Effect of Bromotrifluoromethane on the Ignition in Methane and Ethane-Oxygen-Argon Mixtures behind Shock Waves

Akimichi SUZUKI, Tadaaki INOMATA,* Hiroshi JINNO, and Takao MORIWAKI
Department of Chemistry, Faculty of Science and Technology,
Sophia University, Kioi-cho, 7-1, Chiyoda-ku, Tokyo 102
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The ignition delay times behind shock waves in CH_4–, and C_2H_6–O_2–Ar systems containing CF_3Br were measured for a range of temperatures between 1400 and 2100 K and pressures between 1.5 and 3.5×10^5 Pa. These measurements indicated that CF_3Br promotes the ignition of CH_4 but inhibits the ignition of C_2H_6. Although the inhibition effect for C_2H_6 increases with increasing CF_3Br concentration and decreasing temperature, the promotion effect in CH_4 was independent of both the CF_3Br concentration and the temperature in this experiment. We calculated the induction times for conditions similar to the experiments using a model which included 49 elementary reactions related to CF_3Br. Calculations using this model gave induction times that were in good agreement with the experiments. The calculated values, however, depended on several effective reactions among the 49 reactions.

Ignitions of methane and ethane in shock tubes under various experimental conditions have been investigated since 1959.[1-21] It is well-known that methyl halides accelerate the ignition of CH_4 but retard the ignition of C_2H_6; these effects are due to chemical reasons.[22-23] Methyl bromide was the most effective substance as an ignition promoter for CH_4 and methyl iodide had the greatest effect as an ignition inhibitor for C_2H_6. The different effects in CH_4 and C_2H_6 ignitions have been clarified from the rates of reactions involving halogen species as well as the differences of predominant reactions in both fuels. We have already reported the effect of CH_3Br addition on the ignition of CH_4 and C_2H_6.[22-24]

In this study, in order to examine the influence of the substitution of hydrogen by fluorine, we investigated the effect of CF_3Br addition on the ignition of CH_4 or C_2H_6, compared with the effect of CH_3Br addition. Although this species has received much attention in experimental studies regarding flame inhibition,[25-29] the number of reports concerning its effects on ignition has been extremely small. We therefore provide new experimental information concerning addition effects of CF_3Br in methane– and ethane–oxygen–argon mixtures, as well as a numerical analysis of the mechanism.

Experimental

Measurements. The shock tube used in this experiment was made of 8.0 cm i.d. stainless-steel pipe. The reaction and driver sections were 450 and 80 cm in length, respectively. Thus, dwell times of about 500 microseconds behind a reflected shock wave could be obtained using helium driver gas. A poly(ethylene-terephthalate) diaphragm was ruptured by increasing the driver gas pressure up to a certain value. The reaction gases were mixtures of methane or ethane, bromotrifluoromethane, and oxygen diluted with argon (Table 1). The shock wave velocities were controled by changing the pressure ratio of helium and nitrogen gas in the driver section. The incident shock velocities were measured by PZT-type pressure transducers placed along the reaction section and a digital counter. The state of the test gas behind the shock wave was determined using ideal one-dimensional shock equations with thermodynamic properties. The onsets of ignition were detected by OH radical absorption with a photomultiplier fitted with a 306 nm interference filter on the end of reaction section. A typical oscillograph is shown in Fig. 1. The ignition delay times, defined as the time interval between the pressure rise due to the arrival of a shock wave and the rise of an optical signal by the photomultiplier, were obtained under various conditions.

Calculations: In order to discuss the effect of CF_3Br on the reaction mechanism for methane and ethane oxidations, we calculated the ignition delay times using a model. The model used for methane and ethane oxidations are described in Refs. 30—33. This mechanism consists of 35 species and 113 elementary reactions, including forward and reverse reactions.

Table 1. Test Gas Mixture Composition (%)

No.	CH_4	C_2H_6	CF_3Br	CH_3Br	O_2	Ar
1	2.0				4.0	94.0
2	2.0		0.1		4.0	93.9
3	2.0		0.2		4.0	93.8
4		1.0			3.5	95.5
5		1.0	0.1		3.5	95.4
6		1.0	0.2		3.5	95.3
7	2.0			0.1	4.0	93.9
8	2.0			0.2	4.0	93.8
9		1.0		0.1	3.5	95.4

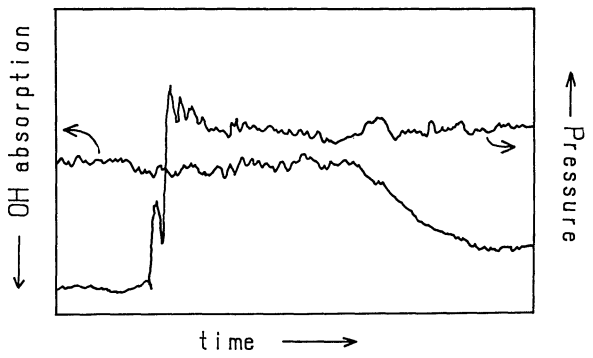


Fig. 1. Typical oscillograms of pressure and OH absorption.

Considering that the pressure is constant within the induction time (Fig. 1), a model calculation was performed that assumed a constant pressure.

We calculated the OH concentration and defined the calculated ignition delay time as being the time interval of a sudden rise in the OH concentration. This gives ignition delay times closer to the observed values.[23] Elementary reactions related to CF_3Br were obtained from the literature.[34] (Table 2)

Results and Discussion

CH_4 System. The ignition delay times of mixtures 2 and 3 including CF_3Br are slightly short compared with those of mixture 1, excluding CF_3Br over the entire temperature region, as shown in Fig. 2. The points are the observed values and the lines are the calculated values. It is obvious that CF_3Br has a promotion effect for methane ignition. The concentration dependence of

Table 2. Reaction Mechanisms and Rate Constants[a]

