The Addition Effect of CH_3Br and CH_3Cl on Ignition of CH_4 by Shock Wave

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Ignition delay times were measured in the CH_4–CH_3X (X: Cl or Br)–O_2 system diluted in Ar using a shock tube. The times were shorter than those without CH_3X, indicating that CH_3X accelerates the ignition of CH_4. A theoretical model including 8 elementary reactions concerning CH_3X, with a CH_4 oxidation mechanism consisting of 93 reactions, was used to examine the role of halogen for the ignition. The compounds containing Br formed a chain reaction with CH_4 and accelerated the decomposition of CH_4, while CH_3Cl acted only as a fuel which was easily decomposed.

Ignition delays in mixtures involving CH_4 and additives have been studied under various experimental conditions.[1–6)] The results showed that additives generally promoted ignition in a CH_4–O_2 mixture, except for substances like N_2 which act as diluents only. The addition effect of some hydrocarbons or hydrocarbon derivatives can be attributed principally to a chemical reaction due to the alkyl radicals generated from the decomposition of the additives.

The ignition delay in CH_4–O_2 strongly depends on the rate of initiation reaction (R1) and the rate of CH_3 generation (R2 and R4), as reported previously.[7)] The promotion of ignition by CH_3Br, well-known as an inhibitor for flame propagation, was caused by the additional production of the CH_3 radical, because the activation energy in CH_3Br decomposition (R94) was smaller than that in CH_4 decomposition. However, in addition to insufficient discussion for the role of Br atom, other problems remain, including how other halomethanes influence the ignition of CH_4 and what happens in the reaction mechanism due to the differences of kinds of halogen.

In this investigation, the measurements of ignition delay by using a shock tube and the analytical treatments are performed in the mixtures containing CH_3Br or CH_3Cl, to understand the reaction of halogenated compounds through the induction period. Although the CH_4–CH_3Br–O_2 system has already been studied,[7)] CH_3Br had acted as a part of the main fuel, because the test mixture had involved a large amount of CH_3Br (about 30% of CH_4). So this system involving a small amount of CH_3Br was reexamined.

Experimental

The shock tube used in the experiment was made of 6.2 cm i.d. stainless steel pipe. The reaction and driver sections were 3.8 m and 1.7 m long, respectively, so dwell time above 1.5 ms could be obtained in all experimental regions. Other apparatus for measurements of shock velocity and of ignition delay time and the procedures were already reported in detail.[7)] The composition of the gas mixtures in Table 1 was employed; the accuracy for preparation of gas mixture is below 0.01%, because silicone oil and mercury manometers were used. The pressure and temperature behind the reflected shock wave were 1.9—3.9 atm and 1500—2000 K, respectively.

Analytical Treatment

To clarify the role of halogen atoms for the ignition, ignition delay times were calculated based on the reaction mechanism presented in Table 2, under the constant pressure conditions.[8)] Figure 5 shows that the OH concentration as a function of the time after the arrival of the shock wave increased gradually in the middle stage of the induction period, while the concentration in the last stage rose rapidly. These two sections are regarded as linear, and the ignition delay time was defined as the intersection of the two straight lines. When the profile between time and concentration of H atom, concentration of CH_4, or temperature was used, the ignition delay times were the same as that from the concentration profile of OH.

Rate constants for forward reactions accumulated by Westbrook[9)] were used, except R94 and R102, which are not involved in Ref. 9. Most of these rate constants which had been used for the calculation of burning velocity are regarded as being reasonable at present. However, the rate constants of reactions involving CHCO, CH_2CO, or CH_2 are uncertain and more exact values need. In this calculation, reactions involving CHCO, CH_2CO, or CH_2 did not greatly affect an ignition delay time, so the values in Ref. 9 were used as presented. Rate constants for reverse reactions were calculated from forward ones and equilibrium constants.

