MODELLING OF THE DECOMPOSITION OF CCl$_4$ IN THERMAL PLASMA

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Abstract

Perhalogenated hydrocarbons were popular materials in many areas of the chemical industry and in the household. Their applications have been banned by international treaties because of their stratospheric ozone depleting property. However, large quantities are still stored waiting for a safe decomposition technology. Many experimental articles were published in the last few years showing that plasma technology is applicable for the decomposition of halogenated hydrocarbons in an environmentally friendly way. We have modelled the kinetics of the decomposition of carbon tetrachloride in thermal plasma in argon bulk gas in the temperature range of 300 K to 7000 K. The reaction mechanism contains 34 irreversible reaction steps and 12 species. The thermodynamic data and the kinetic parameters were obtained from Burcat's Thermodynamic Database and the NIST Chemical Kinetics Database, respectively. The conditions of the modelling were in accordance with that was used in a recent experimental paper of Föglein *et al.* to allow the comparison of the modelling and the experimental results. The modelled reactor was an inductively coupled plasma (ICP) reactor. The CCl$_4$/Ar mixture was injected to the high temperature (7000 K) region of the reactor. The modelled temperature profile was in accordance with that of the laboratory reactor. The kinetic calculations provided the concentration−time profiles for each species. All initial carbon tetrachloride was consumed within a few microseconds, but a part of the CCl$_4$ was regenerated from the decomposition products. Our calculations predicted 70% net conversion of CCl$_4$, which is close to the experimentally determined 60%. Apart from the regenerated CCl$_4$, other main products of the incineration were C$_2$Cl$_2$ and Cl$_2$. The simulations were also repeated by a thermodynamic equilibrium model. Results of the kinetic and thermodynamic modelling were in good accordance above 2000 K, but our calculations showed that below 2000 K the thermodynamic equilibrium model gave wrong predictions. Therefore, application of detailed kinetic mechanisms is recommended in the modelling of plasma incineration of harmful materials. Similar modelling studies can be used for planning efficient plasma reactors for incineration technologies.

Introduction

In the 1960s, halogenated hydrocarbons like chloroform and carbon tetrachloride were frequently used as solvents in the organic chemical industry. Freons were also used in many areas of the industry because of their advantageous properties like being non-toxic, cheap and easily producible. In the last decades it became clear that these materials are directly responsible for the global warming and the depletion of the stratospheric ozone. Therefore, their applications have been banned by international treaties. However, large quantities are still stored waiting for a safe decomposition technology. Traditional technologies like burning or catalytic decomposition are not efficient enough and sometimes generate products that are dangerous for the environment and the human heath.

Methodology

Decomposition in plasma mains a safe and environmental friendly technology for the incineration of halogenated hydrocarbons. In the last few years several experimental works have been done and many articles have been published that show the interest in this new technology. But, only few papers are available about the modelling of plasma incineration of halogenated hydrocarbons. We have modelled the kinetics of the decomposition of carbon tetrachloride in thermal plasma in argon bulk gas in the temperature range of 300 K to 7000 K. The simulations were carried out with the SENKIN code [6] of the CHEMKIN-II gas kinetics simulation program package [7].

Results

Orlandini and Riedel [4] examined the reactions of NO in a thermal plasma at atmospheric pressure. They showed that the ionic reactions at such conditions are slow comparing to the thermal, non-ionic reactions, and therefore can be neglected from the kinetic mechanism. Consequently, in our mechanism the non-ionic reaction steps were considered only. This can be justified since at atmospheric pressure the ionization rate of plasma and the concentration of electrons are low. Besides, the rate constants of ionic reaction steps are much smaller than that of the non-ionic ones.

First, a detailed reaction mechanism for the decomposition of CCl_4 in argon bulk gas was created. It contains 34 reactions and 12 species. The thermodynamic data and the kinetic parameters were obtained from Burcat's Thermodynamic Database [1] and the NIST Chemical Kinetics Database [2], respectively. Arrhenius parameters were not found for reaction steps 3 and 7 and these Arrhenius parameters were estimated on the basis of the parameters of the analogous fluorine reactions. The mechanism is presented in Table 1. The temperature dependence of the rate parameters was described by the extended Arrhenius expression in the form of $k = AT^n \exp(-C / RT)$. For the even-numbered reaction steps, the rate parameters were calculated using the kinetic parameters of the preceding reaction steps and the equilibrium constant determined from the thermodynamic data. These rate parameters were established by a mechanism modifier program called MECHMOD [5].

