Comparison of the Efficiencies and Kinetic Analysis of the Carbon Tetrachloride Decomposition in RF Thermal Plasma in Inert and Oxidative Environments

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Abstract: Decomposition of carbon tetrachloride was investigated in an RF inductively coupled thermal plasma reactor in inert CCl_4-Ar and in oxidative CCl_4-O_2-Ar systems. The exhaust gas mixtures were analyzed by GC-MS. Kinetics of CCl_4 decomposition at the experimental conditions was modeled in the temperature range of 300 K – 7000 K. Kinetic analysis was performed on the basis of atom fluxes.

Keywords: carbon tetrachloride, decomposition, RF thermal plasma, modeling

1. Introduction

Because of their many advantages the halogenated hydrocarbons had been widely used in the industry and in the household until the 70s when it turned out that these materials were dangerous for the environment. After realizing this fact international treaties banned to use them. Since the 80s several papers have been published on this topic using incineration technology like burning, catalytic oxidation or plasma technology. Most of these papers are experimental work [1-19]. In our previous papers the decomposition of CCl_4 in thermal RF plasma was investigated in inert (CCl_4-Ar) [20] and in oxidative (CCl_4-O_2-Ar) [21] environments. We pointed out that the kinetic modeling is essential because at lower temperatures the most commonly used thermodynamic calculations cannot give good results [20].

2. Results and discussion

In this work the concentration profiles of the most important species have been recalculated during the thermal plasma decomposition of the CCl_4 in inert (CCl_4-Ar) and in oxidative (CCl_4-O_2-Ar) environments. The experimental conditions applied for the simulations were the same as in the experiments [21, 22] that were carried out in thermal RF plasma where argon was used as the plasma and the cooling gases. Therefore, it was possible to compare the efficiency of the decomposition in the two cases and also to compare the experimental and the simulation results.

The inductively coupled plasma was generated at atmospheric pressure in a 150 mm long, 26 mm diameter quartz tube by an RF generator operating at 27.17 MHz. The initial gas mixture contained 0.24 n% carbon tetrachloride and 99.76 n% argon in the case of CCl_4-Ar, and 0.93 n% carbon tetrachloride, 0.73 n% oxygen and 98.34 n% argon in the case of CCl_4-O_2-Ar. The exhaust gases were analyzed immediately with GC-MS. A Perkin-Elmer 1750 type FT IR was used for the calibration.

The first step of the simulations was creating a reaction mechanism. For the simulations it was assumed that only species containing one and two carbon atoms play important role in the mechanism. It was a good assumption because according to the experiments no higher products were formed during the process. Solid products were also formed in the experiments; however, in the simulation it was not possible to model the heterogeneous reactions. On the other hand, their mole fraction was much less than the mole fraction of the gas phase products, therefore their absence did not change significantly the distribution of the most important products.

For the CCl_4–O_2–Ar mechanism 25 reactive species and the inert argon were considered. The full mechanism altogether contained 134 irreversible reactions of 25 reactive species. The CCl_4–Ar mechanism was constructed from the CCl_4–O_2–Ar mechanism by eliminating the reactions of the oxygen containing species. In this way a 34 irreversible reaction and 12 reactive species (and the argon) containing mechanism was created.

For the simulations a time dependent temperature profile was created in the centerline of the RF thermal plasma reactor (Fig. 1).

The symbols represent the points of time for kinetic analysis. The mole fractions were calculated with CHEMKIN [23] and SENKIN [24], respectively. The

results are shown in Figs. 2 and 3. Simulations revealed that CCl_4 decomposes at the very beginning of the reaction in both cases. In oxidative environment, its re-formation does not take place at lower temperatures, while in the inert case 33 % of the original carbon tetrachloride is re-formed. Therefore, in oxidative environment the decomposition is more effective.
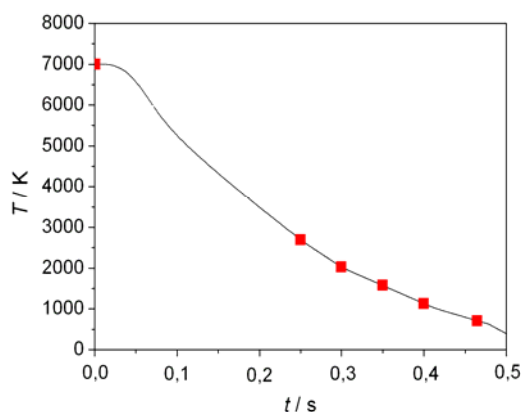
mole fraction than 10^{-5}, while in oxygen-argon atmosphere those products which have bigger final mole fraction than 10^{-5} are the Cl_2, CO, CO_2 and $COCl_2$. All of these are toxic materials except the CO_2. It is interesting that species containing two carbon atoms are forming in very small quantity only (their mole fraction is always smaller than 10^{-8}).

