



## Influence of chlorine on methane oxidation

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### Abstract

Experiments on CH<sub>4</sub>/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> oxidation were conducted in an atmospheric pressure flow reactor to understand the influence of chlorine on hydrocarbon oxidation in hazardous waste incineration. The reaction temperature varied from 973 to 1273 K and the chlorine to hydrogen mole ratio (Cl/H) of the inlet mixture varied from 0 to 0.44. The species produced in the reaction were measured online with Fourier transform infrared spectroscopy (FT-IR). It was found that the destruction and removal efficiency of CH<sub>4</sub> increased with Cl/H mole ratio. Increasing Cl/H favored COCl<sub>2</sub> and CO formation and inhibited the CO oxidation process. As Cl/H approached 0.44, the concentrations of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl first increased, and then declined. Reaction temperature greatly affected the reaction system. Increasing temperatures raised the destruction removal efficiency of CH<sub>4</sub> and decreased the concentrations of CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub>. With a certain ratio of Cl/H, the concentrations of CO and COCl<sub>2</sub> first increased and then declined. The CO and COCl<sub>2</sub> concentration peak was observed around 1100 K and 1023 K, respectively. When the reaction temperature exceeded 1273 K, carbon in CH<sub>4</sub> was mostly converted to CO<sub>2</sub>. It could be concluded that the presence of chlorine enhanced the destruction of CH<sub>4</sub>, but resulted in the more toxic incomplete combustion products emission such as COCl<sub>2</sub> when the reaction temperature was not high enough.

**Key words:** hazardous waste; incineration; methane; oxidation; chlorine

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### Introduction

Incineration is an attractive technique for waste disposal, because hazardous organics can be destroyed and the mass can be significantly reduced through it. Chlorinated hydrocarbons are important components of hazardous wastes disposed in liquid injection incinerators or rotary kilns (Oppelt, 1987; Santoleri, 1973; Saxena and Jotshi, 1996). The incineration process of chlorinated hydrocarbons is usually inhibited by chlorine. The chlorinated hydrocarbons flames have lower flame velocity and are more prone to soot formation (Gupta, 1986). The inhibition effect of chlorine on isolated nonane/tetrachloro-ethane mixture droplet burning velocities was investigated using laminar flow combustors (Chang *et al.*, 1989; Law, 1990; Sorbo and Chang, 1992). This inhibition effect was further studied with electrically heated combustion apparatus and high-speed video photography technology (Stry *et al.*, 2003). It was demonstrated that the burning rate for chlorinated droplet exhibited sharp decline toward the pure compound vaporization rate, as the chlorine to hydrogen atom mole ratio (Cl/H) approached a certain value.

High concentration of incomplete combustion products such as CO is also formed in chlorinated hydrocarbons combustion process. In trichloroethylene flame generated

by oxygen enriched air, the concentration of CO was as high as 16% (V/V) (Bose and Senkan, 1983). Bissonier *et al.* (2002) investigated the combustion of tetrachlorobenzene, and reported that when the heavily chlorinated hydrocarbon was completely destroyed, only very small part of carbon was converted into the final product CO<sub>2</sub>. Thermal oxidation of chloroform was studied by Lou and Chang (1997). Their results demonstrated that high concentrations of incomplete combustion products such as CO were formed even at 1400 K with equivalence ratio 0.05 and residence time 2 s. The CO oxidation process is demonstrated to be inhibited by HCl (Ho *et al.*, 1992a; Wei *et al.*, 2004; Zhang *et al.*, 2005).

Because the presence of chlorine decreases the heat value and complicates the combustion chemistry, sometimes natural gas is supplied as auxiliary fuel to maintain the combustion process. Senger *et al.* (1987) investigated the chemical species and temperature profiles of laminar CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/air flames. Cicek and Senkan (1993) studied the chemical structures of fuel-rich, premixed laminar flames of C<sub>6</sub>H<sub>5</sub>Cl/CH<sub>4</sub>/O<sub>2</sub>/Ar mixture. The oxidation of trichloroethene with methane was also studied by Wu and Lin (2004). All these works focused on the destruction products and pathways of the chlorinated hydrocarbons.