Table 1. The detailed mechanism of the decomposition of CCl_4 in argon bulk gas

num-ber	Reactions	$A\,/\,s^{-1}$	n	$C\,/\,kJ\,mol^{-1}$
1.	$CCl_4 + Ar \rightarrow CCl_3 + Cl + Ar$	$8{,}33\times10^{54}$	$-10{,}6$	313
2.	$CCl_3 + Cl + Ar \rightarrow CCl_4 + Ar$	$1{,}71\times10^{47}$	$-9{,}1$	19,8
3.	$CCl_3 + Ar \rightarrow CCl_2 + Cl + Ar$	$1{,}57\times10^{49}$	$-9{,}0$	386
4.	$CCl_2 + Cl + Ar \rightarrow CCl_3 + Ar$	$8{,}63\times10^{43}$	$-8{,}1$	90,0
5.	$CCl_2 + Ar \rightarrow CCl + Cl + Ar$	$4{,}40\times10^{15}$	$0{,}0$	283
6.	$CCl + Cl + Ar \rightarrow CCl_2 + Ar$	$1{,}91\times10^{10}$	$1{,}2$	$-99{,}6$
7.	$CCl + Ar \rightarrow C + Cl + Ar$	$4{,}32\times10^{15}$	$0{,}0$	290
8.	$C + Cl + Ar \rightarrow CCl + Ar$	$2{,}30\times10^{13}$	$0{,}5$	$-56{,}3$
9.	$CCl_2 + C \rightarrow 2CCl$	$1{,}62\times10^{12}$	$0{,}0$	196
10.	$2CCl \rightarrow CCl_2 + C$	$1{,}34\times10^{9}$	$0{,}7$	153
11.	$CCl_4 + Cl \rightarrow CCl_3 + 2Cl$	$5{,}75\times10^{13}$	$0{,}0$	65,8
12.	$CCl_3 + 2Cl \rightarrow CCl_4 + Cl$	$1{,}18\times10^{6}$	$1{,}5$	-227
13.	$CCl_4 + C \rightarrow CCl_3 + CCl$	$9{,}04\times10^{12}$	$0{,}0$	0,0
14.	$CCl_3 + CCl \rightarrow CCl_4 + C$	$3{,}54\times10^{7}$	$0{,}9$	46,6
15.	$2\,CCl_3 \rightarrow C_2Cl_6$	$4{,}55\times10^{12}$	$-1{,}6$	1,5
16.	$C_2Cl_6 \rightarrow 2\,CCl_3$	$3{,}83\times10^{26}$	$-4{,}5$	288
17.	$C_2Cl_6 + CCl_3 \rightarrow CCl_4 + C_2Cl_5$	$7{,}94\times10^{11}$	$0{,}0$	59,9
18.	$C_2Cl_5 + CCl_4 \rightarrow CCl_3 + C_2Cl_6$	$2{,}95\times10^{8}$	$0{,}8$	39,5
19.	$C_2Cl_5 + Cl_2 \rightarrow C_2Cl_6 + Cl$	$2{,}04\times10^{11}$	$0{,}0$	9,9
20.	$C_2Cl_6 + Cl \rightarrow C_2Cl_5 + Cl_2$	$3{,}51\times10^{17}$	$-1{,}1$	64,7
21.	$C_2Cl_5 \rightarrow C_2Cl_4 + Cl$	$1{,}12\times10^{16}$	$0{,}0$	62,4
22.	$C_2Cl_4 + Cl \rightarrow C_2Cl_5$	$3{,}82\times10^{13}$	$0{,}7$	$-0{,}61$
23.	$C_2Cl_5 + Cl \rightarrow C_2Cl_4 + Cl_2$	$2{,}45\times10^{13}$	$0{,}0$	0,00
24.	$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_5 + Cl$	$6{,}37\times10^{15}$	$-0{,}4$	195
25.	$2Cl + Ar \rightarrow Cl_2 + Ar$	$2{,}00\times10^{15}$	$0{,}0$	0,00
26.	$Cl_2 + Ar \rightarrow 2\,Cl + Ar$	$1{,}52\times10^{20}$	$-1{,}1$	258
27.	$2\,CCl + Ar \rightarrow C_2Cl_2 + Ar$	$5{,}40\times10^{14}$	$0{,}0$	63,5
28.	$C_2Cl_2 + Ar \rightarrow 2CCl + Ar$	$4{,}56\times10^{24}$	$-1{,}9$	858
29.	$2\,CCl_2 + Ar \rightarrow C_2Cl_4 + Ar$	$5{,}70\times10^{15}$	$0{,}0$	24,9
30.	$C_2Cl_4 + Ar \rightarrow 2\,CCl_2 + Ar$	$4{,}14\times10^{26}$	$-1{,}9$	527
31.	$C_2Cl_2 + Cl + Ar \rightarrow C_2Cl_3 + Ar$	$3{,}55\times10^{7}$	$0{,}9$	46,6
32.	$C_2Cl_3 + Ar \rightarrow C_2Cl_2 + Cl + Ar$	$6{,}59\times10^{11}$	$-0{,}1$	192
33.	$C_2Cl_3 + Cl \rightarrow C_2Cl_4$	$2{,}45\times10^{13}$	$0{,}0$	0,00
34.	$C_2Cl_4 \rightarrow C_2Cl_3 + Cl$	$6{,}03\times10^{20}$	$-1{,}4$	327

