

CCl₄ Decomposition in RF Thermal Plasma in Inert and Oxidative Environments

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Abstract The decomposition of carbon tetrachloride was investigated in an RF inductively coupled thermal plasma reactor in inert CCl₄-Ar and in oxidative CCl₄-O₂-Ar systems, respectively. The exhaust gases were analyzed by gas chromatography-mass spectrometry. The kinetics of CCl₄ decomposition at the experimental conditions was modeled in the temperature range of 300–7,000 K. The simulations predicted 67.0 and 97.9% net conversions of CCl₄ for CCl₄-Ar and for CCl₄-O₂-Ar, respectively. These values are close to the experimentally determined values of 60.6 and 92.5%. We concluded that in RF thermal plasma much less CCl₄ reconstructed in oxidative environment than in an oxygen-free mixture.

Keywords Carbon tetrachloride · Decomposition · Thermal plasma

Introduction

Because of their many advantages the halogenated hydrocarbons had been widely used in the economy until the 1970s when it turned out that these materials were environmental unfriendly. After realizing this, international treaties banned to use them. Since the 1980s several papers have been published on this topic using incineration technology like

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burning, catalytic oxidation or even 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 ($\text{CCl}_4\text{-Ar}$) [20] and in oxidative ($\text{CCl}_4\text{-O}_2\text{-Ar}$) [21] environments. We pointed out that the kinetic modelling is essential because at lower temperatures the most commonly used thermodynamic calculations cannot give accurate results [20].

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 ($\text{CCl}_4\text{-Ar}$) and in oxidative ($\text{CCl}_4\text{-O}_2\text{-Ar}$) 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 central and sheath gas, respectively. 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. These calculations use the same mechanisms as in References [21, 22] but the rate parameters were updated and the concentrations were calculated as mole fractions. In this study, the atom fluxes in the two systems can be compared directly, which was not possible in the earlier works.

A 150 mm long, 26 mm diameter quartz tube was used as the reactor and the inductively coupled plasma thermal plasma operated at atmospheric pressure. The initial gas mixture contained 0.24 n% carbon tetrachloride and 99.76 n% argon in the $\text{CCl}_4\text{-Ar}$ case and 0.93 n% carbon tetrachloride, 0.73 n% oxygen and 98.34 n% argon in the $\text{CCl}_4\text{-O}_2\text{-Ar}$ case. The exhaust gases were analyzed immediately with GC-MS. A Perkin-Elmer 1750 type FT IR (MCD—HgCdTe—detector) was used for the calibration.

In the $\text{CCl}_4\text{-O}_2\text{-Ar}$ experiments the specific energy was 0.022 kWh g^{-1} , while in $\text{CCl}_4\text{-Ar}$ it was changed between 0.022 kWh g^{-1} and 0.081 kWh g^{-1} . Table 1 summarizes the percentage of carbon tetrachloride re-formation as the function of specific energy.

It is already seen here that the CCl_4 decomposition is more effective in oxidative environment than in $\text{CCl}_4\text{-Ar}$. In the latter case the decomposition is only 60.6% compared to 92.5% for $\text{CCl}_4\text{-O}_2\text{-Ar}$. Note that in the case of $\text{CCl}_4\text{-Ar}$ higher specific energy provides higher decomposition efficiency (with 0.089 kWh g^{-1} it is 89.6%), however this is still lower than 92.5% obtained for $\text{CCl}_4\text{-O}_2\text{-Ar}$.

In the experiments polycyclic aromatic hydrocarbons were also formed, which are the products of the complicated organic reactions taking place below 2,000 K. These appeared as a condensate on the wall of the reactor. Free radicals (CCl_2 and CCl) formed by reactions taking place at high temperature were condensed to alkanes and alkenes at the cooler places of the reactor. When the experiments were carried out in the presence of

Table 1 Specific energy dependence of CCl_4 re-formation

System	Specific energy (kW g ⁻¹)	CCl_4 re-formation
$\text{CCl}_4\text{-Ar}$	0.089	10.4
$\text{CCl}_4\text{-Ar}$	0.072	17.3
$\text{CCl}_4\text{-Ar}$	0.061	22.9
$\text{CCl}_4\text{-Ar}$	0.022	39.4
$\text{CCl}_4\text{-O}_2\text{-Ar}$	0.022	7.5

oxygen the formation of polycyclic hydrocarbons were inhibited and mostly Cl_2 , CO and CO_2 were formed. By increasing the specific energy the CO and chlorine yields increased.