Reaction	Forward			Reverse		
	A	n	E	A	n	E
(A1) $CH_3Br=CH_3+Br$	1.5849E+13	0.000	71.70	2.8853E+08	0.928	2.91
(A2) $CH_3Br+H=CH_3+HBr$	1.7378E+14	0.000	6.90	1.0000E+13	0.000	5.50
(A3) $CH_3Br+Br=CH_3+Br_2$	5.0119E+13	0.000	22.90	1.0000E+13	0.000	1.00
(A4) $CH_4+Br=CH_3+HBr$	1.0000E+14	0.000	18.30	1.3183E+12	0.000	0.93
(A5) $HBr+H=H_2+Br$	7.5858E+11	0.500	1.11	3.4674E+10	1.000	16.64
(A6) $Br_2+H=Br+HBr$	6.4565E+12	0.500	1.11	6.4565E+10	1.000	42.52
(A7) $Br+Br+M=Br_2+M$	1.0000E+16	0.000	0.00	1.4454E+18	−0.500	46.05
(A8) $Br+H+M=HBr+M$	1.0000E+18	−0.710	0.00	6.4565E+21	−1.710	90.55
(A9) $C_2H_5Br+H=C_2H_5+HBr$	3.4674E+14	0.000	5.90	5.6234E+13	0.000	28.67
(A10) $C_2H_5Br+Br=C_2H_5+Br_2$	1.0000E+14	0.000	19.00	2.5119E+13	0.000	0.00
(A11) $C_2H_6+Br=C_2H_5+HBr$	7.9433E+13	0.000	13.40	1.1482E+13	0.000	3.47
(A12) $C_2H_3Br+H=C_2H_3+HBr$	3.4674E+14	0.000	7.00	1.0000E+13	0.000	25.00
(A13) $C_2H_3Br+Br=C_2H_3+Br_2$	5.0119E+13	0.000	20.00	1.0000E+13	0.000	0.00
(A14) $CF_3Br+H=CF_3+HBr$	2.1850E+14	0.000	9.46	6.9420E+12	0.000	31.32
(A15) $CF_3Br=CF_3+Br$	5.0100E+13	0.000	66.30	3.8020E+11	0.000	0.50
(A16) $CF_3Br+Br=CF_3+Br_2$	6.0256E+13	0.000	23.00	1.8620E+12	0.000	1.00
(A17) $CF_3Br+CH_3=CH_3Br+CF_3$	9.7723E+12	0.000	5.20	1.3489E+13	0.000	12.59
(A18) $CF_3+H=CF_2+HF$	3.9811E+12	0.000	0.00	5.0118E+13	0.000	110.00
(A19) $CF_3+O=CF_2+FO$	1.2882E+14	0.000	2.00	5.0118E+14	0.000	83.42
(A20) $CF_3+OH=CF_2O+HF$	3.9811E+12	0.000	0.00	4.8977E+13	0.000	115.65
(A21) $CF_3+CH_4=CF_3H+CH_3$	1.0000E+12	0.000	11.00	3.8905E+11	0.000	11.75
(A22) $CF_3+CH_3=CH_2CF_2+HF$	6.7608E+13	0.000	0.00	6.4565E+15	0.000	95.67
(A23) $CF_3+O_2=CF_2O+FO$	6.9183E+11	0.000	9.06	3.8905E+11	0.000	23.43
(A24) $CF_3H+M=CF_3+H+M$	2.8184E+15	0.000	110.30	5.0118E+13	0.000	4.00
(A25) $CF_3H=CF_2+HF$	1.2022E+12	0.000	63.00	7.4131E+05	1.000	5.87
(A26) $CF_3H+H=CF_3+H_2$	5.0118E+12	0.000	5.00	4.8978E+11	0.000	3.78
(A27) $CF_3H+O=CF_3+OH$	1.9953E+13	0.000	9.20	8.7096E+11	0.000	5.88
(A28) $CF_3H+OH=CF_3+H_2O$	3.2359E+12	0.000	3.77	1.4125E+12	0.000	17.70
(A29) $CF_3H+Br=CF_3+HBr$	1.9952E+13	0.000	23.00	6.7608E+11	0.000	4.88
(A30) $CH_2CF_2+OH=CF_2O+CH_3$	1.0000E+13	0.000	1.00	1.2882E+12	0.000	20.99
(A31) $CH_2CF_2+O=CF_2O+CH_2$	1.5136E+13	0.000	0.00	1.7378E+11	0.000	13.19
(A32) $CH_2CF_2+O=CF_2+CH_2O$	1.5135E+13	0.000	0.00	1.7378E+11	0.000	13.19
(A33) $CF_2O+H=FCO+HF$	1.2882E+11	0.000	0.00	2.3442E+09	0.000	8.50
(A34) $CF_2O+O=FCO+FO$	5.0118E+12	0.000	4.60	5.3703E+10	0.000	0.00
(A35) $CF_2O+OH=FCO+HOF$	7.5858E+11	0.000	0.00	3.4673E+10	0.000	0.00
(A36) $CF_2+CH_3=CH_2CF_2+H$	1.9953E+13	0.000	0.00	1.5849E+16	0.000	44.14
(A37) $FCO+M=F+CO+M$	1.4454E+14	0.000	30.00	1.0000E+10	1.000	0.00
(A38) $FCO+H=HF+CO$	1.9953E+14	0.000	0.00	3.6308E+14	0.000	105.00
(A39) $FCO+O=CO+FO$	1.0000E+14	0.000	0.00	1.0000E+14	0.000	19.96
(A40) $FCO+OH=CO+HOF$	1.0000E+14	0.000	0.00	4.6774E+14	0.000	19.18
(A41) $FCO+OH=CO_2+HF$	1.0000E+14	0.000	0.00	1.0000E+14	0.000	128.00
(A42) $Br+HO_2=HBr+O_2$	5.0119E+12	0.000	0.50	1.0000E+13	0.000	41.31
(A43) $HBr+OH=H_2O+Br$	1.0000E+14	0.000	0.00	1.2882E+14	0.000	31.80
(A44) $HBr+O=OH+Br$	1.0000E+14	0.000	0.00	1.2885E+13	0.000	14.90
(A45) $H_2O_2+Br=HBr+HO_2$	1.0000E+13	0.000	5.00	1.2589E+12	0.000	4.83
(A46) $CF_2+H=HF+CF$	1.0000E+13	0.000	0.00	9.1201E+11	0.000	14.89
(A47) $CF_2+O=FCO+F$	1.0000E+13	0.000	0.00	5.8884E+12	0.000	38.38
(A48) $CF_2+OH=FCO+HF$	1.0000E+13	0.000	0.00	1.8621E+13	0.000	72.62
(A49) $CF_2+OH=CF_2O+H$	1.0000E+13	0.000	0.00	1.0000E+15	0.000	64.12

