

The Addition Effect of CH₃Cl on Methane Ignition behind Reflected Shock Waves

Kuan Soo Shin,* Kisoo Park, and Kilyoung Kim

Department of Chemistry, Soongsil University, Seoul 156-743, Korea

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World wide use of incineration for disposal of industrial and municipal wastes has led to increasing interests in the high temperature chemistry of halogens. Chlorine has drawn the most attention, since chlorine containing compounds are prominent in consumer and industrial wastes. A major problem arising in the incineration of chlorine-containing organic compounds is that their presence slows down the combustion process and enhance the output of products of incomplete combustion, some of them partially chlorinated are toxic.¹⁻³ The inhibition effects of CH₃Cl, CH₂Cl₂, and CHCl₃ on the methane-air flame have been reported by measuring flame velocities.⁴ The inhibition effect of chlorine-containing species on the combustion of hydrocarbons is caused mainly by reactions of these species with hydrogen atom: such reactions compete against the H + O₂ reaction.⁵ H atoms react more rapidly with HCl or Cl₂ than with O₂. For example, the rate constant of H + HCl → H₂ + Cl is about 50 times larger than the rate constant of the H + O₂ → OH + O reaction at 1000 K. As temperature increases, however, the H + O₂ reaction becomes faster than the reactions of H + HCl or H + Cl₂, therefor the chlorine species such as HCl and Cl₂ no longer divert H atoms. The reason for this difference is that the activation energy for the H + HCl reaction (16 kJ/mol) is lower than the value for the H + O₂ reaction (68 kJ/mol). These effects lead to markedly decreased inhibition effect at high temperatures and even to promotion of ignition, as found for methane oxidation in the presence of CH₃Cl by Takahashi *et al.*⁶

In our previous works,^{7,8} we have shown the addition effect of CH₃Br on CH₄ ignition and the effect of CH₃Cl on C₂H₆ ignition. The small amount of CH₃Cl inhibited the ignition of C₂H₆ in the temperature range of 1270-1544 K.⁷ However, CH₃Br was found to promote the ignition of CH₄ significantly.⁸ In this investigation, in order to examine the addition effect of CH₃Cl on the ignition of CH₄, the ignition delay time for stoichiometric CH₄-O₂-Ar mixtures in the presence and absence of CH₃Cl with respect to the arrival of the reflected shock wave was measured in the temperature range of 1588-1920 K and the pressure range of 1.05-1.39 bar. It was found that the small amount of CH₃Cl also promoted the ignition of CH₄.

Experimental Section

The experiments were done behind reflected shock waves in stainless-steel shock tube which was described in detail elsewhere.^{8,9} Therefore, only a brief description of the sys-

tem will be presented here. The apparatus consists of a 514 cm (6.02 cm i.d.) 304 stainless-steel tube separated from the He driver chamber by a 0.1 mm thickness unscored aluminium diaphragm. The tube was routinely pumped between experiments to < 10⁻⁷ torr by turbo molecular pump (Varian, 969-9002) system. The velocity of shock wave was measured with 5 pressure transducers (PCB 113A21) mounted along the end portion of the shock tube, and the temperature and the density in the reflected shock wave regime were calculated from this velocity. This procedure has been given previously, and the corrections for boundary-layer perturbation were applied.^{10,11}

Ignition delay time (τ) was defined as the time interval between the arrival of the reflected shock and the onset of the ignition. The pressure measurements were made using a pressure transducer (PCB 113A21) which was located at 1.0 cm from the reflecting surface. The characteristic ultraviolet emission from OH radicals at 306.7 nm was monitored using a photomultiplier tube (ARC DA-781) with a band path filter (Andover, 307 nm) through the sapphire window which was mounted flush at 1.0 cm from the shock tube end plate. The window was masked to 1 mm slit width in order to reduce emission intensity and improve the time resolution of the system. Both traces were fed into a digital oscilloscope (HP45601A). Figure 1 shows the typical oscilloscope trace of the pressure and OH emission profiles. The upper beam records the pressure and the lower beam the OH emission.

