

# The Addition Effect of CH<sub>3</sub>Cl on Methane Ignition behind Reflected Shock Waves

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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.<sup>1-3</sup> The Inhibition effects of CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub> on the methane-air flame have been reported by measuring flame velocities.<sup>4</sup> 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 + O<sub>2</sub> reaction.<sup>5</sup> H atoms react more rapidly with HCl or Cl<sub>2</sub> than with O<sub>2</sub>. For example, the rate constant of H + HCl → H<sub>2</sub> + Cl is about 50 times larger than the rate constant of the H + O<sub>2</sub> → OH + O reaction at 1000 K. As temperature increases, however, the H + O<sub>2</sub> reaction becomes faster than the reactions of H + HCl or H + Cl<sub>2</sub>, therefor the chlorine species such as HCl and Cl<sub>2</sub> 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 + O<sub>2</sub> 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 CH<sub>3</sub>Cl by Takahashi *et al.*<sup>6</sup>

In our previous works,<sup>7,8</sup> we have shown the addition effect of CH<sub>3</sub>Br on CH<sub>4</sub> ignition and the effect of CH<sub>3</sub>Cl on C<sub>2</sub>H<sub>6</sub> ignition. The small amount of CH<sub>3</sub>Cl inhibited the ignition of C<sub>2</sub>H<sub>6</sub> in the temperature range of 1270-1544 K.<sup>7</sup> However, CH<sub>3</sub>Br was found to promote the ignition of CH<sub>4</sub> significantly.<sup>8</sup> In this investigation, in order to examine the addition effect of CH<sub>3</sub>Cl on the ignition of CH<sub>4</sub>, the ignition delay time for stoichiometric CH<sub>4</sub>-O<sub>2</sub>-Ar mixtures in the presence and absence of CH<sub>3</sub>Cl 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 CH<sub>3</sub>Cl also promoted the ignition of CH<sub>4</sub>.

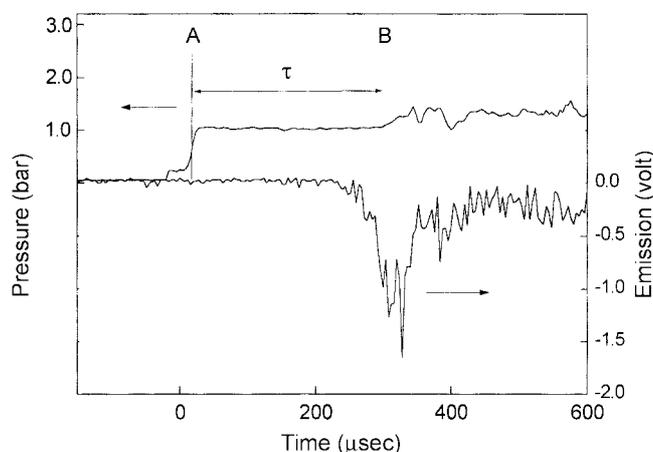
## Experimental Section

The experiments were done behind reflected shock waves in stainless-steel shock tube which was described in detail elsewhere.<sup>8,9</sup> 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<sup>-7</sup> 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.<sup>10,11</sup>

Ignition delay time ( $\tau$ ) 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  $T_5=1732$  K in mixture 2. (A: an arrival of a reflected shock wave; B: onset of the ignition;  $\tau$ : ignition delay time).

**Table 1.** Experimental conditions

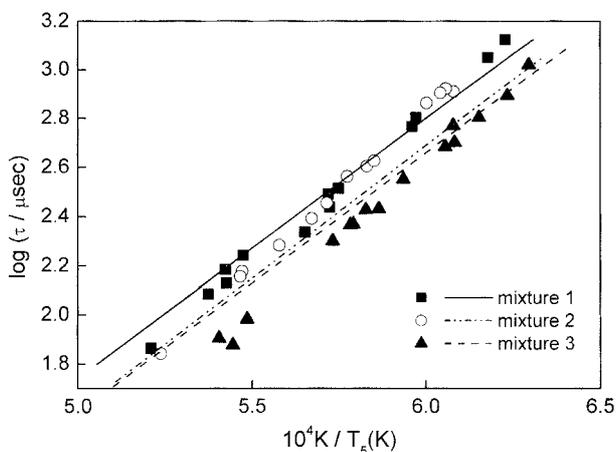
	CH <sub>4</sub> (%)	O <sub>2</sub> (%)	CH <sub>3</sub> Cl (%)	Ar (%)	T <sub>5</sub> (K)	τ (μs)
Mixture 1	3.5	7.0		89.50	1618-1920	72-1176
Mixture 2	3.5	7.0	0.18	89.32	1645-1909	76-852
Mixture 3	3.5	7.0	0.35	89.15	1588-1850	92-1096