In the incineration chamber, chlorine not only influences the destruction of chlorinated hydrocarbons, but also in-

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teracts with hydrocarbons such as methane in gas phase. Therefore, it is necessary to understand the influence of chlorine on hydrocarbons oxidation process. But this has not been sufficiently studied and published in literature. In the present work,  $\text{CH}_4/\text{Cl}_2/\text{O}_2/\text{N}_2$  reaction was studied in a flow reactor to determine the inhibition effect of chlorine at different temperatures and Cl/H ratios. The products were analyzed online and the reaction mechanism was discussed.

## 1 Materials and methods

Experiments were performed in an atmospheric pressure flow reactor. A schematic of the apparatus is shown in Fig. 1. The reactor consisted of a quartz tube 2 cm in diameter and 35 cm long with capillary inlet and outlet legs. The inlet leg and outlet leg were 2 mm in diameter and total length was 50 cm. Reactants were heated to the reaction temperature in the inlet leg in very short time, and then entered the reaction zone. The residence time in the inlet and outlet legs was less than 4% of the total residence time in the reaction zone. The reactor was heated in a SK2-4-12 tubular electric resistance furnace (Shanghai Y-feng Electrical Furnace Co., Ltd., China).

The gases from cylinders were at least 99.999% purity (New Century Co., China). Methane and chlorine in the cylinders were diluted with nitrogen, and the concentration was 0.5% (mol/mol) for methane and 0.4375% (mol/mol) for chlorine. After metering with mass flow controller, complete feed gas mixing occurred in a glass coil. Then the mixture flowed into the reactor at the flow rate of 0–3 L/min for  $\text{N}_2$  and  $\text{O}_2$ , 0–300 mL/min for  $\text{Cl}_2$  and  $\text{CH}_4$ . The accuracy of all the mass flow controllers was  $\pm 1\%$ , and the linearity was  $\pm 0.5\%$ . (Beijing Seven Star Co., China). The tube of the glass coil was 12 mm in diameter and 100 cm long.

The reaction products entered the analyzer through heated polytetrafluoroethylene tube. Quantitative analysis of  $\text{CH}_4$ ,  $\text{HCl}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_2\text{H}_2\text{Cl}_2$  and  $\text{COCl}_2$  in effluent could be performed online using a Gasmet Fourier Transform Infrared Spectroscopy (FT-IR) gas analyzer (Gasmet Technologies, Finland). The analysis was performed with 500 cm path length at 453 K sample cell temperature and  $1.024 \times 10^5$  Pa ambient pressure. The calibrated concentration range for species were as follows:  $\text{CO}$ : 2000–2150  $\text{cm}^{-1}$ , 0.002%–0.1% (mol/mol);  $\text{CO}_2$ : 2150–2300  $\text{cm}^{-1}$ , 0.002%–0.1% (mol/mol);  $\text{CH}_4$ : 3000–3300  $\text{cm}^{-1}$ , 0.002%–0.1% (mol/mol);  $\text{HCl}$ : 2500–2800  $\text{cm}^{-1}$ , 0.001%–0.1038% (mol/mol);  $\text{COCl}_2$ : 1810–2000  $\text{cm}^{-1}$ , 0.001%–0.0174% (mol/mol);  $\text{CH}_3\text{Cl}$ : 2802–3188  $\text{cm}^{-1}$ , 0.001%–0.0098% (mol/mol);  $\text{CH}_2\text{Cl}_2$ : 1100–1300  $\text{cm}^{-1}$ , 0.001%–0.02% (mol/mol). The concentration uncertainty was less than 5%.

To obtain good analysis results, the total inlet volumetric flow rate of reactants was set constant at 2.0 L/min at every reaction temperature. The pressure at the inlet was maintained about  $1.0 \times 10^5$  Pa by the pump inside the FT-IR sampling component at this flow rate, and the pressure in the reactor was kept near  $1.024 \times 10^5$  Pa accordingly. The reaction temperature varied from 973 to 1273 K with a step of 50 K. The residence time of reactants in the reactor was calculated to be 0.93, 0.88, 0.8, 0.77, 0.74, and 0.71 s with the increase in temperature. Six tests were performed at every reaction temperature, in which the initial  $\text{CH}_4$  concentration,  $\text{O}_2$  concentration and residence time were kept constant. The flow rate of  $\text{Cl}_2$  and  $\text{N}_2$  was adjusted, and the initial Cl/H varied from 0 to 0.44, accordingly. All reactions were under fuel lean conditions. The initial concentrations of reactants in experiments are listed in Table 1.