R94 and R102 were estimated as calculated induction times so as to agree with experimental ones in 1500—2000 K. The rate constant of R94 in high pressure limit was expressed by

$$k_{94} = 1.58 \times 10^{14} \exp(-71700/RT).^{10)}$$

However, the agreement of experimental and calculated values could not be attained by using this expression. This experimental conditions are correspond to the so called fall-off region for R94, so the ratio of k/k_∞ was estimated by unimolecular reaction theory. The ratio was 0.07—0.11; then the one-tenth of pre-exponential factor of the above expression was most suitable. Because the data for k_{102} could not be obtained, the expression in Table 2 was estimated. The estimated activation energy of R102 is located between the bond energy of CH_3–Cl and the activation energy of R94 and the pre-exponential factor is reasonable for a unimolecular reaction in fall-off region. Because the variation below 3% of k_{94} or k_{102} does not cause any important change to calculated ignition delay times, both estimated expressions include errors of ±3%.

Although most thermochemical and thermodynamic data which were needed to calculate induction time or reverse rate constants were obtained from Refs. 11 and 12, the data for nine compounds shown below, which were not published, were evaluated by the general statistical method.[11] From the moments of inertia and fundamental vibrational frequencies for C_2H_3 and C_2H_5,[12] C_2H_6,[13] CH_3O,[14] CH_3Cl and CH_3Br,[15] H_2O_2,[16] CHCO,[17] and CH_2CO,[18] we calculated the data for these compounds in the 0—4000 K range. The data in the 0—1500 K range was reported for the former seven compounds;[12—16] calculated values in the 0—1500 K range agree well with the data in the references, supporting the adequacy of calculated values for 1500—4000 K, because values in high temperature can be estimated more exactly. On the other hand, the calculated data for CHCO and CH_2CO may involve some error, because of using unreliable fundamental vibrational frequencies, but small changes of thermodynamic data for CHCO and CH_2CO do not affect calculations of ignition delay times.

Results and Discussion

Additives used in this study are a kind of fuel, so we must determine how a small additional amount of fuel changes the ignition delay. As shown in Fig. 1, ignition delay times are slightly longer in mixture 2 than that in mixture 1; namely, CH_4 acts as a self-inhibitive compound. Therefore, to discuss the role of halogen, we used the mixture containing only CH_4 as fuel and some mixtures in which a part of CH_4 was replaced by halomethane. For example, the concentrations of O_2 and Ar and the number of C atoms are constant in mixtures 2, 3, and 4 (Table 1) and it is proper to use them to examine the role of the halogen atom, as previously reported.[7]

Ignition delay times of mixtures including CH_3Br or CH_3Cl (in Fig. 1) are short in comparison with the times for the mixtures 1 and 2, indicating that these compounds accelerate an ignition of CH_4; the acceleration effect of CH_3Br is more predominant than CH_3Cl. The lines between $1/(10^{-4}\,T_5)$ and $\log(\tau/s)$ are straight. The slopes are 1.04, 1.02, 1.08, and 1.09 K for the mixtures 1, 2, 3, and 4, respectively; namely, the addition effect is quite different absolutely each case but the dependence on temperature is almost identical in all mixtures. The fact that ignition delay times in mixtures 3 and 4 are shorter than that in mixtures 1 or 2 may be explained qualitatively by only the difference of bond energies of C–H and C–X. However it is hardly possible that only the initiation reactions (R1, R94, R102) control the ignition delay, even though they are the main factor.

Table 1. Test Gas Mixture Composition (%)

No.	CH_4	CH_3Br	CH_3Cl	O_2	Ar
1	2.00	—	—	4.00	94.00
2	2.10	—	—	4.00	93.90
3	2.00	0.10	—	4.00	93.90
4	2.00	—	0.10	4.00	93.90

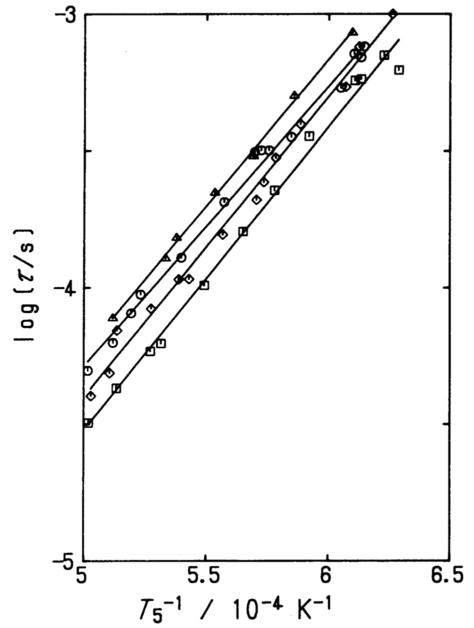


Fig. 1. Observed ignition delay times. ○, mixture 1; △, mixture 2; □, mixture 3; ◇, mixture 4.