The compositions of the mixtures used in this work are

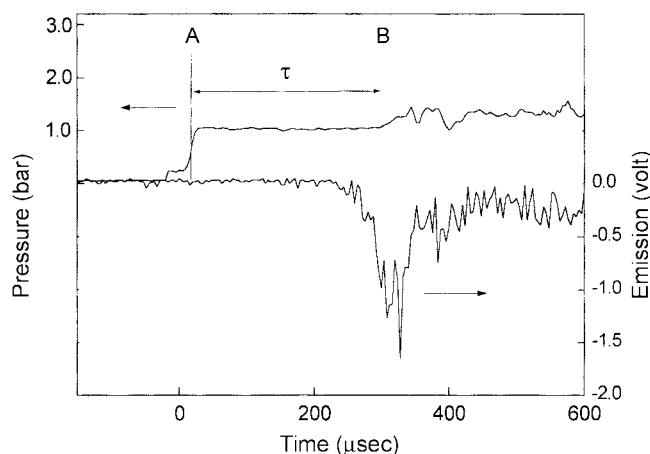


Figure 1. Typical experimental record showing pressure (upper) and OH emission (lower). Experimental conditions were $P_1=20$ torr and $T_3=1732$ K in mixture 2. (A: an arrival of a reflected shock wave; B: onset of the ignition; τ : ignition delay time).

Table 1. Experimental conditions

	CH ₄ (%)	O ₂ (%)	CH ₃ Cl(%)	Ar (%)	T ₃ (K)	τ(μs)
Mixture 1	3.5	7.0		89.50	1618-1920	72-1176
Mixture 2	3.5	7.0	0.18	89.32	1645-1909	76-852
Mixture 3	3.5	7.0	0.35	89.15	1588-1850	92-1096

given in Table 1. CH₄ (99.99%), CH₃Cl (99.5%), O₂ (99.999%) and Ar (99.999%) were used without further purification. He (99.9999%) was used as a driver gas. Four test gas mixtures were prepared manometrically and stored at aluminium cylinders. The initial pressure (P_1) was fixed to 20 torr and the shock velocity could be controlled by changing the pressure of the He driver gas.

Results and Discussion

The ignition delay times of mixtures 2 and 3 (including CH₃Cl) are slightly short compared with those of mixture 1 (excluding CH₃Cl), as shown in Figure 2. At low CH₃Cl loading as in mixture 2, the promotion effect does not seem to be clear. However, as the amount of CH₃Cl increases as in mixture 3, it becomes obvious that CH₃Cl has a promotion effect for methane ignition. A correlation between ignition delay time and concentration of CH₃Cl could be summarized in the form of mass-action expression.¹² In this investigation, the ignition delay time can be expressed as $\tau \propto [\text{CH}_3\text{Cl}]^{-0.75}$, where the concentration of CH₃Cl is in mol/cm³. The reliability of this empirical formula was tested by plotting all data as $\log(\tau/[\text{CH}_3\text{Cl}]^{-0.75})$ vs. $10^4/T$. As shown in Figure 3, all points lie close to a single line and the slope of line gives an apparent activation energy of 56.7 kcal/mol. The power dependence of CH₃Cl shows promotion effect: the ignition delay time decreases by increasing the concentration of CH₃Cl.

The numerical calculations were performed to elucidate the important steps in the reaction scheme of CH₄ oxidation in the presence of CH₃Cl during the ignition period using the reaction mechanism proposed by Leylegian *et al.*⁴ Their

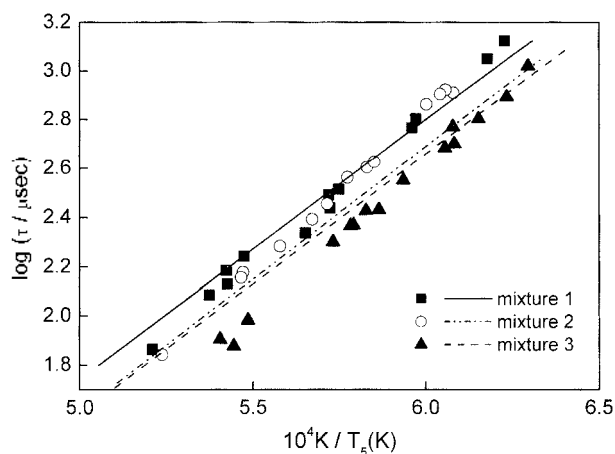


Figure 2. Comparison of calculated ignition delay times with observed ones. Straight lines represent calculated values for the corresponding mixtures.