given in Table 1. CH<sub>4</sub> (99.99%), CH<sub>3</sub>Cl (99.5%), O<sub>2</sub> (99.999%) and Ar (99.999%) were used without further purification. He (99.999%) 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.

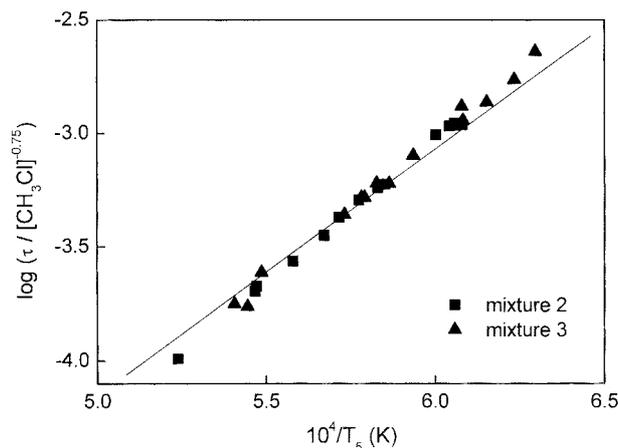
### Results and Discussion

The ignition delay times of mixtures 2 and 3 (including CH<sub>3</sub>Cl) are slightly short compared with those of mixture 1 (excluding CH<sub>3</sub>Cl), as shown in Figure 2. At low CH<sub>3</sub>Cl loading as in mixture 2, the promotion effect does not seem to be clear. However, as the amount of CH<sub>3</sub>Cl increases as in mixture 3, it becomes obvious that CH<sub>3</sub>Cl has a promotion effect for methane ignition. A correlation between ignition delay time and concentration of CH<sub>3</sub>Cl could be summarized in the form of mass-action expression.<sup>12</sup> In this investigation, the ignition delay time can be expressed as  $\tau \propto [\text{CH}_3\text{Cl}]^{-0.75}$ , where the concentration of CH<sub>3</sub>Cl is in mol/cm<sup>3</sup>. 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 CH<sub>3</sub>Cl shows promotion effect; the ignition delay time decreases by increasing the concentration of CH<sub>3</sub>Cl.

The numerical calculations were performed to elucidate the important steps in the reaction scheme of CH<sub>4</sub> oxidation in the presence of CH<sub>3</sub>Cl during the ignition period using the reaction mechanism proposed by Leylegian *et al.*<sup>4</sup> Their



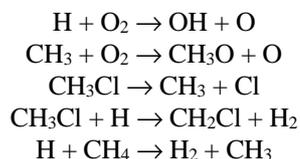
**Figure 2.** Comparison of calculated ignition delay times with observed ones. Straight lines represent calculated values for the corresponding mixtures.



**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.*<sup>13,14</sup> for the reaction chemistry involving Cl and the GRI-Mech 1.2<sup>15</sup> 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.<sup>16</sup> As shown in Figure 2, the calculations also represent the promotion effect of CH<sub>3</sub>Cl 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 CH<sub>3</sub>Cl in methane ignition compared with the observed one.

In order to understand more details on the role of CH<sub>3</sub>Cl in methane combustion, the sensitivity and flow analyses were performed.<sup>17</sup> 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 analysis<sup>17</sup> 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 CH<sub>4</sub>-CH<sub>3</sub>Cl-O<sub>2</sub>-Ar mixtures are the following reactions.



