.00	54.70	10
R2	$CH_3I+H=CH_3+HI$	125	126	14.54	0.00	4.50	9
R3	$CH_3I+I=CH_3+I_2$	125	125	14.30	0.00	19.80	9
R4	$CH_4+I=CH_3+HI$	143	139	14.70	0.00	33.90	9
R5	$HI+H=H_2+I$	122	123	13.52	0.00	0.00	9
R6	$I_2+H=HI+I$	124	125	14.39	0.00	0.00	9
R7	$I+I+M=I_2+M$	125	126	13.00	1.00	0.00	9
R8	$I+H+M=HI+M$	138	136	13.08	1.00	0.00	9

a) Reaction in which both forward and reverse rate constants are changed. The ignition-delay time calculated by the normal rate constants is 124 μs. b) Forward rate constants in the form $A{\times}T^n\exp(-E/RT)$, in cm^{-3}, mol, s, kcal, and K units.

in the corresponding reaction).

Although the thermal-decomposition reaction, R1$_{\mathrm{I}}$, contributes most to the acceleration of an ignition like those of CH_3Cl and CH_3Br, each situation is different. When the forward and reverse rate constants of thermal decomposition, R1$_{\mathrm{Br}}$ or R1$_{\mathrm{Cl}}$, are changed by 10% in systems including CH_3Br or CH_3Cl, the ignition-delay time changes a small percentage, but it does not change at all in this case, and it only decreases about 1% with one-tenth of the R1$_{\mathrm{I}}$. On the other hand, when both rate constants of thermal decomposition (R1) are zero, the ignition delay times are similar (about 220 μs) in the three halomethanes. The forward rate constant of R1$_{\mathrm{I}}$ is two orders of magnitude larger than those of R1$_{\mathrm{Br}}$ and R1$_{\mathrm{Cl}}$, so the greater part of the CH_3I is decomposed in the early stage of the induction period, as is shown in Figs. 2 and 3. This means that the decomposition rate of CH_3I is very fast and that a small change in the decomposition rate does not affect the ignition-delay time.

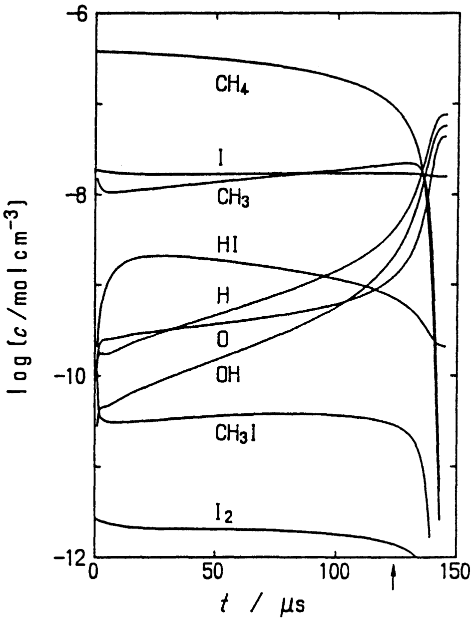

Fig. 2. Calculated concentration profiles at 1800 K. t is time after the arrival of shock wave. Arrow indicates the ignition-delay time.

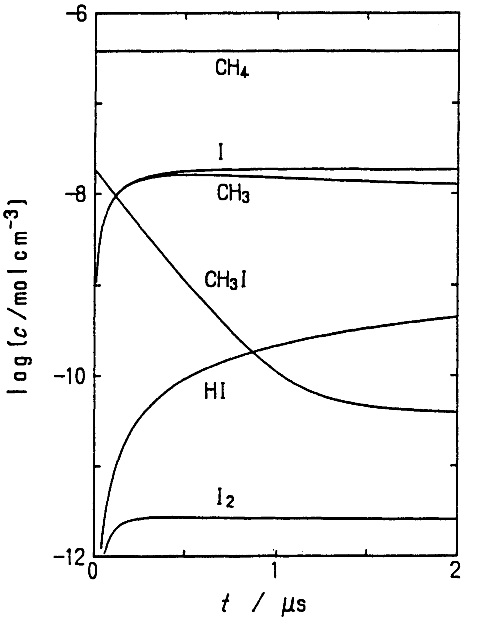

Fig. 3. Calculated concentration profiles at 1800 K in early stage of induction period.