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

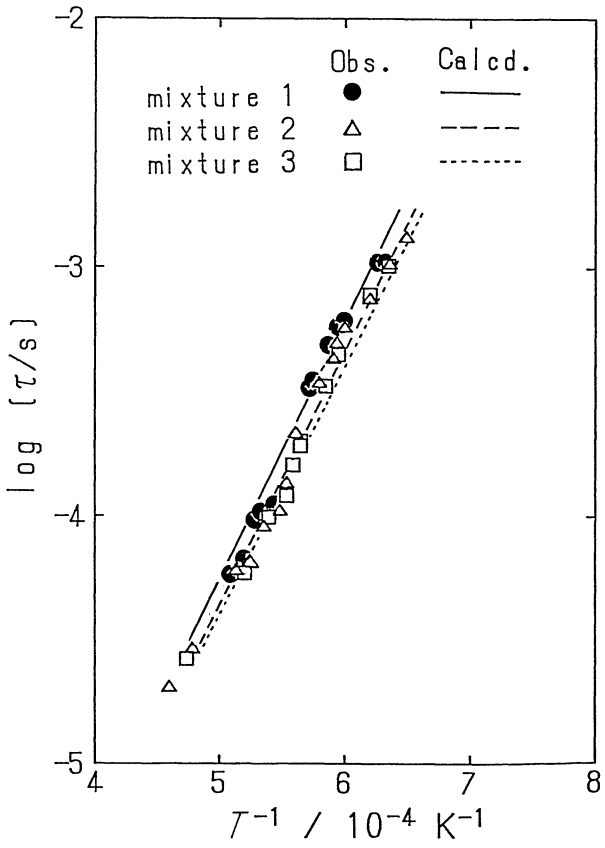


Fig. 2. Comparison of the calculated and observed ignition delay times in CH_4 systems. T is temperature behind shock wave.

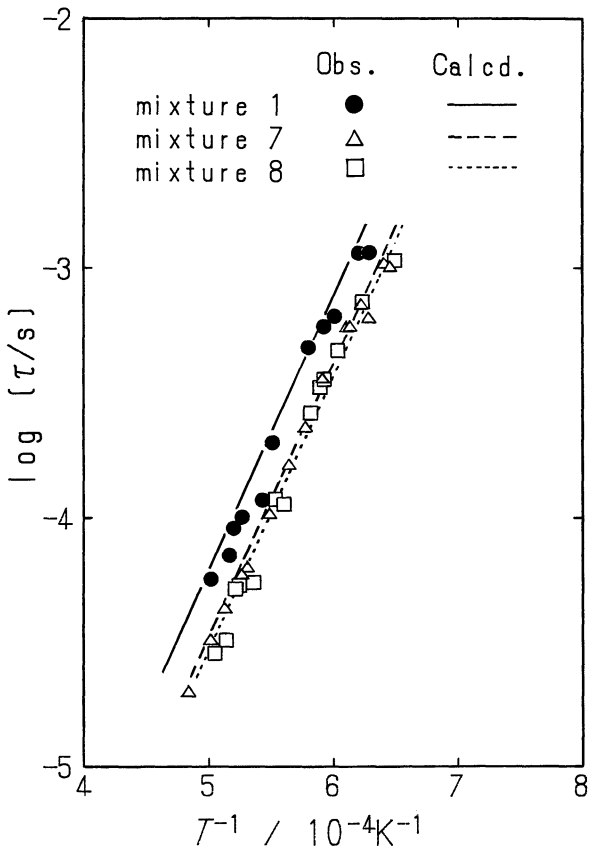


Fig. 3. Comparison of the calculated and observed ignition delay times in CH_4 systems.

CF_3Br, however, is small. These experimental data can be expressed by the least-square method as follows:

$$\log \tau = -9.85 + 1.08\ (10^4/T) \qquad \text{for mixture 1,}$$

$$\log \tau = -9.48 + 1.02\ (10^4/T) \qquad \text{for mixture 2,}$$

and

$$\log \tau = -9.55 + 1.03\ (10^4/T) \qquad \text{for mixture 3.}$$

The slopes of mixtures 1—3 are almost the same, indicating that the promotion effect at high temperature is almost the same as that at low temperature. The ignition delay times of CH_4–O_2–Ar–CH_3Br are shown in Fig. 3 together with those of mixture 1. The tendency was the same for mixtures 7 and 8 including CH_3Br. Accordingly, we try to analyze the kinetics of methane combustion including CF_3Br in comparison with that including CH_3Br.

When comparing the results in Figs. 2 and 3 we considered that the concentration dependence of CF_3Br is smaller than that of CH_3Br.

The reaction mechanism of the CH_4–O_2–Ar system has already been studied. In order to realize a difference in the addition effects between both fuels, we express the consumption route of CH_4 according to the induction time.[35,36] An initiation reaction of this system is a thermal decomposition of fuel, as follows:

$$CH_4 = CH_3 + H. \qquad \text{(R1)}$$

Though the time interval during which reaction (R1) effects the ignition delay times is short, this reaction is important, considering the fact that no ignition occurs without reaction (R1). CH_3 produced by the initiation reaction reacts with O or O_2, as follows:

$$CH_3 + O_2 = CH_3O + O \qquad \text{(R2)}$$

and

$$CH_3 + O = CH_2 + OH. \qquad \text{(R3)}$$

Since O atoms are scarcely produced during the early stage of the induction period, reaction (R2) is dominant. The route in flame, however, is reaction (R3), since O atoms are produced in a region of high temperature. The CH_3O produced by reaction (R2) decomposes immediately, as follows:

$$CH_3O = CH_2O + H. \qquad \text{(R4)}$$

Any H atoms produced react with CH_4 and O_2:

$$CH_4 + H = CH_3 + H_2 \quad (R5)$$

and

$$H + O_2 = OH + O. \quad (R6)$$

The reaction with O_2 as a chain-branching reaction produces two radicals. Of the two radicals the O atom reacts with CH_3; on the other hand, the OH radical reacts with CH_4, as follows:

$$CH_4 + OH = CH_3 + H_2O. \quad (R7)$$

As mentioned above, CH_4 is consumed within the early stage of the induction period by a chain mechanism comprising reactions (R2), (R4), (R5) or reactions (R2), (R4), (R6), (R7).