Fig. 1 Time dependent temperature profile

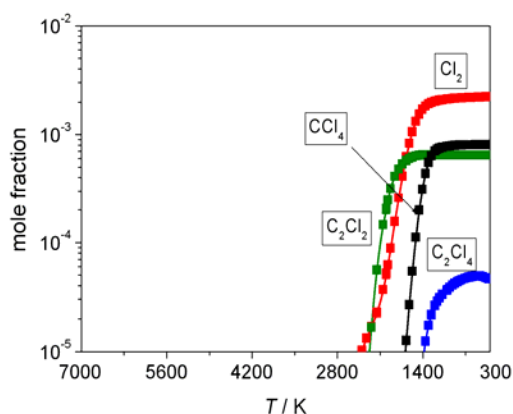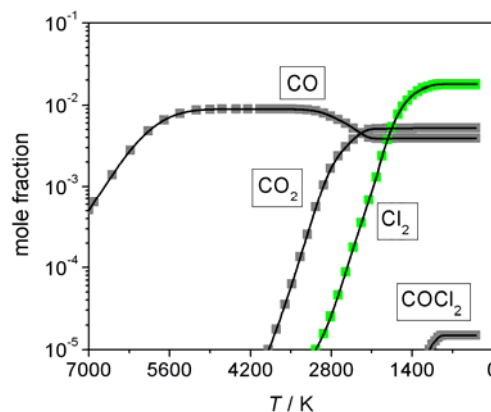Fig. 3 Concentration profiles of the most important products in the CCl_4–O_2–Ar system

Fig. 2 Concentration profiles of the most important products in the CCl_4–Ar system

As it is seen from Figures 2 and 3, Cl_2 is the most important product in both cases. In inert atmosphere, besides Cl_2, C_2Cl_2 and C_2Cl_4 are formed in higher

The simulated results could be directly compared with the experimental ones in the oxidative case because calibration was carried out only for this system. Note that no calibration was done for CO. Therefore, the quantity of the CO formed in the experiments is uncertain. On the other hand, the phosgene is formed in small quantity and its quantitative measurement was not possible. According to the calculations in oxidative system the most possible products are the Cl_2, CO_2, CO and $COCl_2$ in smaller amount, while in inert system are the Cl_2, C_2Cl_2 and C_2Cl_4. Tables 1 and 2 show a good qualitative agreement between the theory and the experiments: the same gas phase products were formed (the + sign labels the products which could be identified during the experiments).

The reaction mechanism was reduced with KINALC [25, 26] by identifying the unimportant species and selecting the unimportant reactions from the principal component analysis of matrix **F** [26, 27, 28].

Table 1. Comparison of simulated and experimental results for the CCl_4–Ar case

	Conversion / %	C_2Cl_2	C_2Cl_4	Cl_2
Theory	67.0	$x = 6.5 \cdot 10^{-4}$	$x = 4.7 \cdot 10^{-5}$	$x = 2.2 \cdot 10^{-3}$
Experiment	60.6	+ (uncertain)	uncertain	+ (uncertain)

Table 2. Comparison of simulated and experimental results for the CCl_4–O_2–Ar case

	Conversion / %	CO	CO_2	Cl_2	$COCl_2$
Theory	97.9	$X = 3.9 \cdot 10^{-3}$	$x = 5.0 \cdot 10^{-3}$	$x = 1.9 \cdot 10^{-2}$	$x = 1.5 \cdot 10^{-5}$
Experiment	92.5	uncertain	$C = 1.2 \cdot 10^{-3}$ mol·dm^{-3}	$c = 2.5 \cdot 10^{-3}$ mol dm^{-3}	+ uncertain

In both cases the reduction was carried out in nine time points between 10^{-7} s and 0.500 s. The reduced CCl_4-Ar mechanism contains 29 irreversible reactions of 12 reactive species and the reduced CCl_4–O_2–Ar

mechanism contains 65 irreversible reactions of 23 reactive species. The mole fractions were recalculated with the reduced mechanisms, too. Good agreement was obtained between the results by the full and re-

duced mechanisms (0.1 %). This is seen in Figures 2 and 3.

The kinetic analysis was performed by investigating the fluxes of C-, Cl- (and O) atoms. Flux analysis revealed the change of inter-conversion rates among species during the process [29]. It was concluded that significant fluxes appear only at high (6000-7000 K) temperatures and that at the beginning of the reaction the CCl_4 and its direct fragments (CCl_3, CCl_2, CCl) were mostly consumed by thermal decomposition.

The main characteristics of the two systems studied in this work can be summarized as follows.

CCl_4-Ar system: Above 6000 K the reactions are fast enough and the system is in thermodynamic equilibrium. The forward and backward reactions have about the same reaction rates. This is the reason why no significant net species production can take place. After $2 \cdot 10^{-5}$ s (when the temperature is still 7000 K) the decomposition is almost complete and only the equilibrium reactions between Cl and CCl are significant. Below 6000 K no significant carbon tetrachloride is present because it was almost totally consumed. The concentration decrease of the CCl, CCl_2 and CCl_3 species is reasoned by their production reactions being more important below 4000 K.

CCl_4-O_2-Ar system: From the O atom fluxes it became clear that the O_2 molecule is in equilibrium with both the O and ClO radicals. This is valid even at lower temperatures. The important role of the ClO radical is not questionable because it has significant fluxes in each time point. The $COCl \rightarrow COCl_2$ reaction becomes slower below 5000 K. Therefore, the slow production rate of phosgene is not surprising. With decreasing temperature the thermodynamic equilibrium falls and the kinetics becomes more important. The reactions are slow but the original O_2 concentration is high enough and comparable with that of CCl_4. There is still a lot of oxygen in the system which gives a reasonable chance for the CO, CO_2 and phosgene production. It is interesting that below 1400 K the COCl radical decomposes to CO and Cl instead of forming $COCl_2$.

3. Conclusions

The decomposition of CCl_4 was investigated in inert and in oxidative environments. The decomposition was kinetically modeled and detailed kinetic analysis including mechanism reduction and atom fluxes analysis was also carried out. Good qualitative agreement was obtained between the experimental and simulation results. According to both the theory and the experiments, in CCl_4-Ar system the most important products are the Cl_2 and C_2Cl_2 and in CCl_4-O_2-Ar system the Cl_2, CO, CO_2 and $COCl_2$. We can conclude that decomposition is more effective in oxidative environment than in inert one.

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