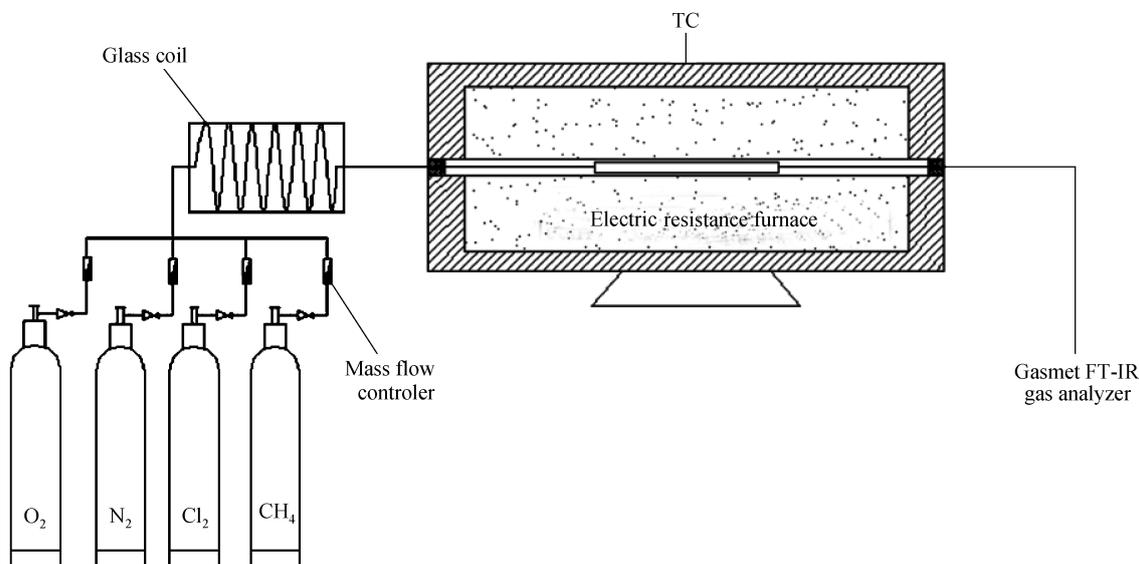


Fig. 1 Schematic of the experimental system.

**Table 1** Initial concentrations of reactants in experiments

CH <sub>4</sub> ( $\times 10^{-6}$ mol/mol)	Cl <sub>2</sub> ( $\times 10^{-6}$ mol/mol)	O <sub>2</sub> ( $\times 10^{-2}$ mol/mol)	N <sub>2</sub> ( $\times 10^{-2}$ mol/mol)	Cl/H (mol/mol)
500	0.0	10	89.95	0.00
500	87.5	10	89.94	0.09
500	175.0	10	89.93	0.18
500	262.5	10	89.92	0.26
500	350.0	10	89.91	0.35
500	437.5	10	89.90	0.44