We indicated[7] that the main reactions controlling the ignition of CH_4 are R1, R2, R4—R6, R8, R9, R13, R14, R22, and R69. CH_3, CH_3O, CH_2O, and CHO species participate in all these reactions, except for R69, which is the most important one to chain branching: These results suggest that the ignition reactions progress through the route of $CH_3 \rightarrow CH_3O \rightarrow CH_2O \rightarrow CHO$. When CH_3Br is added, the reaction scheme will differ; the initiation reaction is not R1 but R94, R1 does not contribute to ignition at all, and R95 and R98, known as inhibition ones, compete with R69 in the consumption of H atoms. Moreover, in CH_4–O_2, the behavior of CH_3 and of H atom made extremely important contribution to an ignition. CH_3, generated by the initiation reaction (R1), reacts

$CH_4 + M = CH_3 + H + M$ (R1)
$CH_4 + OH = CH_3 + H_2O$ (R2)
$CH_4 + O = CH_3 + OH$ (R4)
$CH_3 + HO_2 = CH_3O + OH$ (R5)
$CH_3 + O_2 = CH_3O + O$ (R6)
$CH_3 + O = CH_2O + H$ (R8)
$CH_3 + CH_3 = C_2H_6$ (R9)
$CH_3O + M = CH_2O + H + M$ (R13)
$CH_2O + OH = HCO + H_2O$ (R14)
$HCO + M = CO + H + M$ (R22)
$H + O_2 = O + OH$ (R69)
$CH_3Br = CH_3 + Br$ (R94)
$CH_3Br + H = CH_3 + HBr$ (R95)
$HBr + H = H_2 + Br$ (R98)

with O_2 or O atom. R6 is predominant in the early stage of the induction period and R8 becomes important later, while the concentration of H atom increased continuously. These facts are important in order to comprehend the role of halogen atoms.

Calculated induction times are in good agreement with the observed values, as shown in Fig. 2, indicating that the reaction mechanism in Table 2 is reasonable. Although a large number of reactions for halogen containing compounds have been reported, the set of R94—R109 for halogen containing compounds is enough to explain the ignition delay time. As is obvious from experimental results, additive effects are similar in all temperature regions; therefore, model calculations and various parametric analyses were performed in all mixtures at 1800 K. Calculated induction times are shown in Table 3. This includes the results which were calculated by the reaction mechanism in Table 2 and by deleting reactions concerning halogen species one by one from it.

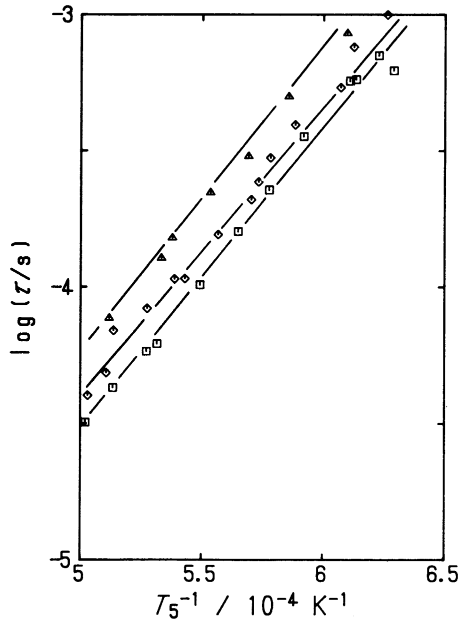
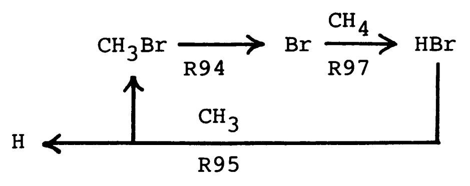


Fig. 2. Comparison of calculated and observed ignition delay times. △, mixtures 2; □, mixture 3; ◇, mixture 4. Straight lines are calculated ones.