During the ignition CF_3Br effects the chain mechanism. As shown in Figs. 2 and 3, the calculated ignition delay times agree with the observed values for all mixtures at both low and high temperatures. We therefore considered that the assumed scheme is reasonable. To make sure which reactions are effective, we performed sensitivity analysis. These were performed on 49 reactions involving F or Br-containing species by increasing both the forward and reverse rate constants, multiplying them by ten times and by deleting each reaction at 1866 and 1517 K. From this sensitivity test, the reactions which had some effects on the ignition delay times are shown in Table 3. We also performed this sensitivity test at 1517 K, as shown in Table 3. Reactions (A4) and (A15) are very sensitive in deleting, but not sensitive in increasing these rate constants. In this study we considered these reactions to be effective, owing to the high sensitivity in deleting.

Time profiles of the rates of these effective reactions involving Br-containing species at both 1517 and 1866 K

Table 3. Percentage Change of the Ignition Delay Times ($\tau_{deleted}$, $\tau_{k\times10}$) to Those (τ) Calculated by Using the Complete Mechanism in Mixture 2

Reaction	1866 K		1517 K	
	$\tau_{deleted}$ [a)]	$\tau_{k\times10}$ [b)]	$\tau_{deleted}$	$\tau_{k\times10}$
(A1)	+22	−19	+24	−31
(A2)	+31	−23	+67	−12
(A4)	+50	−3	+27	+1
(A5)	+1	+3	+1	+7
(A15)	+57	0	+107	−5
(A21)	+7	−11	+3	−5
(A22)	−13	+6	−11	+6
(A23)	+7	−9	+3	−4
(A31)	+5	−10	+6	−10
(A32)	0	+4	0	+4
(A34)	−2	+3	0	+4
(A44)	−1	+8	−1	+10

a) $\frac{(\tau_{deleted} - \tau)\times100}{\tau}$, b) $\frac{(\tau_{k\times10} - \tau)\times100}{\tau}$.

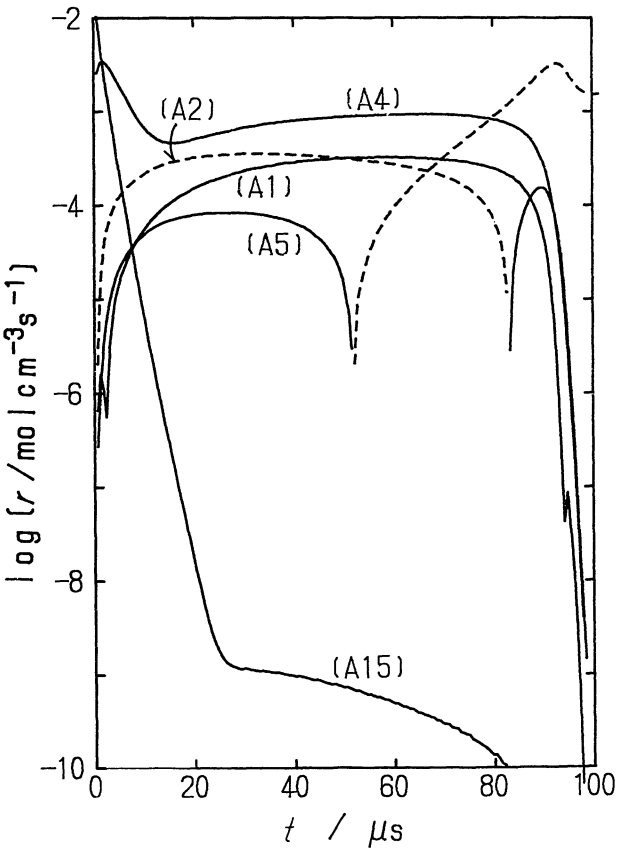


Fig. 4. Net reaction rates at 1866 K in mixture 2. t is the time after the arrival of a shock wave. The solid lines indicate that the net reaction proceeds in the forward direction; the dotted lines indicate the reverse direction.

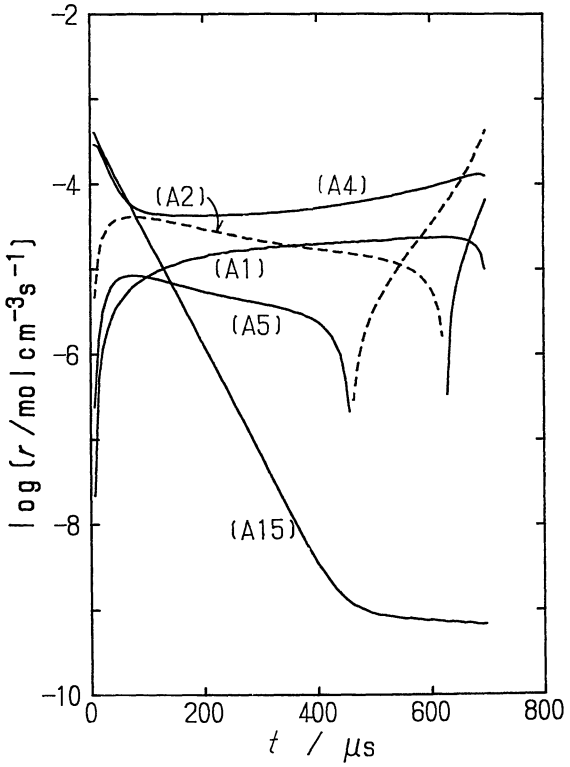


Fig. 5. Net reaction rates at 1517 K in mixture 2.

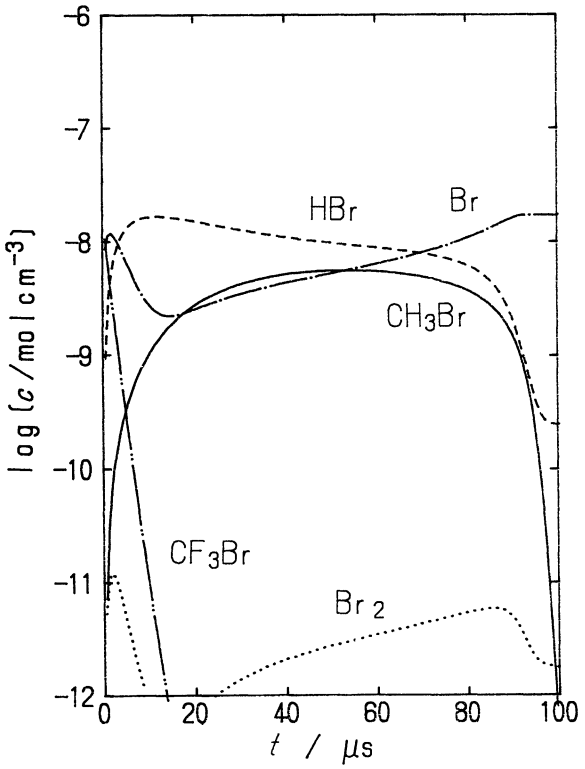


Fig. 6. Calculated concentration profiles of Br-containing species for mixture 2 at 1866 K.