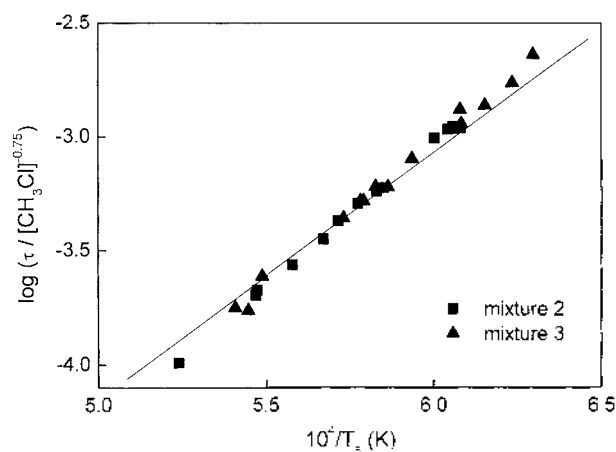
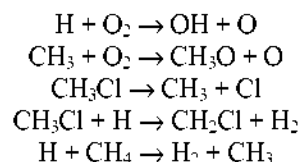


Figure 3. A plot of $\log(\tau/[\text{CH}_3\text{Cl}]^{0.75})$ vs. $10^4/T$ for mixtures 2 and 3. The solid line represents the best fit for the mixtures.

model was based on the work of Ho *et al.*^{13,14} for the reaction chemistry involving Cl and the GRI-Mech 1.2¹⁵ for the methane combustion chemistry. The kinetic model used in this study consists of 82 species and 505 elementary reactions. The ignition delay times were computed using Chemkin III code.¹⁶ As shown in Figure 2, the calculations also represent the promotion effect of CH₃Cl on the ignition of methane. The calculated ignition delay times agree reasonably with the observed ones within the experimental uncertainty, considering that the kinetic model is assembled from literature data and is untuned. However, it is worth noting that the kinetic model predicts small concentration dependence of CH₃Cl in methane ignition compared with the observed one.

In order to understand more details on the role of CH₃Cl in methane combustion, the sensitivity and flow analyses were performed.¹⁷ In the reaction model, not all the elementary reactions contribute equally to the ignition delay time. On the contrary, some of them contribute significantly, some marginally, and some not at all. In order to find the sensitive reactions to the ignition delay time, logarithmic sensitivity analysis¹⁷ was carried out by multiplying the reference rate constants by a factor of 2. As listed in Table 2, the sensitive reactions of the ignition delay times in CH₄-CH₃Cl-O₂-Ar mixtures are the following reactions.



The main reactions controlling the ignition of CH₄ are the reactions involving CH₃, CH₃O, CH₂O, and CHO species, except for the reaction of H + O₂ which is the most important one to chain branching. These results suggest that the ignition reactions may progress through the route of CH₄ → CH₃ → CH₃O → CH₂O → CHO → CO.

When CH₃Cl is added, however, the reaction scheme differs: the initiation reaction is not CH₄ → CH₃ + H but CH₃Cl → CH₃ + Cl. The methane decomposition reaction does not contribute to ignition at all. The CH₃ radical is generated

Table 2. Logarithmic sensitivities of ignition delay time in mixture 3 with $P_1=20$ torr

Reactions	$T_3=1588$ K	$T_3=1850$ K
$\text{CH}_3+\text{H} \rightarrow \text{CH}_3+\text{H}_2$	0.1728	0.1411
$\text{CH}_3+\text{O} \rightarrow \text{OH}+\text{CH}_3$	-0.0529	-0.1255
$\text{CH}_3+\text{OH} \rightarrow \text{CH}_3+\text{H}_2\text{O}$	0.0576	0.0159
$\text{CH}_3+\text{O}_2 \rightarrow \text{O}+\text{CH}_3\text{O}$	-0.3067	-0.1431
$\text{CH}_3+\text{O}_2 \rightarrow \text{OH}+\text{CH}_2\text{O}$	0.0961	-0.0256
$\text{CH}_3+\text{O} \rightarrow \text{H}+\text{CH}_2\text{O}$	0.0953	0.1253
$\text{CH}_3+\text{OH} \rightarrow \text{CH}_2+\text{H}_2\text{O}$	-0.0670	-0.1255
$\text{CH}_3+\text{HO}_2 \rightarrow \text{OH}+\text{CH}_3\text{O}$	-0.1106	-0.1255
$\text{CH}_3+\text{CH}_2\text{O} \rightarrow \text{HCO}+\text{CH}_4$	-0.0530	-0.0229
$2\text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$	0.0824	0.0080
$\text{O}_2+\text{H} \rightarrow \text{O}+\text{OH}$	-0.5577	-0.6611
$\text{O}_2+\text{CH}_2\text{O} \rightarrow \text{HO}_2+\text{HCO}$	-0.0525	-0.0161
$\text{CH}_3\text{Cl} \rightarrow \text{CH}_3+\text{Cl}$	-0.3165	-0.2938
$\text{CH}_3\text{Cl}+\text{H} \rightarrow \text{CH}_3+\text{HCl}$	0.0166	0.0040
$\text{CH}_3\text{Cl}+\text{Cl} \rightarrow \text{CH}_2\text{Cl}+\text{HCl}$	0.0292	0.0093
$\text{CH}_3\text{Cl}+\text{CH}_3 \rightarrow \text{CH}_4+\text{CH}_2\text{Cl}$	0.0229	0.0040
$\text{CH}_2\text{Cl}+\text{H}_2 \rightarrow \text{CH}_3\text{Cl}+\text{H}$	0.1673	0.0969
$\text{CH}_2\text{Cl}+\text{O}_2 \rightarrow \text{CH}_2\text{O}+\text{ClO}$	-0.0325	-0.0067