In eight reactions involving bromine containing species, the reactions, R94, R95, R97, and R98 influence upon ignition delay time. When R94, R95, or R97 is deleted from the complete mechanism (Table 2), the ignition delay is longer than that in the complete mechanism, while deletion of R98 made it shorter, showing that R94, R95, and R97 promote an ignition and R98 inhibits an ignition.

The calculated ignition delay time without R94 is longer than that in mixture 2. This result is caused by R98, in addition, R95 can also inhibit an ignition, when R94 is deleted. R95 proceeds in the reverse direction in a greater part of the induction period, while R94, R97, and R98 proceed in the forward direction, in the complete mechanism. When R94 is deleted, R95 proceeds in the forward direction through the whole induction period, leading to the inhibition of ignition. Of course, the conditions in which R94 does not exist cannot occur in these experiments, but the result suggests that a reaction like R95 has some possibility to act as an inhibition one or as an acceleration one, depending on the rate of thermal decomposition of the halogenated hydrocarbons.

The initiation reaction is, of course, R94, because the rates of other initiation reactions (R1, R74, R92) did not contribute much to the ignition delay time. While CH_3 is consumed through R6 and R8, which are the main reactions for CH_3 consumption, Br atom consumed CH_4 through R97 and then CH_3Br was regenerated through the reverse reaction of R95. R97, including the same species as R95 on its right side, progresses forward, namely CH_4 is not regenerated by R97. Therefore, the next chain cycle is formed and promotes the decomposition of CH_4. Moreover, in the cycle, H atoms are produced, so that the chain branching reaction, R69, or the reaction of CH_4 consumption, R3, is accelerated catalytically. In brief, the net reaction of R94, R95, and R97 corresponds to a process having a fast rate in which CH_4 is decomposed to CH_3 and H atom instead of process R1 having a slow rate.



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The effect of CH_3Cl as ignition promoter is low in comparison to that of CH_3Br; the effective reactions on ignition are R102, R103, R105, and R106. Al-

