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The Addition Effect of Hydrogen Bromide on Methane Ignition behind Reflected Shock Waves

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Synopsis. Ignition delay times were measured in a CH_4–O_2–HBr–Ar mixture behind reflected shock waves. Hydrogen bromide retarded methane ignition, though methyl bromide accelerated it. Model calculations showed that two different chain cycles, promotion and inhibition cycles, were formed for bromine-containing species. The inhibition cycle was predominant in the HBr addition.

Halogenated compounds reduce the burning velocity when they are added to a flame.[1)] However, addition effects of the halogenated compounds on ignition are not always similar to their effects on flame propagation. In ignition, the initial process of complicated chemical reactions for combustion is very significant. We have already reported that several halomethanes, such as CH_3Br and CF_3Br, accelerate methane ignition.[2—6)] This promotion effect is caused by the low dissociation energy of the carbon–halogen bond in the halomethanes. In the presence of halomethanes, most active species leading to ignition are produced in the early stage of the induction period, because the thermal decomposition of halomethanes is faster than that of methane fuel.

The second-order rate coefficient of thermal decomposition of HBr (k_1) is much smaller than that of CH_4 (k_{R1}):

$$\mathrm{HBr} + \mathrm{M} = \mathrm{H} + \mathrm{Br} + \mathrm{M}, \tag{1}$$

$$\mathrm{CH_4} + \mathrm{M} = \mathrm{CH_3} + \mathrm{H} + \mathrm{M}. \tag{R1}$$

According to Westbrook,[7)] the ratios k_1/k_{R1} are 0.11 and 0.06 at 1000 and 2000 K, respectively. Therefore, hydrogen bromide may have a different addition effect from that of halomethanes. In this study, to examine the addition effect of hydrogen bromide on methane ignition, ignition delay times are measured by a shock tube. The difference of addition effects between hydrogen bromide and halomethane is discussed by using model calculations.

Experimental and Computational

The shock tube, the associated vacuum line, and observation arrangements used in this study have all been described previously.[2)] All experiments were done using a mixture of CH_4 (2.0 mol%)-O_2 (4.0 mol%)-HBr (0.1 mol%)-Ar(93.9 mol%) behind reflected shock waves, in the temperature range of 1350—2000 K and the pressure range of 1.9—3.9 atm. Ignition delay times, defined as the time between the arrival of a shock wave and the onset of ignition, were obtained by rapid changes in pressure and OH emission (the 0–0 band of the $A^2\Sigma^+-X^2\Pi_i$ transition, 306.4 nm).

To study the reaction mechanism, we calculated ignition delay times and did sensitivity analyses. The kinetic reaction mechanism for methane oxidation has been reported previously.[3,5)] The methane oxidation mechanism was combined with the 10 elementary reactions involving bromine-containing species shown in Table 1. In the table, the kinetic data on reactions (6) and (7) used in earlier studies[3,5,6)] have been modified within acceptable limits, to improve the fit with the ignition delay times in the CH_4–O_2–HBr–Ar mixture measured in this study. These modifications had no effect on the ignition delay times in the CH_4 (or C_2H_6)-O_2-CH_3Br (or CF_3Br)-Ar mixtures calculated in previous works.[5,6)] All reverse rate coefficients were computed from the forward rate coefficients and the equilibrium constants. Other details concerning the calculation procedure and the definition of calculated ignition delay times have already been described.[3,5)]

Results and Discussion

The ignition delay times (τ) measured in the CH_4–O_2–HBr –Ar mixture are shown in Fig. 1, together with those in the CH_4–O_2–Ar and CH_4–O_2–CH_3Br–Ar mixtures reported in a previous paper.[5)] Hydrogen bromide lengthens τ, i.e., inhibits methane ignition, but methyl bromide promotes it. For the three mixtures, plots of logarithmic τ against the reciprocal temperature are linear with an identical slope, corresponding to the apparent activation energy of 90.6 kJ mol^{-1}. Though the changes of bottleneck reactions caused by the additions of HBr and CH_3Br cannot be found from the activation energy, HBr lengthens τ by 17—18% and CH_3Br shortens τ by 33—34% over the whole temperature range.

In Fig. 1, the ignition delay times calculated in the three mixtures are drawn with straight lines; they show good agreement with the measured times. To clarify the opposite addition effects of HBr and CH_3Br, sensitivity analyses were done on the 10 reactions involving bromine-containing species. In the CH_4–O_2–HBr–Ar mixture (1700 K), the ignition delay times calculated by deleting reactions (1)—(10), one by one, are shown in the sixth column of Table 1. Reactions (2), (6), (7), and (10) greatly influence ignition delay times. When reaction (2) is deleted, the ignition delay time is shorter than that in the complete mechanism, showing that reaction (2) inhibits methane ignition. On the contrary, reactions (6), (7), and (10) promote methane ignition. Not only the inhibition reactions but also the promotion ones occur in the HBr addition.