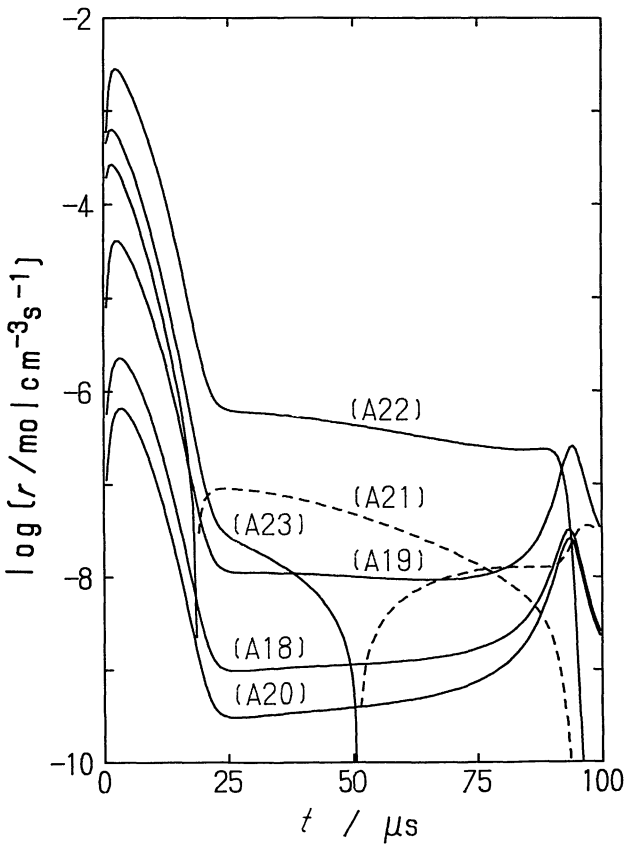
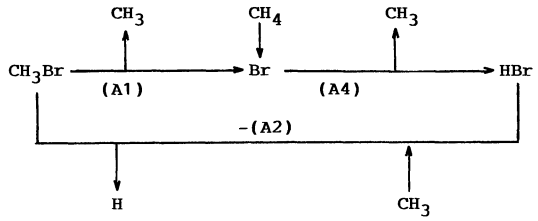


Fig. 7. Net reaction rates at 1866 K in mixture 2.

are shown in Figs. 4 and 5. Also, the time profiles of the main species including Br are shown in Fig. 6. During the early stage of the induction period reaction (A15) is the fastest of these five reactions at both 1517 and 1866 K. Further, since reaction (A15) is faster than reaction (R1), the former reaction acts as an initiation reaction. This may be reasonable, considering that the bond energy of C–Br is smaller than those of C–H and C–F.

As time passes, the rate of reaction (A15) becomes smaller. This means that CF_3Br decomposes during an earlier stage of the induction period. From Fig. 6 we realize that CF_3Br changes into CH_3Br within the ignition delay times.

Lifshitz has shown that most oxidation mechanisms for simple molecules involve closed-loop reactions that determine the behavior of the overall oxidation mechanism. In his investigation he identified the reactions that comprise this closed loop by examining the net reaction rates at half the induction time.[37] In the present study, during the induction period reactions (A1), (A2), and (A4) had high reaction rates. These reactions thus form a loop, as follows:



The total reaction of these reactions is

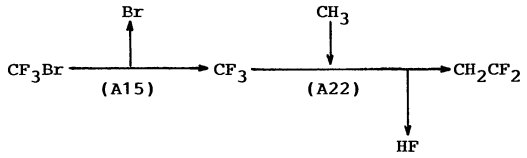
$$CH_4 = CH_3 + H,$$

which provides H atoms that are the active species during combustion. We considered that this loop has a dominant effect on methane ignition. This loop is the same as that obtained in the CH_4–O_2–CH_3Br system.

To make sure how CF_3 produced by the decomposition of CF_3Br effects the ignition delay times, we calculated the time profiles of the reaction rates which had higher values among the reactions involving the F-containing species at 1866 K (Fig. 7). It was found that reactions (A19), (A21), (A22), and (A23) have high reaction rates during the induction period. Especially, reaction (A22) has the fastest rate during the induction period, ten-times larger than other reactions. According to a sensitivity analysis, reaction (A22) has a high inhibition effect on the ignition delay times at both 1517 and 1866 K.

In this system CH_3 is produced from CH_4 by an attack of Br atoms (reaction (A4)), and CH_3 (reaction (A2)) reacts with HBr to produce H atoms, which are the active species during combustion. CH_3 thus plays an important role as a chain carrier in this system. It is further reported that reaction (A22) is also effective in flame.[34] It is therefore reasonable that reaction (A22), which consumes CH_3 as a chain carrier, has a large

inhibition effect in sensitivity analysis. By the reason that the effect suppresses any promotion effect by an attack of Br atoms, we considered that the promotion effect of CF_3Br is smaller than that of CH_3Br. From Fig. 7, the main route of CF_3Br decomposition is as follows:



C_2H_6 System. As shown in Fig. 8, CH_3Br has an inhibition effect on ethane ignition. The lines indicate the calculated results and the points are the observed values. The observed ignition delay times of mixture 4—6 are shown, as follows, by least-squares methods:

$$\log \tau = -9.40 + 0.81\ (10^4/T) \qquad \text{for mixture 4,}$$

$$\log \tau = -9.76 + 0.91\ (10^4/T) \qquad \text{for mixture 5,}$$

and

$$\log \tau = -9.63 + 0.96\ (10^4/T) \qquad \text{for mixture 6.}$$

As the concentration of CF_3Br increases, the slopes of these lines become large. This means that this inhibition effect at high temperature is smaller than that at low temperature. The concentration dependence of CF_3Br was large in comparison with methane ignition. Since this tendency was the same for CH_3Br,[22,23] we analyzed the kinetics of the C_2H_6–O_2–CF_3Br system in comparison with the C_2H_6–O_2–CH_3Br system (already reported).