## 2 Results

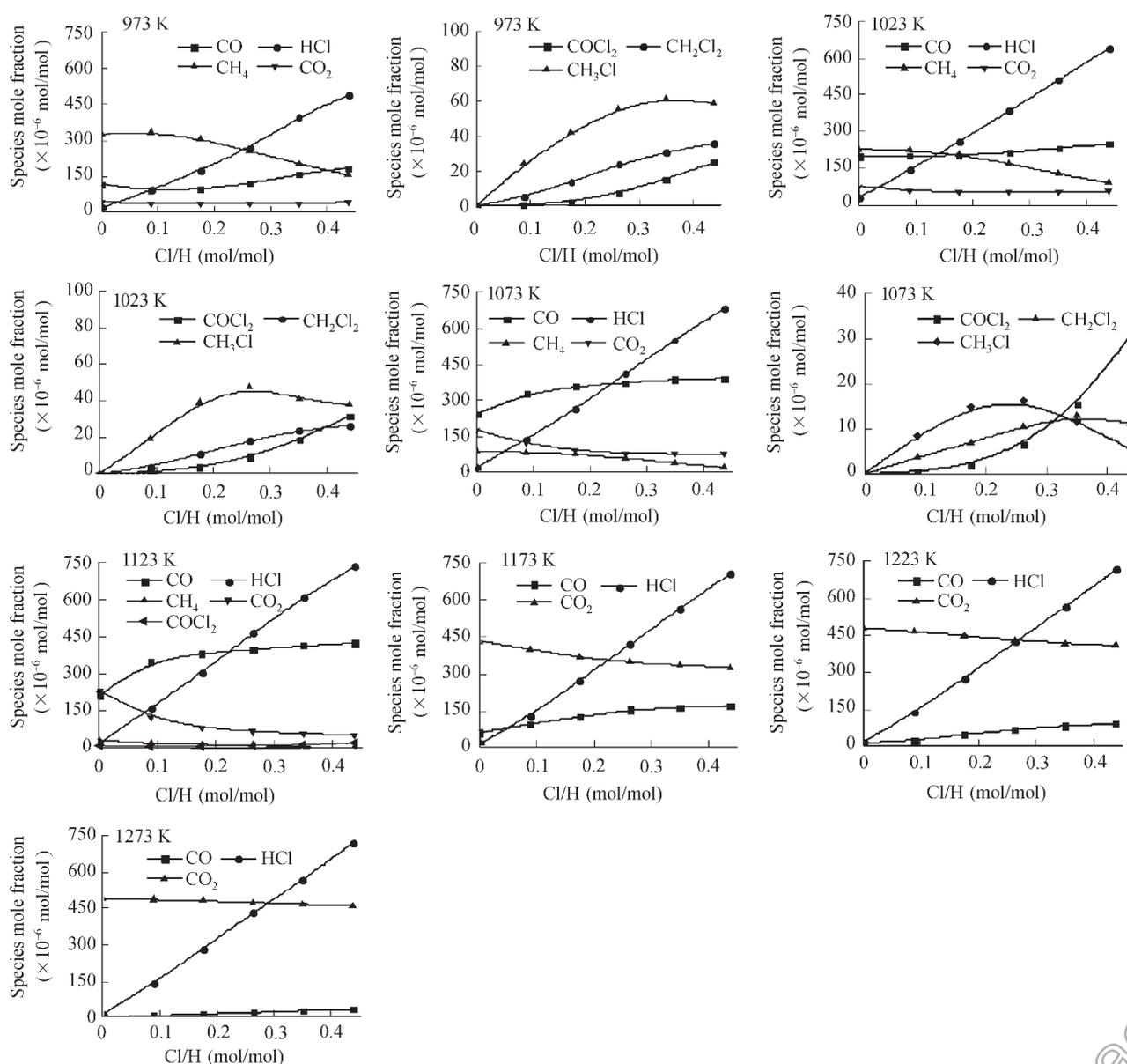
### 2.1 Influence of reaction temperature

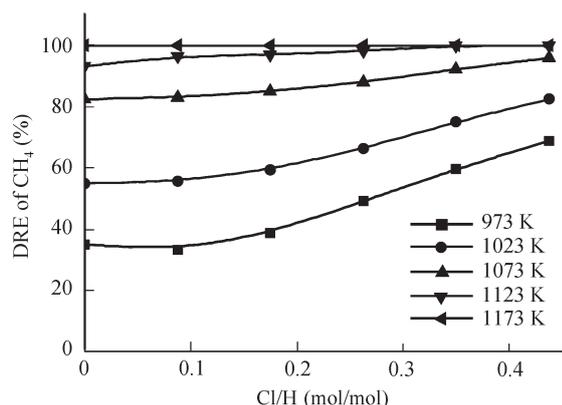
Reaction temperature has important influence on product distributions. For main products include CO, HCl, CO<sub>2</sub> and H<sub>2</sub>O, at temperatures below 1173 K, CH<sub>4</sub> was not completely destroyed. The absorption peaks of COCl<sub>2</sub> at 1837 and 850 cm<sup>-1</sup> were clearly observed in

the experiments. The peaks at 1266, 2949, and 2987 cm<sup>-1</sup> demonstrated the formation of CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub>. However, other chlorinated species such as chloroform and tetrachloride carbon were not detected in the experiments. The species profiles are shown in Fig. 2.

With a certain Cl/H, the concentrations of these organic incomplete combustion products decrease with increasing reaction temperature due to their instability at high reaction temperature. As shown in Fig. 2, CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> were completely destructed at 1123 K. When the temperature exceeded 1173 K, COCl<sub>2</sub> was not detected in the outlet gas.