Table 1. Kinetic Data on Reactions Involving Br-Containing Species and Calculated Ignition Delay Times

Reaction		Forward rate coefficient[a)]				$\tau_{\text{calcd}}/\mu s$[b)]	Effect
		log A	n	E	Ref.	at 1700 K	
(1)	$HBr+M=H+Br+M$	21.81	−1.71	378.9	7	529	Non-effect
(2)	$HBr+H=H_2+Br$	11.88	0.50	4.64	7	503	Inhibition
(3)	$HBr+OH=H_2O+Br$	13.00	0.00	0.00	8	530	Non-effect
(4)	$HBr+O=OH+Br$	13.00	0.00	0.00	8	529	Non-effect
(5)	$HBr+Br=H+Br_2$	10.81	1.00	177.9	7	531	Non-effect
(6)	$HBr+CH_3=H+CH_3Br$	12.00	0.00	23.01	Estimated	627	Promotion
(7)	$CH_3Br=CH_3+Br$	13.20	0.00	272.0	Estimated	580	Promotion
(8)	$CH_3Br+Br=CH_3+Br_2$	13.70	0.00	95.81	7	531	Non-effect
(9)	$Br_2+M=Br+Br+M$	18.16	−0.50	192.7	7	530	Non-effect
(10)	$Br+CH_4=CH_3+HBr$	14.00	0.00	76.57	7	550	Promotion

a) Rate coefficients in the form $k=AT^n \exp(-E/RT)$, in cm^3, mol, s, kJ, and K units. b) Ignition delay times calculated by deleting the reaction in the first column. Ignition delay time calculated using the complete mechanism is 530 µs.

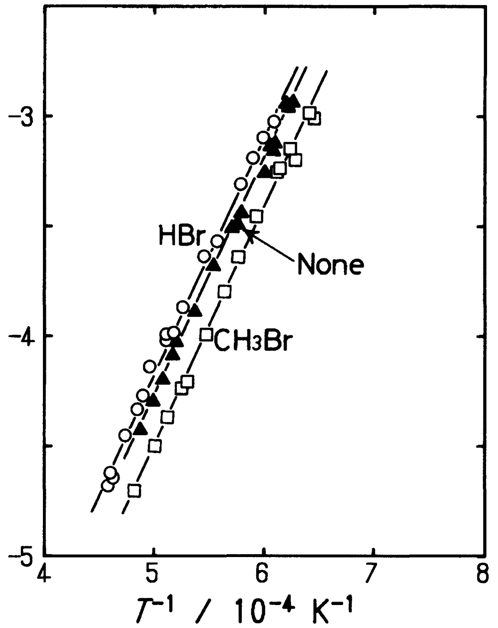

Fig. 1. Comparison between measured and calculated ignition delay times. T is temperature behind reflected shock waves. ○, CH_4–O_2–HBr–Ar mixture; □, CH_4–O_2–CH_3Br–Ar mixture;[5)] ▲, CH_4–O_2–Ar mixture.[5)] Straight lines are calculated.

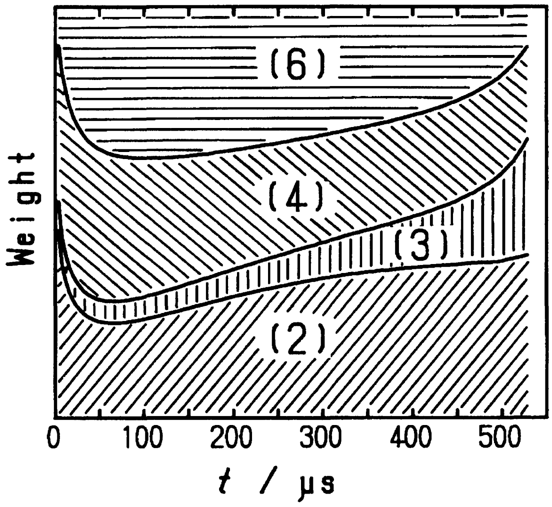

Fig. 2. Weight of HBr consumption channels at 1700 K in CH_4–O_2–HBr–Ar mixture. t is time after the arrival of the reflected shock wave. For each reaction, a relative area enclosed by boundary lines means weight of HBr consumption channels. Calculated ignition delay time is 530 µs.

Figure 2 shows the weight of HBr consumption channels during the induction period in the CH_4–O_2–HBr–Ar mixture (1700 K). Hydrogen bromide is mainly consumed through reactions (2)—(4) and (6). Reaction (1) contributes only 1% at the early stage of the induction period (until a few microseconds). Before the thermal decomposition of HBr (reaction (1)) occurs, methane fuel is appreciably decomposed and oxidized, leading to the consumption of HBr through the reactions with H, OH, O, and CH_3. Reaction (5) has little effect on the HBr consumption under this condition.