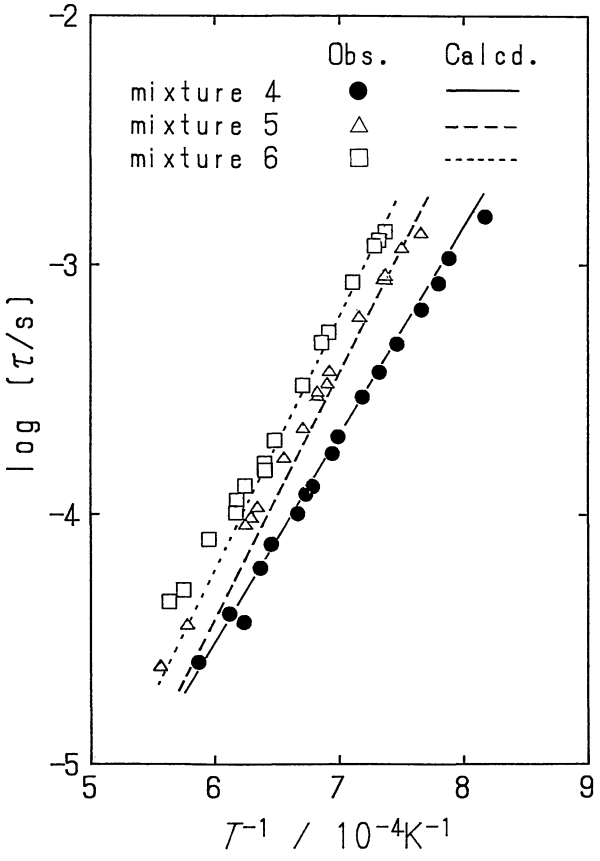


Fig. 8. Comparison of the observed and calculated ignition delay times.

In the C_2H_6–O_2–Ar system we express the consumption route of C_2H_6 during the early stage of the induction period.[35,36] In this system the initiation reaction is a thermal decomposition of C_2H_6,

$$C_2H_6 = CH_3 + CH_3. \qquad \text{(R8)}$$

The gratest part of CH_3 produced reacts with C_2H_6, as follows:

$$C_2H_6 + CH_3 = C_2H_5 + CH_4. \qquad \text{(R9)}$$

The C_2H_5 produced by reaction (R9) decompose immediately,

$$C_2H_5 = C_2H_4 + H, \qquad \text{(R10)}$$

and a part of the H atoms produced react with C_2H_6; some part of the H atoms react with O_2:

$$C_2H_6 + H = C_2H_5 + H_2 \qquad \text{(R11)}$$

and

$$H + O_2 = OH + O. \qquad \text{(R6)}$$

Reaction (R6), which is a chain-branching reaction, produces O atoms and OH radicals. OH radicals react with C_2H_6 and the O atoms react with CH_3:

$$C_2H_6 + OH = C_2H_5 + H_2O. \qquad \text{(R12)}$$

As mentioned above most of the C_2H_6 is consumed by a chain mechanism comprising reactions (R10) and (R11) or ractions (R10), (R6), and (R12).

CF_3Br effects the chain mechanism of C_2H_6 consumption. In this system we also performed a sensitivity analysis at both 1565 and 1717 K in order to realize how CF_3Br effects the mechanism. From this analysis the effective reactions are shown in Table 4. The time profiles of the reaction rates of the effective reactions which contian Br-atom are shown in Figs. 9 and 10. We also show the time profiles of the important reactions in the C_2H_6–CH_3Br system in Fig. 11 (already reported). The reactions which can be considered as an initiation type are reactions (A15) and (R8) in C_2H_6–CF_3Br, and reactions (A1) and (R8) in C_2H_6–CH_3Br. The calculated rate of reaction (R8) during the very early stage is about three times as large as that of reaction (A15) at 1500 K. The calculated rate of reaction (R8) is

Table 4. Percentage Change of the Ignition Delay Times ($\tau_{deleted}$, $\tau_{k\times10}$) to Those (τ) Calculated by Using the Complete Mechanism in Mixture 5

Reaction	1565 K		1717 K	
	$\tau_{deleted}$[a)]	$\tau_{k\times10}$[b)]	$\tau_{deleted}$	$\tau_{k\times10}$
(A2)	−6	+1	−6	0
(A5)	+3	−4	+1	−5
(A11)	+6	−7	+4	−9
(A14)	−13	+20	−6	+12
(A15)	+15	−13	+16	−10
(A17)	−4	+13	−4	+12
(A19)	−3	+10	0	+4
(A22)	+8	−3	+9	−2
(A30)	−4	+8	−3	+6
(A31)	+3	−11	+2	−9
(A32)	−5	+26	−4	+17
(A34)	−1	+5	0	+3
(A35)	−1	+5	−1	+2
(A36)	+7	−4	+3	−3

a) $\frac{(\tau_{deleted}-\tau)\times100}{\tau}$, b) $\frac{(\tau_{k\times10}-\tau)\times100}{\tau}$.

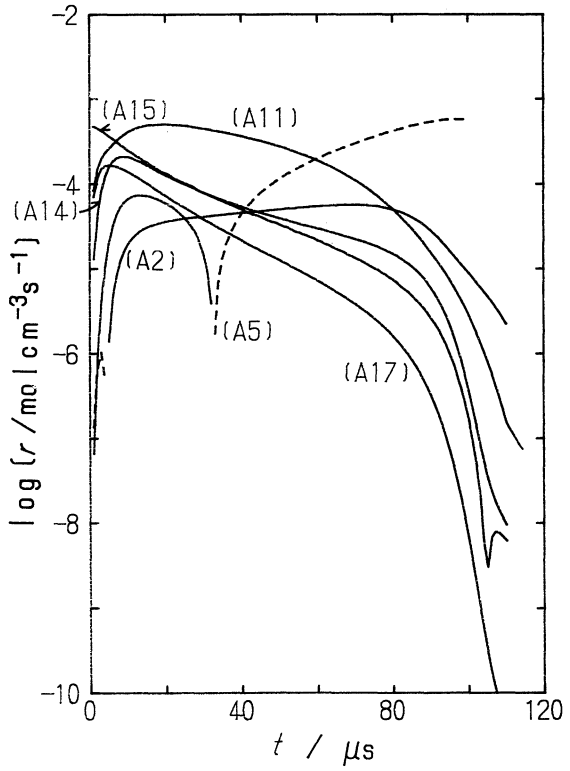


Fig. 9. Net reaction rates at 1565 K in mixture 5. The calculated reactions are those involving Br-containing species.

much faster than that of (A1). Thus, in both systems, reaction (R8) may act as the initiation reaction. However, reaction (A15), which is a thermal decomposition, also has a sufficiently large reaction rate in the C_2H_6–CF_3Br systems.