Table 2. Reaction Mechanism and Rate Constants

	Reaction	log A	n	E
R1	$CH_4+M=CH_3+H+M$	17.15	0.00	88.40
R2	$CH_4+OH=CH_3+H_2O$	3.54	3.08	2.00
R3	$CH_4+H=CH_3+H_2$	14.10	0.00	11.90
R4	$CH_4+O=CH_3+OH$	13.20	0.00	9.20
R5	$CH_4+HO_2=CH_3+H_2O_2$	13.30	0.00	18.00
R6	$CH_3+HO_2=CH_3O+OH$	13.51	0.00	0.00
R7	$CH_3+O_2=CH_3O+O$	13.68	0.00	29.00
R8	$CH_3+OH=CH_2O+H_2$	12.60	0.00	0.00
R9	$CH_3+O=CH_2O+H$	14.11	0.00	2.00
R10	$CH_3+CH_3=C_2H_6$	12.95	0.00	0.00
R11	$CH_3+CH_3=C_2H_5+H$	14.90	0.00	26.52
R12	$CH_3+CH_3=C_2H_4+H_2$	16.00	0.00	32.00
R13	$CH_3+CH_2O=CH_4+CHO$	10.00	0.50	6.00
R14	$CH_3+CHO=CH_4+CO$	11.48	0.50	0.00
R15	$CH_3+HO_2=CH_4+O_2$	12.00	0.00	0.40
R16	$CH_3O+O_2=CH_2O+HO_2$	12.00	0.00	6.00
R17	$CH_3O+M=CH_2O+H+M$	13.70	0.00	21.00
R18	$CH_2O+OH=CHO+H_2O$	12.88	0.00	0.17
R19	$CH_2O+H=CHO+H_2$	14.52	0.00	10.50
R20	$CH_2O+O=CHO+OH$	13.70	0.00	4.60
R21	$CH_2O+HO_2=CHO+H_2O_2$	12.00	0.00	8.00
R22	$CH_2O+M=CHO+H+M$	16.52	0.00	81.00
R23	$CHO+OH=CO+H_2O$	14.00	0.00	0.00
R24	$CHO+H=CO+H_2$	14.30	0.00	0.00
R25	$CHO+O=CO+OH$	14.00	0.00	0.00
R26	$CHO+O_2=CO+HO_2$	12.60	0.00	7.00
R27	$CHO+HO_2=CH_2O+O_2$	14.00	0.00	3.00
R28	$CHO+M=CO+H+M$	14.16	0.00	19.00
R29	$CO+OH=CO_2+H$	7.11	1.30	−0.77
R30	$CO+O+M=CO_2+M$	15.77	0.00	4.10
R31	$CO+HO_2=CO_2+OH$	14.18	0.00	23.65
R32	$CO+O_2=CO_2+O$	11.50	0.00	37.60
R33	$C_2H_6+OH=C_2H_5+H_2O$	13.05	0.00	2.45
R34	$C_2H_6+H=C_2H_5+H_2$	2.73	3.50	5.20
R35	$C_2H_6+O=C_2H_5+OH$	13.40	0.00	6.36
R36	$C_2H_6+CH_3=C_2H_5+CH_4$	−0.26	4.00	8.28
R37	$C_2H_5+O_2=C_2H_4+HO_2$	12.00	0.00	5.00
R38	$C_2H_5+M=C_2H_4+H+M$	15.30	0.00	30.00
R39	$C_2H_4+OH=C_2H_3+H_2O$	12.68	0.00	1.23
R40	$C_2H_4+H=C_2H_3+H_2$	7.18	2.00	6.00
R41	$C_2H_4+M=C_2H_3+H+M$	18.80	0.00	108.72
R42	$C_2H_4+M=C_2H_2+H_2+M$	16.97	0.00	77.20
R43	$C_2H_4+OH=CH_3+CH_2O$	12.30	0.00	0.96
R44	$C_2H_4+O=CH_3+CHO$	12.52	0.00	1.13
R45	$C_2H_4+O=CH_2O+CH_2$	13.40	0.00	5.00
R46	$C_2H_4+C_2H_4=C_2H_5+C_2H_3$	14.70	0.00	64.70
R47	$C_2H_3+H=C_2H_2+H_2$	13.30	0.00	2.50
R48	$C_2H_3+O_2=C_2H_2+HO_2$	12.00	0.00	10.00
R49	$C_2H_3+M=C_2H_2+H+M$	14.90	0.00	31.50
R50	$C_2H_2+OH=C_2H+H_2O$	12.78	0.00	7.00
R51	$C_2H_2+H=C_2H+H_2$	14.30	0.00	19.00
R52	$C_2H_2+O=C_2H+OH$	15.51	−0.60	17.00
R53	$C_2H_2+M=C_2H+H+M$	14.00	0.00	114.00
R54	$C_2H_2+OH=CH_2CO+H$	11.51	0.00	0.20
R55	$C_2H_2+O=CHCO+H$	4.55	2.70	1.39
R56	$C_2H_2+O=CH_2+CO$	13.83	0.00	4.00
R57	$C_2H_2+O_2=CHO+CHO$	12.60	0.00	28.00
R58	$C_2H+O_2=CHO+CO$	13.00	0.00	7.00
R59	$C_2H+O=CH+CO$	13.70	0.00	0.00
R60	$CH_2CO+OH=CHCO+H_2O$	13.00	0.00	0.00
R61	$CH_2CO+H=CHCO+H_2$	13.00	0.00	0.00
R62	$CH_2CO+O=CHCO+OH$	13.00	0.00	0.00
R63	$CH_2CO+OH=CH_2O+CHO$	13.45	0.00	0.00
R64	$CH_2CO+H=CH_3+CO$	13.04	0.00	3.40
R65	$CH_2CO+O=CHO+CHO$	13.00	0.00	2.40
R66	$CH_2CO+M=CH_2+CO+M$	16.30	0.00	60.00

Table 2. (Continued)