The concentration profiles (Fig. 3) in the early stages of the induction period indicate that CH_3, which is importatnt in ignition, is generated from CH_3I, but not from CH_4. The concentration of iodine atoms reaches its maximum value 0.5 μs after the arrival of a shock wave and is the same as the decomposition value of CH_3I. The net reaction rate of R1$_{\mathrm{I}}$ is very fast in the early stage of the induction period, but it is about 10^{-5} mol cm^{-3} s^{-1} during most of the induction period; this value is smaller by one or two orders than those of R1$_{\mathrm{Br}}$ and R1$_{\mathrm{Cl}}$. Therefore, R1$_{\mathrm{I}}$ contributes significantly to the ignition only in the early stage. Since R4$_{\mathrm{I}}$ proceeds in the forward direction and promotes the ignition, R4$_{\mathrm{I}}$ has the possibility of making a chain with R1$_{\mathrm{I}}$, in which the forward reaction is fast, and with R2$_{\mathrm{I}}$, in which the reverse reaction is fast, just as in the case of CH_3Br addition.[8] However, the change of the forward and reverse rate constants of R2$_{\mathrm{I}}$ has no effect on the calculated ignition-delay time (Table 1), and the net rate of R1$_{\mathrm{I}}$ is slow through the greater part of the induction period. Therefore, the chain of R1$_{\mathrm{I}}$, R2$_{\mathrm{I}}$, and R4$_{\mathrm{I}}$ is impossible. On the other hand, R8$_{\mathrm{I}}$ proceeds in the reverse diretion and promotes the ignition. As a result, R4$_{\mathrm{I}}$ forms a chain with R8$_{\mathrm{I}}$, and their net reaction corresponds to the production of one H radical and one CH_3 radical from CH_4 in each chain. This net reaction is equivalent to that which is formed by R1$_{\mathrm{Br}}$,

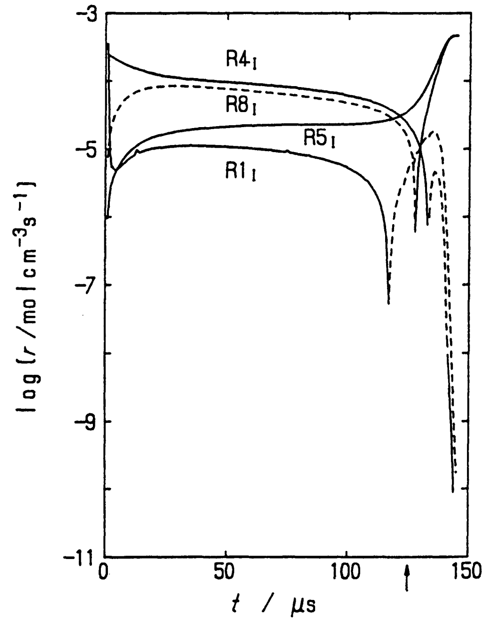

Fig. 4. Net reaction rates. t is time after the arrival of shock wave. Solid and dotted lines indicate that net reaction proceeds in the forward direction and in the reverse direction, respectively. Arrow indicates the ignition-delay time.

$R2_{Br}$, and $R4_{Br}$ when CH_3Br is used. However, the promotion effect of CH_3I is weaker than that of CH_3Br. As is apparent from Fig.4, the net rate of $R4_I$ is nearly equal to the rate of $R8_I$ except for the early stage of the induction period, and the net rates of $R1_{Br}$, $R2_{Br}$, and $R4_{Br}$ previously reported are also equal to each other. However the net rate of $R2_{Br}$ controlling the rate of the chain formed in the CH_4-CH_3Br system is two times faster than that of $R8_I$ controlling the rate of chain formed when CH_3I is used; consequently, we infer that CH_3Br promotes the ignition better than CH_3I does.

Only $R5_I$ inhibits the ignition in the system involving CH_3I. When $R5_I$ or $R5_{Br}$ is deleted from the reaction mechanism in a system including CH_3I or CH_3Br, the calculated ignition-delay time becomes too short by 2 μs or 5 μs respectively. Although the forward reaction of $R5_I$ is fast and should greatly inhibit ignition, its reverse reaction is also fast, in spite of the low reverse rate constant, because iodine above 90% exists as iodine atoms, as is shown in Fig. 2. Therefore, the net rate of $R5_I$ is lower than that of $R2_I$ and $R8_I$ and has only a little effect on the inhibition of the ignition. In the system involving CH_3Br, the concentration of HBr is about three times that of Br atoms, and the rate constant of $R5_{Br}$ in the reverse direction is smaller by 2 orders than that in the forward direction, so the net rate of $R5_{Br}$ also becomes slow compared with those of other reactions which have a large effect on the ignition.

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