In C_2H_6–CH_3Br (already reported) CH_3Br reacts with

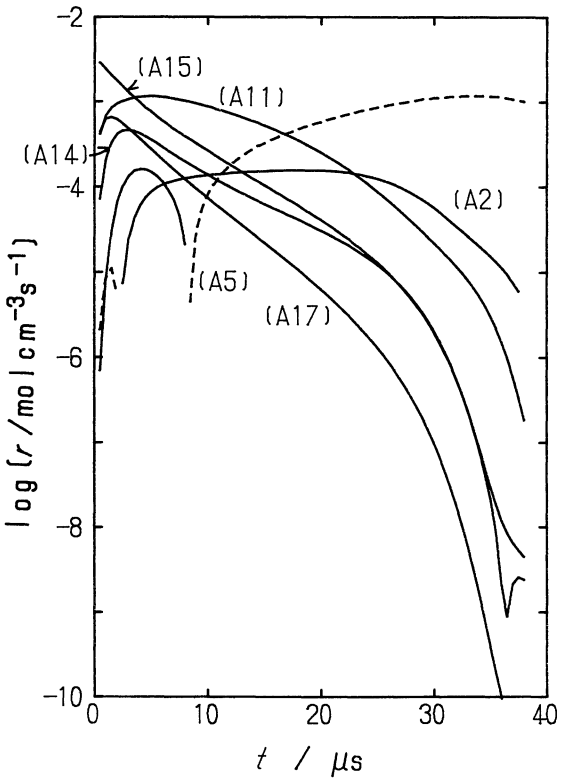


Fig. 10. Net reaction rates at 1717 K in mixture 5. The calculated reactions are those involving Br-containing species.

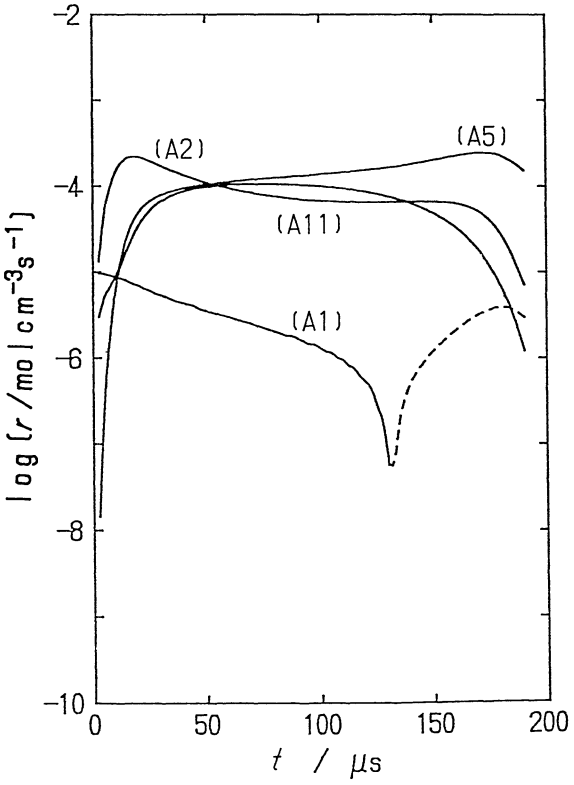


Fig. 11. Net reaction rates at 1500 K in mixture 9. The calculated reactions are those involving Br-containing species.

H produced by ethane decomposition, as follows:

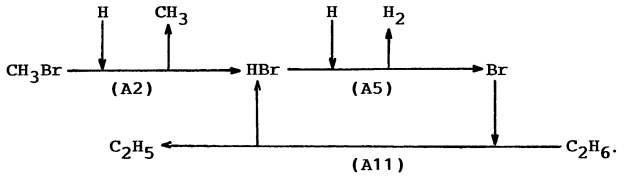
$$CH_3Br + H = CH_3 + HBr, \quad (A2)$$

$$HBr + H = H_2 + Br, \quad (A5)$$

and

$$C_2H_6 + Br = C_2H_5 + HBr. \quad (A11)$$

Most of the CH_3Br is consumed by reaction (A2). This fact is reasonable considering that the ignition temperature in the C_2H_6–O_2 system is lower than that in the CH_4–O_2 system, and that the concentration of H atoms in the C_2H_6 system is larger than that in the CH_4 system. Reaction (A5), which follows reaction (A2), has a large inhibition effect, since the HBr produced by reactions (A2) and (A11) consumes H as the active species. These three reactions can be expressed by the following loop:



In the C_2H_6–CF_3Br system, although reaction (R8) is dominant during the early stage, the rate of reaction (A15) is sufficiently large. Further, since the H and CH_3 concentrations increase in this system, reactions (A14) and (A17) became faster, as shown in Figs. 9 and 10. It is thus considered that reactions (A14), (A15), and (A17) are competitive. Reactions (A14) and (A17) have large inhibition effects and reaction (A15) has a promotion effect according to sensitivity analysis. If CF_3Br is consumed by reaction (A14), the HBr produced by reaction (A14) may react through the same route mentioned above in the C_2H_6–CH_3Br system. However, considering that reaction (A5) has a small promotion effect, this route may not be the main one. It is interesting that reaction (A5), which has a large inhibition effect in C_2H_6–CH_3Br, has a promotion effect in C_2H_6–CF_3Br. This might be caused by a difference in the relative concentration ([HBr]/[Br]), as shown in Figs. 12 and 13. [HBr]/[Br] in a mixture including CH_3Br is much larger than that in a mixture including CF_3Br. This indicates that in a CF_3Br mixture the concentration of Br is larger than that of HBr; in this system the reverse reaction rate thus becomes larger after the middle of induction period, as shown in Figs. 9 and 10.