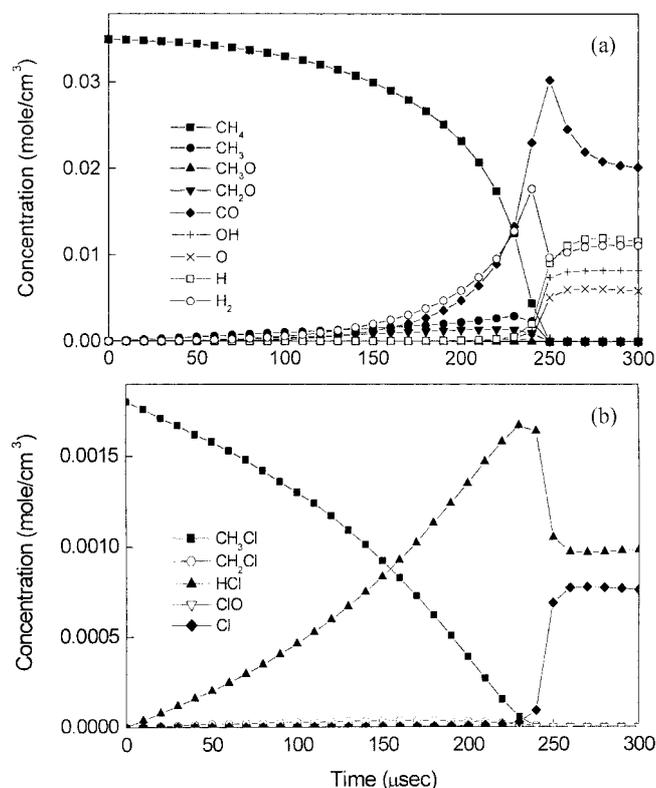
The main reactions controlling the ignition of CH<sub>4</sub> are the reactions involving CH<sub>3</sub>, CH<sub>3</sub>O, CH<sub>2</sub>O, and CHO species, except for the reaction of H + O<sub>2</sub> which is the most important one to chain branching. These results suggest that the ignition reactions may progress through the route of CH<sub>4</sub> → CH<sub>3</sub> → CH<sub>3</sub>O → CH<sub>2</sub>O → CHO → CO.

When CH<sub>3</sub>Cl is added, however, the reaction scheme differs; the initiation reaction is not CH<sub>4</sub> → CH<sub>3</sub> + H but CH<sub>3</sub>Cl → CH<sub>3</sub> + Cl. The methane decomposition reaction does not contribute to ignition at all. The CH<sub>3</sub> radical is generated

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

Reactions	$T_5=1588$ K	$T_5=1850$ K
$\text{CH}_4+\text{H} \rightarrow \text{CH}_3+\text{H}_2$	0.1728	0.1411
$\text{CH}_4+\text{O} \rightarrow \text{OH}+\text{CH}_3$	-0.0529	-0.1255
$\text{CH}_4+\text{OH} \rightarrow \text{CH}_3+\text{H}_2\text{O}$	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  $\text{CH}_3\text{Cl}$  or from the reaction of  $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$ . The  $\text{CH}_3$  radical is consumed through  $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$  reaction, and  $\text{CH}_3\text{O}$  decomposes quickly to  $\text{CH}_2\text{O}$  and  $\text{H}$ . Once  $\text{H}$  atom is formed,  $\text{H}$  can react

**Figure 4.** (a) Calculated concentration profiles of  $\text{CH}_4$ ,  $\text{CH}_3$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{OH}$ ,  $\text{O}$ ,  $\text{H}$ , and  $\text{H}_2$  at 1750 K in mixture 2. (b) Calculated concentration profiles of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{HCl}$ ,  $\text{ClO}$ , and  $\text{Cl}$  at 1750 K in mixture 2.

with  $\text{CH}_3\text{Cl}$  or  $\text{CH}_4$ . This scheme shows that the additive,  $\text{CH}_3\text{Cl}$ , changes the rate of ignition reaction but not the main ignition mechanism. The promotion effect by addition of  $\text{CH}_3\text{Cl}$  on  $\text{CH}_4$  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  $\text{CH}_3\text{Cl}$ .

In our previous work,<sup>8</sup> it was found that the small amount of  $\text{CH}_3\text{Br}$  also promoted the ignition of  $\text{CH}_4$  significantly. The main ignition schemes for addition effect of  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{Cl}$  on the  $\text{CH}_4$  ignition are the same. However, this work shows that the promotion effect of  $\text{CH}_3\text{Cl}$  is smaller than that of  $\text{CH}_3\text{Br}$ . 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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