	Reaction	log *A*	*n*	*E*
R67	$CHCO+OH=CHO+CHO$	13.00	0.00	0.00
R68	$CHCO+H=CH_2+CO$	13.70	0.00	0.00
R69	$CHCO+O=CO+CHO$	13.53	0.00	2.00
R70	$CH_2+OH=CH+H_2O$	11.43	0.67	25.70
R71	$CH_2+H=CH+H_2$	11.43	0.67	25.70
R72	$CH_2+O=CH+OH$	11.28	0.68	25.00
R73	$CH_2+O_2=CHO+OH$	14.00	0.00	3.70
R74	$CH+O_2=CHO+O$	13.00	0.00	0.00
R75	$CH+O_2=CO+OH$	11.13	0.67	25.70
R76	$H+O_2=OH+O$	14.27	0.00	16.79
R77	$O+H_2=OH+H$	10.26	1.00	8.90
R78	$OH+OH=O+H_2O$	12.50	0.00	1.10
R79	$OH+H_2=H+H_2O$	13.34	0.00	5.15
R80	$H+H+M=H_2+M$	15.48	0.00	0.00
R81	$O+O+M=O_2+M$	15.67	−0.28	0.00
R82	$H+O+M=OH+M$	16.00	0.00	0.00
R83	$OH+H+M=H_2O+M$	23.15	−2.00	0.00
R84	$H+O_2+M=HO_2+M$	15.22	0.00	−1.00
R85	$H+HO_2=H_2+O_2$	13.40	0.00	0.70
R86	$H+HO_2=OH+OH$	14.40	0.00	1.90
R87	$H+HO_2=O+H_2O$	11.95	0.50	3.97
R88	$OH+HO_2=H_2O+O_2$	13.70	0.00	1.00
R89	$O+HO_2=OH+O_2$	13.70	0.00	1.00
R90	$H_2O_2+OH=H_2O+HO_2$	13.00	0.00	1.80
R91	$H_2O_2+H=HO_2+H_2$	12.23	0.00	3.75
R92	$H_2O_2+O_2=HO_2+HO_2$	13.60	0.00	42.64
R93	$H_2O_2+M=OH+OH+M$	17.08	0.00	45.50
R94	$CH_3Br=CH_3+Br$	13.20	0.00	71.70
R95	$CH_3Br+H=CH_3+HBr$	14.24	0.00	6.90
R96	$CH_3Br+Br=CH_3+Br_2$	13.70	0.00	22.90
R97	$CH_4+Br=CH_3+HBr$	14.00	0.00	18.30
R98	$HBr+H=H_2+Br$	11.88	0.50	1.11
R99	$Br_2+H=HBr+Br$	12.81	0.50	1.11
R100	$Br+Br+M=Br_2+M$	16.00	0.00	0.00
R101	$Br+H+M=HBr+M$	18.00	−0.71	0.00
R102	$CH_3Cl=CH_3+Cl$	13.90	0.00	79.80
R103	$CH_3Cl+H=CH_3+HCl$	14.54	0.00	9.00
R104	$CH_3Cl+Cl=CH_3+Cl_2$	14.00	0.00	25.00
R105	$CH_4+Cl=CH_3+HCl$	13.41	0.00	3.85
R106	$HCl+H=H_2+Cl$	13.36	0.00	3.50
R107	$Cl_2+H=HCl+Cl$	14.57	0.00	1.80
R108	$Cl+Cl+M=Cl_2+M$	14.30	0.00	−1.79
R109	$Cl+H+M=HCl+M$	8.78	1.00	−36.52

Rate constants in the form $A \times T^n \exp(-E/RT)$, in cm^{-3}, mol, s, kcal, and K units.

Table 3. Calculated Induction Times

Reaction[a)]	Ignition delay time/10^{-6} s			
	Mixture 1	Mixture 2	Mixture 3	Mixture 4
None	215	221	119	154
$CH_3X=CH_3+X$(R94, R102)			233	236
$CH_3X+H=CH_3+HX$(R95, R103)			142	145
$CH_3X+X=CH_3+X_2$(R96, R104)			118	154
$CH_4+X=CH_3+HX$(R97, R105)			140	152
$HX+H=H_2+X$(R98, R106)			115	150
$X_2+H=HX+X$(R99, R107)			119	153
$X+X+M=X_2+M$(R100, R108)			119	154
$X+H+M=HX+M$(R101, R109)			118	153

a) Reaction which is delected from the complete mechanism. X is Br or Cl.