To summarise our interpretation of the results, we can say that the total inhibition effect in this system depends on a balance of the consumption reactions of CF_3Br (reactions (A14), (A15), and (A17)) during the early stage of the induction period. Thus, in this system the

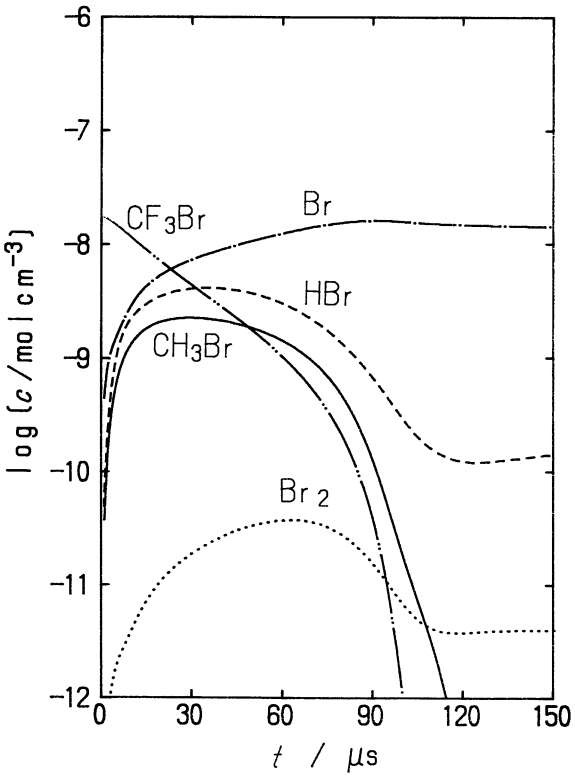


Fig. 12. Calculated concentration profiles of Br-containing species at 1565 K in mixture 5.

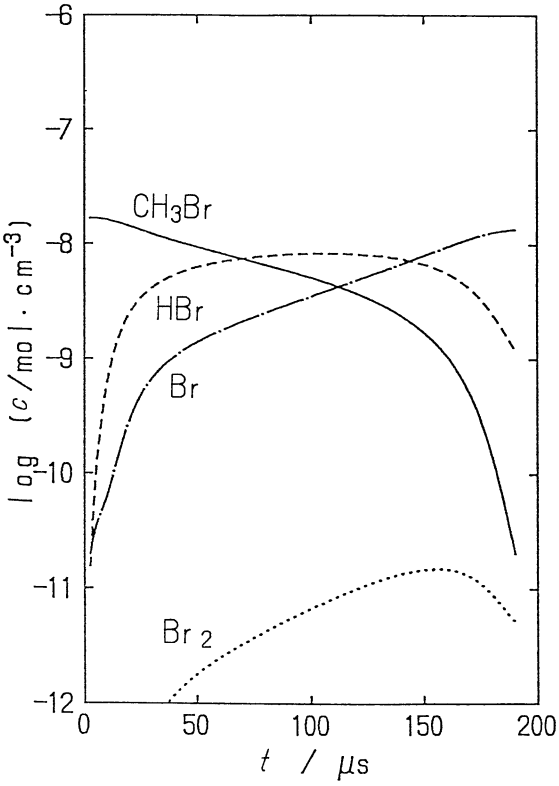


Fig. 13. Calculated concentration profiles of Br-containing species at 1500 K in mixture 9.

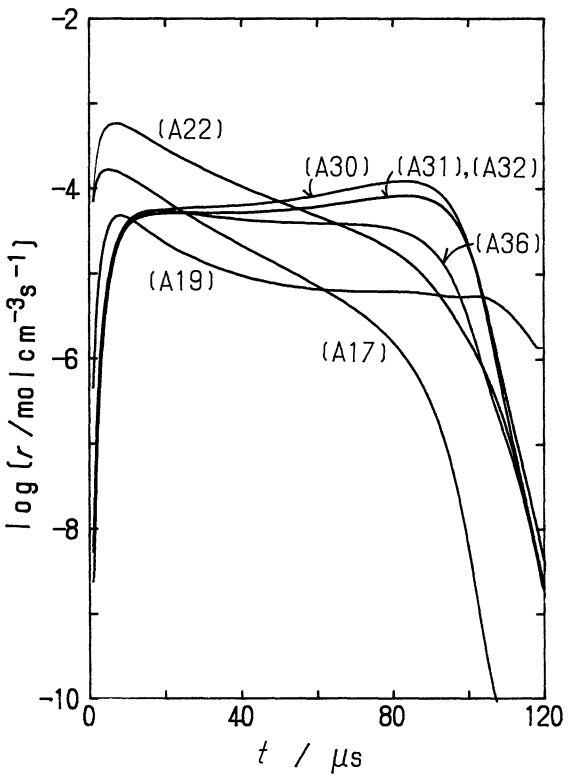


Fig. 14. Net reaction rates at 1565 K in mixture 5. The calculated reaction are the effective reactions involving F-containing species.

inhibition effects of reactions (A14) and (A17) surpass any promotion effect of reaction (A15). To make sure how CF_3 effects ethane ignition and how CF_3 is consumed, the rates of the effective reactions at 1565 K (which involve F-containing species) are shown in Fig. 14. This result indicates that reactions (A22), (A30), and (A36) have large rates during the induction period. During the earlier stage of the induction period, reaction (A22) has the fastest reaction rate.

In this system CH_3 is produced by the decomposition of C_2H_6. CH_3 is the source of active species, H. It is thus reasonable that reaction (A22), which consumes CH_3 radicals as the source of H atoms, has an inhibition effect in sensitivity analysis. This may show that the rate of reaction (A14) in this system is slower than reaction (A2) in the CH_3Br system.

CF_3 is consumed in a similar way as in the CH_4–CF_3Br system, considering that the effective reactions involving F-containing species are almost the same as in the CH_4–CF_3Br system.

Conclusion

In this study the ignition delay times were dependent on the reactions during the earlier stage. This may indicate that during the induction times the decomposition of fuel is important. Therefore, we can think that the effective reactions which formed loops didn't include O-containing reactions in the same reasons. In this study it is especially important to identify the initiation reaction. Although in the CH_4 system CF_3Br decomposition is an initiation reaction, in the C_2H_6 system C_2H_6 decomposition is an initiation reaction. This deference may cause these opposite effects.

In order to make the mechanism clearer, modifications of the used model and the concentration measurements of radicals during the induction time are essential.

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