In the main reactions of HBr consumption shown in Fig. 2, reactions (2) and (6) have contrasting effects on the ignition delay times (Table 1). Reaction (2) has an inhibition effects, because it extinguishes H atoms, which are one of the important chain carriers driving a combustion reaction. Reaction (6) has a promotion effect, producing H atoms. The other reactions (3) and (4) have no effect on the ignition delay times as shown in Table 1, although these reactions quench the chain carriers, OH radicals and O atoms. This suggests that the addition effect of HBr results from controlling the rate of a chain-branching reaction (R76), $H+O_2=OH+O$, which is the rate-determining step for the combustion reaction.

The dashed line in Fig. 3 shows the rate of consumption of HBr through reactions (2)—(4) and (6) during the induction period in the CH_4–O_2–HBr–Ar mixture (1700 K). The dotted line in the figure shows the rate

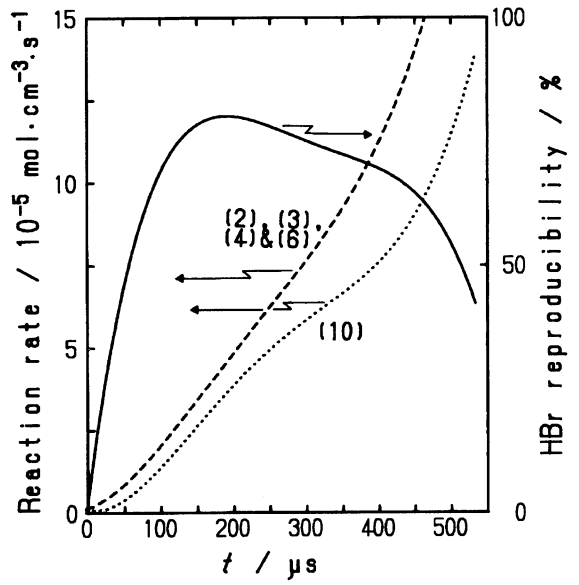

Fig. 3. Reaction rates and HBr reproducibility at 1700 K in CH_4–O_2–HBr–Ar mixture. Dashed and dotted lines show total rates of the reactions consuming and reproducing HBr, respectively. The solid line shows reproducibility of HBr.

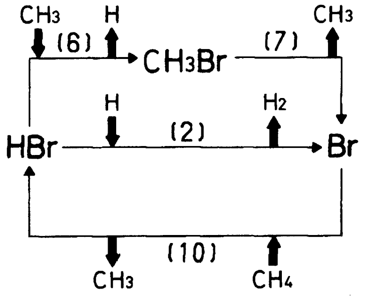

Fig. 4. Chain cycles for Br-containing species formed in CH_4–O_2–HBr–Ar mixture.

of reaction (10) through which HBr is reproduced. The rate ratio of reaction (10) to reactions (2)—(4) and (6), i.e., the reproducibility of HBr, is very high, with a maximum value of 80%, as drawn with a solid line in Fig. 3. This shows that chain cycles are formed for bromine-containing species during the induction period.

From the calculated results of reaction rates and the sensitivity analyses, we propose two chain cycles for bromine-containing species. These are shown in Fig. 4. One consists of reactions (6), (7), and (10) (Cycle I), the other of reactions (2) and (10) (Cycle II). Other cycles such as reactions (3) and (10), and reactions (4) and (10) are excluded from the discussion, because of having no effect on ignition delay times. The ignition delay time calculated using only Cycle I is 495 μs at 1700 K. Similarly, the time calculated using only Cycle II is 621 μs. Considering that the ignition delay time calculated using the complete mechanism is 530 μs, Cycle I has a promotion effect, but Cycle II has an inhibition one. The overall reactions of Cycles I and II are $CH_4=CH_3+H$ and $CH_4+H=CH_3+H_2$, respectively. Thus the different effects for Cycles I and II can be explained by the production and consumption of H atoms.

Reaction (10) is a common step in Cycles I and II, and overall acts as a promotion reaction, as shown in Table 1. However, reaction (10) amplifies the inhibition effect of reaction (2) in Cycle II. When Cycle I is deleted, the ignition delay time calculated by coupling reaction (2) with (10) is much longer than that calculated by reaction (2) only.

We have already reported that Cycle I is formed in the CH_3Br addition, and causes methane ignition to be accelerated.[5] In the HBr addition, although Cycles I and II are simultaneously formed, methane ignition is apparently inhibited, due to the superiority of Cycle II. The difference of the predominant cycle formed in the CH_3Br and HBr addition seems to be caused by methyl radicals produced during the induction period. In the CH_3Br addition, many more methyl radicals are produced at the early stage of induction period through the fast initiation reaction (7). At $t=10$ μs, the concentration of methyl radicals in the CH_3Br addition is about two orders of magnitude higher than that in the HBr addition (1700 K). A high concentration of methyl radicals increases the rate of reaction (6), resulting in the superiority of Cycle I. On the contrary, since a low concentration of methyl radicals decreases the rate of reaction (6), the contribution of reaction (6) to the HBr consumption becomes smaller than that of reaction (2), leading to the superiority of Cycle II. Therefore, Cycle I predominates in the CH_3Br addition, but Cycle II in the HBr addition.

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