though the initiation reaction is changed from R1 to R102, the chain reaction like (I) does not exist. This is because R102 is 100 times faster than R1 and R105 proceeds in the forward direction and promotes the decomposition of CH_4, but R103 progresses forward (Fig. 4), so CH_3Cl could not be regenerated during the whole induction period. The difference of rates between R95 and R103 depends on the rate constant. The forward and net rates of R103 are about 1/10 of R95 and the reverse rate of R103 is about 1/500 of R95, while the concentration of HCl is two times that of HBr (Figs. 5 and 6).

$CH_3Cl = CH_3 + Cl$ (R102)
$CH_3Cl + H = CH_3 + HCl$ (R103)
$CH_4 + Cl = CH_3 + HCl$ (R105)
$HCl + H = H_2 + Cl$ (R106)

As R103 proceeds in the forward direction and the

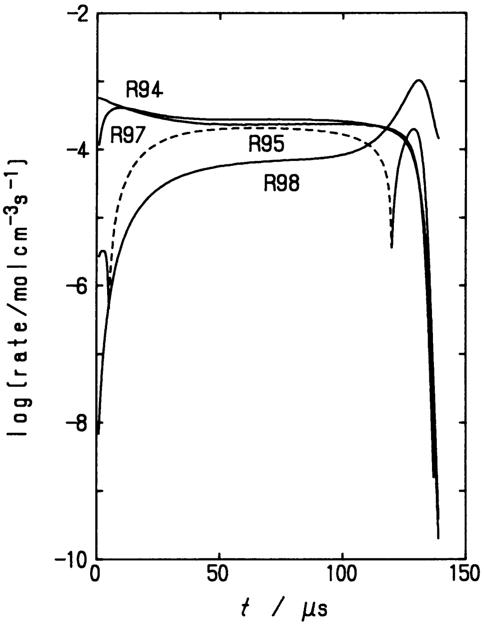


Fig. 3. Net reaction rates of R94, R95, R97, and R98 at 1800 K in mixture 3. *t* is time after the arrival of shock wave. Solid line: net reaction proceeds in forward direction, dotted line: in reverse direction.

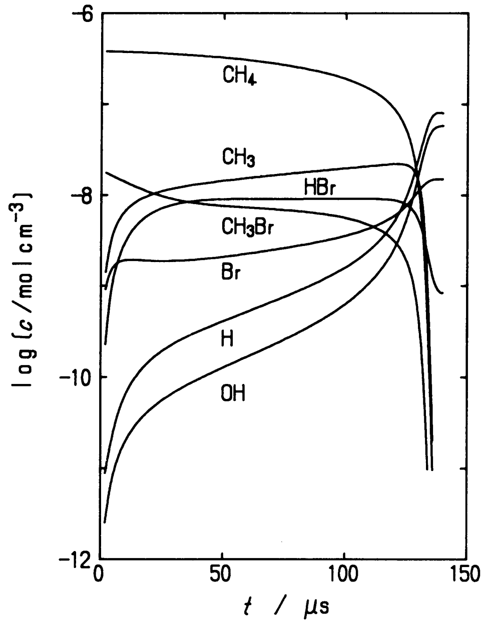


Fig. 5. Calculated concentration profiles of CH_4, CH_3, H, OH, CH_3Br, HBr, and Br at 1800 K in mixture 3.

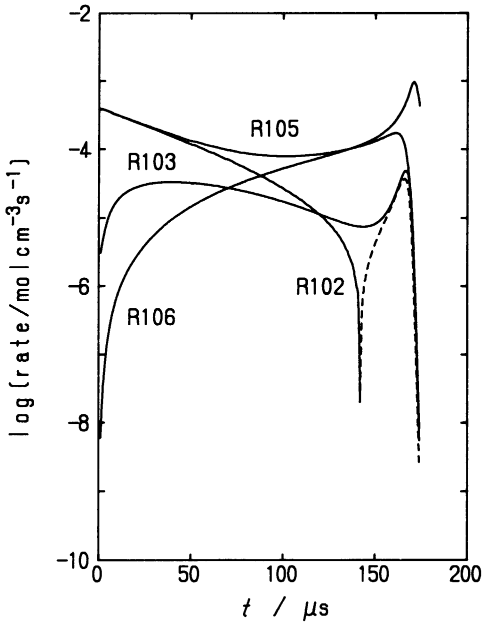


Fig. 4. Net reaction rates of R102, R103, R105, and R106 at 1800 K in mixture 4.