from the decomposition of CH_3Cl or from the reaction of $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$. The CH_3 radical is consumed through $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$ reaction, and CH_3O decomposes quickly to CH_2O and H . Once H atom is formed, H can react

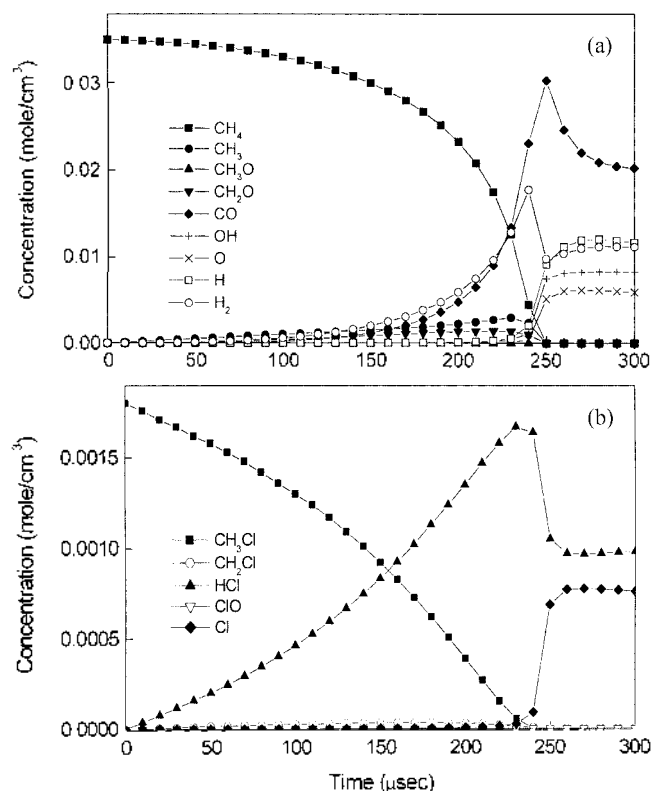


Figure 4. (a) Calculated concentration profiles of CH_4 , CH_3 , CH_3O , CH_2O , CO , OH , O , H , and H_2 at 1750 K in mixture 2. (b) Calculated concentration profiles of CH_3Cl , CH_2Cl , HCl , ClO , and Cl at 1750 K in mixture 2.

with CH_3Cl or CH_4 . This scheme shows that the additive, CH_3Cl , changes the rate of ignition reaction but not the main ignition mechanism. The promotion effect by addition of CH_3Cl on CH_4 ignition is due to the relatively fast decomposition rate of the additive. The concentration profiles of the important species calculated using this trial reaction mechanism, shown in Figure 4, confirm that reactions progress through the decomposition of CH_3Cl .

In our previous work,⁸ it was found that the small amount of CH_3Br also promoted the ignition of CH_4 significantly. The main ignition schemes for addition effect of CH_3Br or CH_3Cl on the CH_4 ignition are the same. However, this work shows that the promotion effect of CH_3Cl is smaller than that of CH_3Br . The difference in the promotion effects of the additives originated from the difference in the bond dissociation energy of $\text{CH}_3\text{-Br}$ and $\text{CH}_3\text{-Cl}$.

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