Simulations

In the first step reaction mechanisms were created. For the simulations, we assumed that species containing only 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 also formed in the experiments; however, in the simulation it was not possible to model the heterogeneous reactions. On the other hand, heterogeneous reactions can be usually well separated from the gas phase ones.

In the case of $\text{CCl}_4\text{-O}_2\text{-Ar}$ 25 reactive species were considered as possible species taking place in the mechanism. Theoretically, many reactions are possible, however only the thermal dissociation reactions and those reactions were considered which are important in the formation of experimentally detected and estimated products.

According to the experiments there were no gas phase products which contain three or more carbon atoms. Therefore, these were neglected in the simulations. Although solid products were important, according to the experiments, but, because of the extreme complication caused by them, no heterogeneous reactions were considered in the simulations. Furthermore, this is a reasonable approximation as the molar ratio of the high carbon containing species was much lower than of the small main products, therefore their ignorance did not affect the estimation of the product distribution significantly.

The full mechanism altogether contained 134 irreversible reactions of the 25 reactive species. Arrhenius parameters were adopted from the NIST database [23], while there for the reverse reactions they were calculated by the MECHMOD [24]. In the mechanism—due to the low concentrations of the ionic species and the small reaction rates, no ionic species were considered [25].

The $\text{CCl}_4\text{-Ar}$ mechanism was constructed from the $\text{CCl}_4\text{-O}_2\text{-Ar}$ 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 centreline of the experimental ICP reactor (Fig. 1).

The symbols represent the times of kinetic analysis. Mole fractions were calculated with CHEMKIN [26] and SENKIN [27]. Figures 2 and 3 show the results.

Fig. 1 The time dependent temperature profile

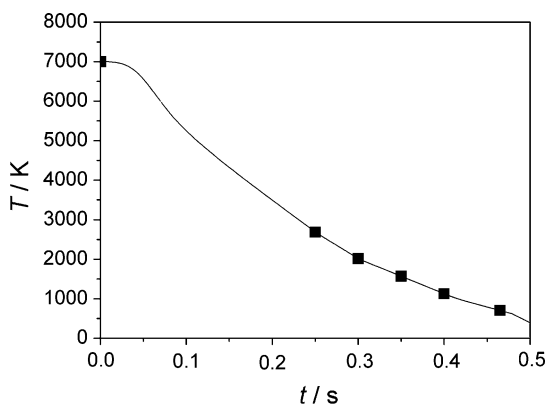


Fig. 2 Concentration profiles of the most important products in the $\text{CCl}_4\text{-Ar}$ system

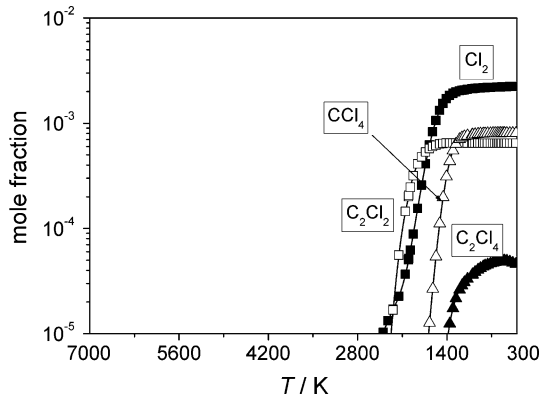
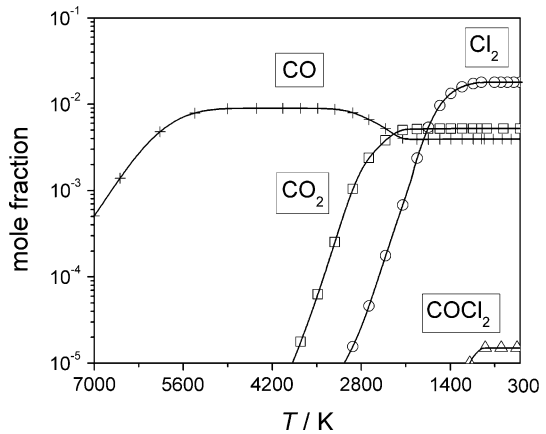


Fig. 3 Concentration profiles of the most important products in the $\text{CCl}_4\text{-O}_2\text{-Ar}$ system



As it turned out during the simulations, 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 recombined. Therefore, in oxidative environment the decomposition is more effective. As it is seen from Figs. 2 and 3 the 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 mole fraction than 10^{-5} , while in oxygen-argon atmosphere those products, which have bigger final mole fraction than 10^{-5} are 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 formed only in very small amount (their mole fraction is always smaller than 10^{-8}).