As shown in Fig. 3, the destruction and removal efficiency (DRE) of CH<sub>4</sub> increased with temperature increasing from 973 to 1173 K. The oxidation of CO was relatively slow under HCl inhibition, thus the destruction of CH<sub>4</sub> resulted in the CO formation and accumulation. When temperature reached 1173 K or above, CH<sub>4</sub> was completely destructed and the CO oxidation reaction accelerated. As

**Fig. 2** Species profiles of reaction product at different temperatures.



**Fig. 3** Variation of destruction and removal efficiency (DRE) of CH<sub>4</sub> with Cl/H mole ratio at different temperatures.

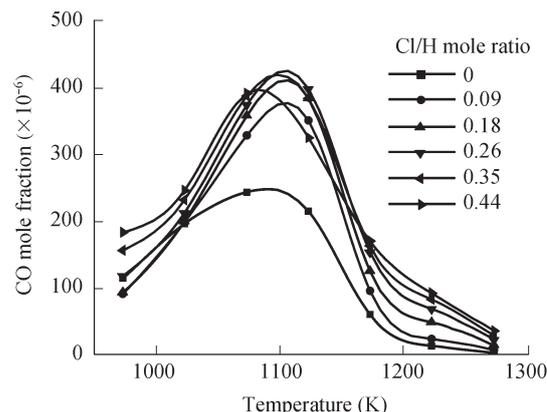
a result, CO concentration first increased as temperature increasing, then declined with the concentration peak around 1100 K (Fig. 4). To completely convert CO to CO<sub>2</sub>, the reaction temperature should be higher than 1273 K. The percentage of carbon in CH<sub>4</sub> converted to CO<sub>2</sub> ( $x(\text{CO}_2)/x(\text{CH}_4)_0$ ) increased with temperature (Fig. 5). At 973 and 1023 K, less than 10% of CH<sub>4</sub> was oxidized to CO<sub>2</sub>, whereas the conversion could approach 100% at 1273 K. The conversion increased sharply when reaction temperature varied from 1023 to 1223 K.

## 2.2 Influence of Cl/H mole ratio

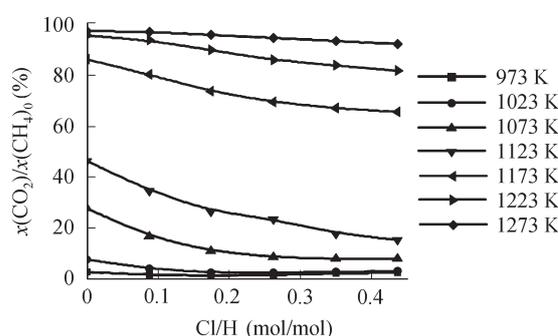
The influence of Cl/H mole ratio on methane destruction and removal efficiency is illustrated in Fig. 3. Adding chlorine to the inlet mixture obviously increased the DRE of CH<sub>4</sub>, especially at low temperatures. For instance, the DRE of CH<sub>4</sub> varied from 34.9% to 68.8% when Cl/H mole ratio varied from 0 to 0.44 at 973 K. When the reaction temperature was 1173 K or above, more than 99% of CH<sub>4</sub> was destructed and the influence of chlorine became mild.

The effect of Cl/H mole ratio on organic incomplete combustion products formation is more complicated. For COCl<sub>2</sub>, the concentration steadily increased with Cl/H mole ratio, as summarized in Fig. 6a. The variations of CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> mole fraction with Cl/H mole ratio are shown in Figs. 6b and 6c. The concentrations of both chlorinated methane exhibited a peak and the peak move to low Cl/H region as temperature increasing, especially for CH<sub>3</sub>Cl. This demonstrated the further destruction of these species at higher chlorine concentration or temperature. Chlorine in the system reacted with carbonaceous radicals to form CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub>. At the same time, CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> reacted with Cl<sub>2</sub> or Cl, which led to a further destruction of these intermediate species.