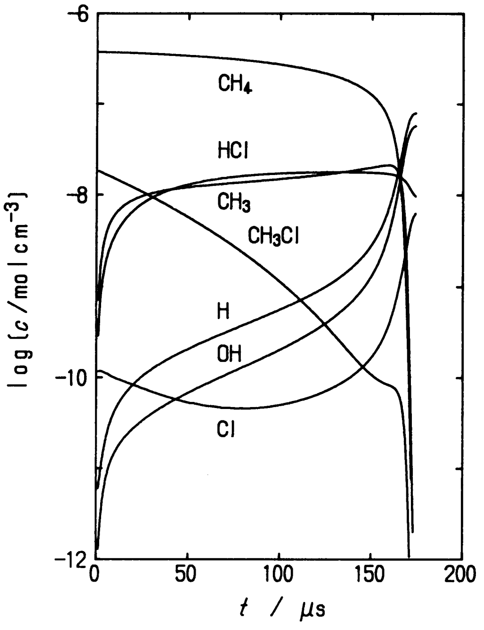
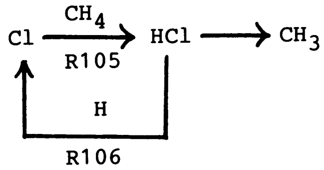


Fig. 6. Calculated concentration profiles of CH_4, CH_3, H, OH, CH_3Cl, HCl, and Cl at 1800 K in mixture 4.

reverse rate of R105 is very slow, HCl generated by R103 reacts through R106; as a result, R105 and R106, which have comparable rates, form chain (II). The



(II)

chain promotes the decomposition of CH_4, while consumes H simultaneously. H atom promotes R69 directly, while CH_3 needs two or more steps, which have low rate constants, to generate H atom, so the chain (II) inhibits the ignition. In CH_3Br, the chain like (II) is probably created too, but it contributes little to an ignition as the reverse rate of R96 is faster than that of forward rate of R98 through the whole induction period.

When R102 is deleted, the ignition delay is almost equal to that in mixture 3, as shown in Table 3. If R102 does not exist, it is predicted that CH_3Cl should consume H through R103; H is consumed furthermore by the chain (II), causing inhibition of an ignition. Exclusion of R103, R105, or R106 makes the ignition delay shorter by a few percent; this result indicates that these reactions certainly inhibit an ignition and that H atom has more effect on the ignition than CH_3 does.

The concentration profile of CH_3Br or of Br differ from that of CH_3Cl or of Cl, respectively. On the other hand, the profiles of CH_4, CH_3, OH, H, or HX (X: Br or Cl) are very similar in the mixtures 3 and 4. When the reaction is initiated, Br is first generated by R94 and then HBr rapidly increases, following Br, until it reaches a constant value at about 30 μs. The consumption of CH_3Br is retarded practically with increase of concentration of HBr. CH_3Cl is consumed gradually through the induction period and its concentration did not become constant. Moreover, Cl atom is produced in the early stages of induction period, but it generates HCl soon because of fast R105, resulting in the greater parts of Cl existing as HCl even in early stages. Although these profiles may be easily expected from Figs. 3 and 4, they express fully the difference of addition effect between CH_3Br and CH_3Cl. At the same time, they show that both additives change the rate of ignition reaction but not the main ignition mechanism.

In conclusion, the promotion mechanism by the addition of CH_3Br and CH_3Cl to methane is because of the relatively fast decomposition rates in both additives, which lead to easy generation of CH_3 radical; this is especially clear in CH_3Br, because of the existence of the chain reaction constructed by R94, R95, and R97. The fundamental discrepancy in CH_3Br and CH_3Cl depends on the relative rates of R95 or R103 and R98 or R106, in addition to the low rate in R102.

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