The conditions of the simulations were in accordance with an experimental inductively coupled plasma (ICP) reactor that had been used by Föglein *et al.* [3] for decomposition experiments of carbon tetrachloride. The modelled reactor was an ICP reactor with a 27.17 MHz frequency; its dimensions were 150 mm in length and 26 mm in diameter. The initial gas composition was also the same as in Föglein's experiments (0.93 m% CCl_4, 99.93 m% Ar). Also, the volumetric flow rate of the gas mixture was 8 L min^{-1}, in accordance with the experiments. The conditions of the calculations referred to the centerline of the reactor where the linear flow velocity was in the range

of 30-60 cm/s. Using calculated flow and temperature profiles [3], the retention times for the different temperature parts of the reactor were determined.
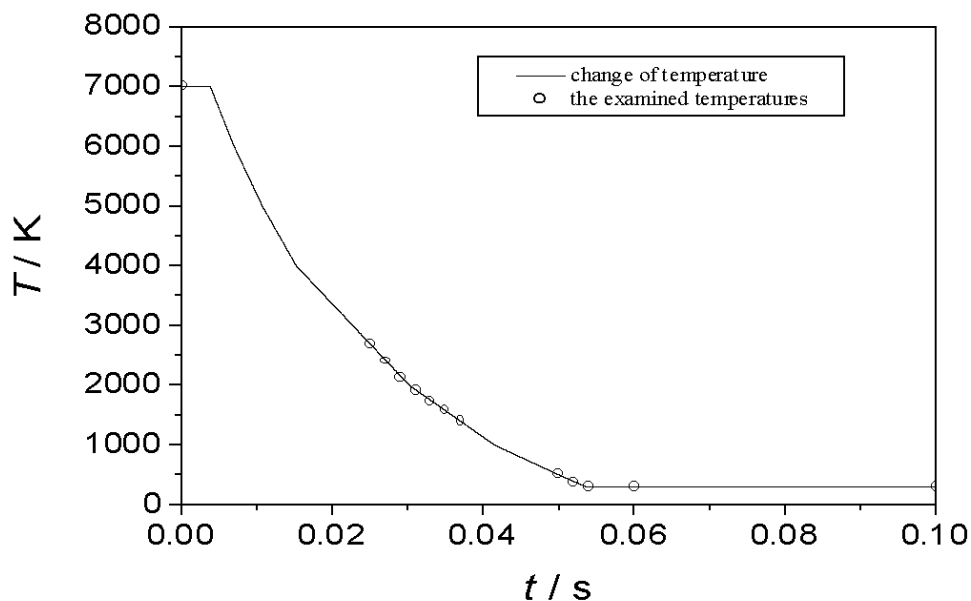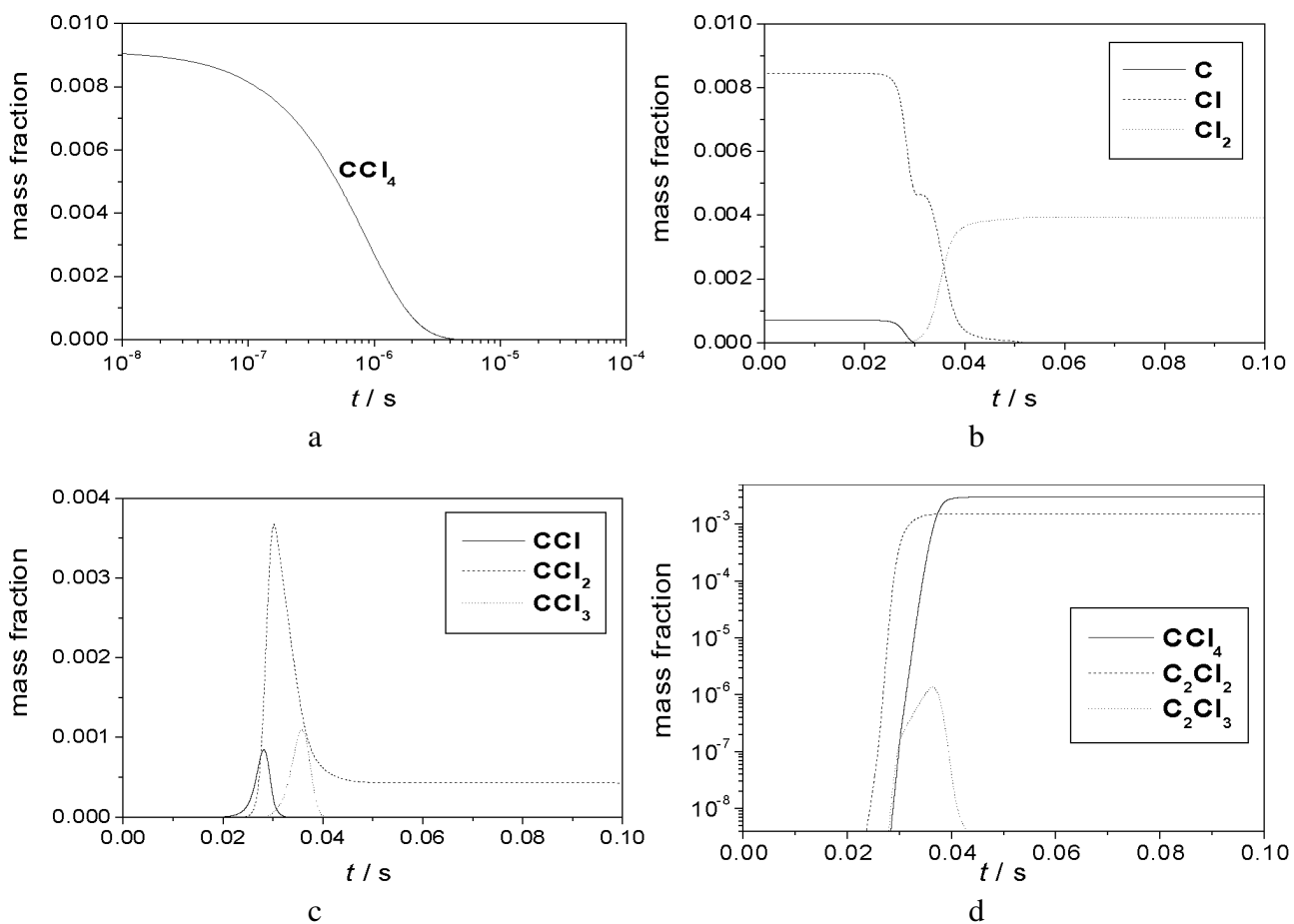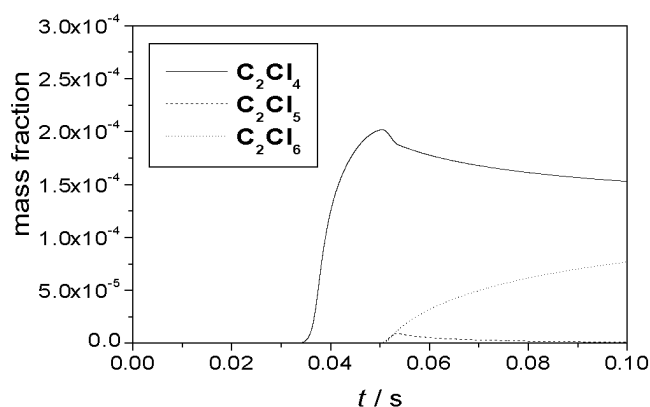