The direct comparison of the simulation and the experimental results was possible only in the oxidative case because we could calibrate this system only. 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 calculations in oxidative system the most probable products are Cl_2 , CO_2 , CO and COCl_2 , while in inert system they are Cl_2 , C_2Cl_2 and C_2Cl_4 . Tables 2 and 3 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).

Table 2 Comparison of the simulated and experimental results in the $\text{CCl}_4\text{-Ar}$ case

	Conversion/%	C_2Cl_2	C_2Cl_4	Cl_2
Theory	67.0	6.5×10^{-4}	4.7×10^{-5}	2.2×10^{-3}
Experiment	60.6	+Uncertain	Uncertain	+Uncertain

Table 3 Comparison of the simulated and experimental results in the $\text{CCl}_4\text{-O}_2\text{-Ar}$ case

	Conversion/%	CO	CO_2	Cl_2	COCl_2
Theory	97.9	3.9×10^{-3}	5.0×10^{-3}	1.9×10^{-2}	1.5×10^{-5}
Experiment	92.5	Uncertain	2.9×10^{-2}	6.1×10^{-2}	+Uncertain

Kinetic analysis was carried out by using KINALC [28] by investigating the fluxes of C-, Cl- (and O) atoms. Flux of an atom is defined as the sum of the rates of all reaction steps that convert a given species to another, multiplied by the change of the number of atom investigated in the reaction steps. Flux analysis revealed the change of inter-conversion rates among species during the process [29].

It was concluded for both cases that significant fluxes appear only at high temperatures, above 6,000 K. At the beginning of the reactions the main consuming reactions of the carbon tetrachloride and its fragments are the thermal decompositions (like $\text{CCl}_4 + \text{Ar} \rightarrow \text{CCl}_3 + \text{Cl} + \text{Ar}$). A bit later (at around 2×10^{-5} s reaction time, when the temperature is still 7,000 K) the thermal decompositions are still dominant, however there is no CCl_4 present. Here, only CCl- and Cl containing reactions are important. Above 6,000 K the reactions are fast and the system is in thermodynamic equilibrium.

$\text{CCl}_4\text{-Ar}$ System

The only consuming reaction of the CCl_4 is $\text{CCl}_4 + \text{Ar} \rightarrow \text{CCl}_3 + \text{Cl} + \text{Ar}$, which is also the main production step of the CCl_3 in the first 10 μs . This consumes mainly in the $\text{CCl}_3 + \text{Ar} \rightarrow \text{CCl}_2 + \text{Cl} + \text{Ar}$ reaction. The CCl_2 and CCl are also consumed mainly by thermal decomposition. At 20 μs the rate of the decomposition is very high and only the equilibrium reaction between Cl and CCl has a role. According to the simulation the equilibrium is valid over the entire reaction time. The reason why the concentrations of CCl, CCl_2 and CCl_3 increase is that at lower temperatures (below 4000 K) their slower production steps become also important.

$\text{CCl}_4\text{-O}_2\text{-Ar}$ System

The O_2 molecule is in equilibrium with the O atom and also with the ClO radical. This is valid at lower temperatures, too. The ClO has significant fluxes at all reaction time. The most important interconversions (like $\text{C} \rightleftharpoons \text{CO}$, $\text{CO} \rightleftharpoons \text{CO}_2$ and $\text{CO} \rightleftharpoons \text{COCl}$) are in equilibrium at later times, too. The $\text{COCl} \rightarrow \text{COCl}_2$ steps slow down even above 5,000 K, therefore the phosgene production is not surprising. With the temperature drop the system comes out from the equilibrium and the kinetics become dominant. Although the reactions are slow but the initial O_2 concentration was comparable with the carbon tetrachloride concentration, there is still enough oxygen, which makes the CO, CO_2 and COCl_2 productions possible. With further temperature drop there are more ways for their production.

Conclusions

The decomposition of CCl_4 was investigated in inert and in oxidative environments, respectively. The decomposition was kinetically modelled 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 the $\text{CCl}_4\text{-Ar}$ system the most important products are Cl_2 and C_2Cl_2 and in $\text{CCl}_4\text{-O}_2\text{-Ar}$ system they are Cl_2 , CO , CO_2 and COCl_2 . The decomposition was more effective in oxidative conditions than in the inert one.

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