For CO and CO<sub>2</sub>, adding chlorine to the inlet mixture enhanced CH<sub>4</sub> destruction and CO formation, whereas inhibited the CO oxidation reactions. As shown in Figs. 4 and 5, these factors led to an increase in CO concentration with Cl/H and temperature below 1073 K. At temperatures above 1173 K, CH<sub>4</sub> was completely destructed and CO was produced rapidly. The reaction was dominated by the inhibition of CO oxidation reactions. Therefore, the CO concentration also increases with Cl/H ratio. However, it



**Fig. 4** Variation of CO concentration with temperature at different Cl/H mole ratios.

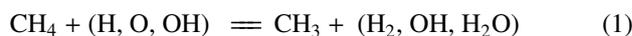


**Fig. 5** CH<sub>4</sub> conversion at different temperatures and Cl/H mole ratios.

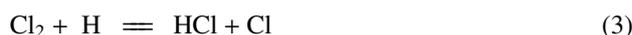
declined at high temperature. In the temperature range 973–1273 K, CO<sub>2</sub> concentration declined with increasing Cl/H ratio at a certain reaction temperature.

## 2.3 Formation mechanism of intermediate species

On the basis of the experimental results, the main reaction pathways were qualitatively analyzed as follows. According to the work by Warnatz (1984), the initiation steps of CH<sub>4</sub> destruction in methane/air flame are:



when chlorine is added to the system, chlorine radical can be generated through unimolecular dissociation or the reaction with H.



Then the reaction between Cl and CH<sub>4</sub> enhances the destruction of CH<sub>4</sub>:

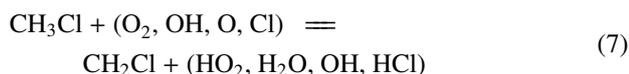


CH<sub>3</sub>Cl is mainly produced through Reactions (5) and (6):

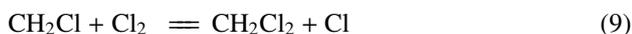


As demonstrated by Ho *et al.* (1992 b), H on CH<sub>3</sub>Cl is more likely to be eliminated than Cl through Reaction (7)

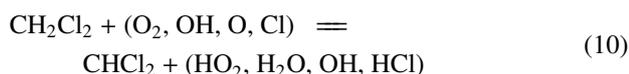
for lower activation energy:



The  $\text{CH}_2\text{Cl}$  radical reacts with  $\text{Cl}$  or  $\text{Cl}_2$  to form  $\text{CH}_2\text{Cl}_2$ :



According to the work by Sgro *et al.* (2000),  $\text{CH}_2\text{Cl}_2$  is mainly converted to  $\text{CHCl}_2$  through bimolecular reactions in fuel lean experimental conditions (Reaction (10)):



The  $\text{CHCl}_2$  radical reacts with  $\text{Cl}$  or  $\text{Cl}_2$  to form  $\text{CHCl}_3$ :



$\text{CHCl}_3$  is the least stable one of chloromethanes (Taylor *et al.*, 1991). It is rapidly dissociated:



Then  $\text{COCl}_2$  is formed through this reaction:



It has been demonstrated that  $\text{COCl}_2$  can only be formed from a structure with two  $\text{Cl}$  which are already bonded to a  $\text{C}$  atom (Thomson *et al.*, 1994). If the reaction temperature and initial concentration of  $\text{CH}_4$  are constant, higher  $\text{Cl}/\text{H}$  favors the  $\text{CCl}_2$  formation and leads to a higher concentration of  $\text{COCl}_2$ . At the same  $\text{Cl}/\text{H}$  and initial concentration of  $\text{CH}_4$ , increasing temperature enhances  $\text{CHCl}_3$  dissociation (Reaction (13)) and  $\text{COCl}_2$  formation (Reaction (14)). Meanwhile, the  $\text{COCl}_2$  consumption reactions also accelerate.



The equilibrium between these two effects leads to the  $\text{COCl}_2$  concentration peak at 1023 K.  $\text{CO}$  in the reaction system is mostly oxidized to  $\text{CO}_2$  by  $\text{OH}$ .



The chlorine inhibition effect on  $\text{CO}$  oxidation is mainly due to the reaction between  $\text{HCl}$  and  $\text{OH}$ , which decreases the  $\text{OH}$  concentration (Ho *et al.*, 1992).



When reaction temperature is elevated, the rate constant of Reaction (17) increases. The reaction rate between  $\text{H}$  and  $\text{O}_2$  to form  $\text{OH}$  increases rapidly. The reaction between  $\text{HCl}$  and  $\text{O}$  also abates the  $\text{OH}$  consumption:



As a result, the effect of chlorine inhibition on  $\text{CO}$  oxidation is reduced. Kinetic modeling of this reaction system with detailed reaction mechanism to obtain further understanding of the inhibition mechanism is going on.

## 2.4 Hints for chlorinated waste incineration

From the experimental results, some hints for chlorinated waste incineration can be drawn. In hazardous waste incinerators, stable combustion of highly chlorinated hydrocarbons is always maintained by adding auxiliary fuel. Auxiliary fuel such as methane will promote highly chlorinated hydrocarbons destruction, and the chlorine in flame will promote hydrocarbons destruction as well. However, the chlorine will inhibit  $\text{CO}$  oxidation and react with carbonaceous species to form toxic incomplete combustion products. It will be important to set suitable incineration temperature and chlorinated waste injection position to eliminate toxic intermediate species formation. Compared with directly mixing the chlorinated hydrocarbons and auxiliary fuels before combustion, the pollutants emission may be lower if the auxiliary fuel is combusted first and then the chlorinated hydrocarbons are injected into the high temperature flue gas, which means a two-stage combustion mode. More work is needed to verify this supposition.

## 3 Discussion and conclusions

Experimental study on  $\text{CH}_4/\text{Cl}_2/\text{O}_2/\text{N}_2$  oxidation was conducted in flow reactor. Products profiles were measured online with FT-IR. It is shown that the presence of chlorine enhances the destruction of methane, but it will lead to more toxic incomplete combustion products emission such as  $\text{COCl}_2$ . The destruction and removal efficiency of  $\text{CH}_4$  increases with  $\text{Cl}/\text{H}$  mole ratio at a constant temperature.

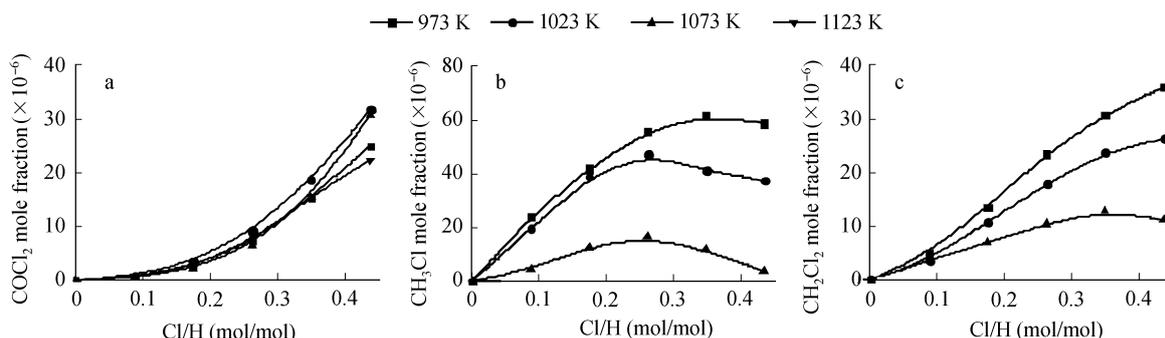


Fig. 6 Variation of  $\text{COCl}_2$  (a),  $\text{CH}_3\text{Cl}$  (b), and  $\text{CH}_2\text{Cl}_2$  (c) concentration with  $\text{Cl}/\text{H}$  mole ratio at different temperatures.

Increasing Cl/H also favors  $\text{COCl}_2$  and CO formation and inhibits the CO oxidation process. As Cl/H approaching 0.44, the concentrations of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$  first increase, and then decline. The concentration peak moves to the low Cl/H region with increasing temperature. This phenomenon is due to the instability and further destruction of these organic species through reactions with chlorine.

Reaction temperature has significant effect on this reaction system. As temperature increases, the destruction and removal efficiency of methane increases, and the concentration of organic incomplete combustion products decreases, including  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ . With a certain Cl/H ratio, the concentrations of CO and  $\text{COCl}_2$  first increase and then decline. The CO concentrations peak is around 1100 K, and the  $\text{COCl}_2$  concentration peak is around 1023 K. At temperatures below 1100 K, the oxidation of CO is relatively slow, and higher temperature favors methane oxidation and CO accumulation. At 1123 K or above, methane is completely destructed. The CO concentration gradually decreases with increasing temperature because the chlorine inhibition effect is abated. When the reaction temperature exceeds 1273 K, carbon in methane is mostly converted to  $\text{CO}_2$ .

Finally, the reaction pathways are qualitatively analyzed. These experimental data can be used for detailed kinetic modeling of this reaction system to obtain more comprehensive understanding of the reaction mechanism.

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