Figure 1. The temperature-time profile

Using the SENKIN program [6] and the above reaction mechanism we calculated the mass fractions for the various species. Tables 2a to 2e show the profiles of the mass fractions till 0.1 s reaction time.

a

b

c

d

e

Figure 2.a-e. Concentration profiles of the most important species

The most important end products were Cl_2, CCl_4 and C_2Cl_2 with mass fractions 4.10×10^{-3}, 3.24×10^{-3} and 1.06×10^{-3}, respectively. Our calculations predicted 70% net conversion of CCl_4, which is close to the experimentally determined 60%. The experimental value was determined using GC-MS analysis.

Discussion

Figure 2.a shows that the initial CCl_4 is totally consumed in the first 10^{-5} s. When the temperature is above 3000 K (till 2×10^{-2} s), the C and Cl radicals have an almost stationary concentration (see Figure 2.b.). According to our calculations, these stationary values are reached within 10^{-4} s. The mass fraction of the CCl_2 radical has a maximum at 3×10^{-2} s (2050 K) and it decreases to mass fraction 5×10^{-4} at the end of the investigated time interval. After 5×10^{-2} s (below 500 K) the dominant process is the regeneration of the CCl_4.

So far, there have been only thermodynamic calculations for the decomposition of CCl_4. Above the kinetic modelling, we have also carried out thermodynamic equilibrium calculations for the same reactant mixtures between 1000 K and 7000 K, and compared the two results. In Figures 3.a and 3.b, the kinetic and the thermodynamic equilibrium results are compared for the simulated mass fractions of Cl_2 and CCl_4. Above 2000 K, the calculations of these two kinds predicted the same concentrations. Below 2000 K the results are different, since at such low temperatures the chemical reactions are slow and there is no time to reach the thermodynamic equilibrium. Therefore, application of chemical kinetic simulations based on detailed mechanisms is recommended for the modelling of plasma incineration of harmful materials.
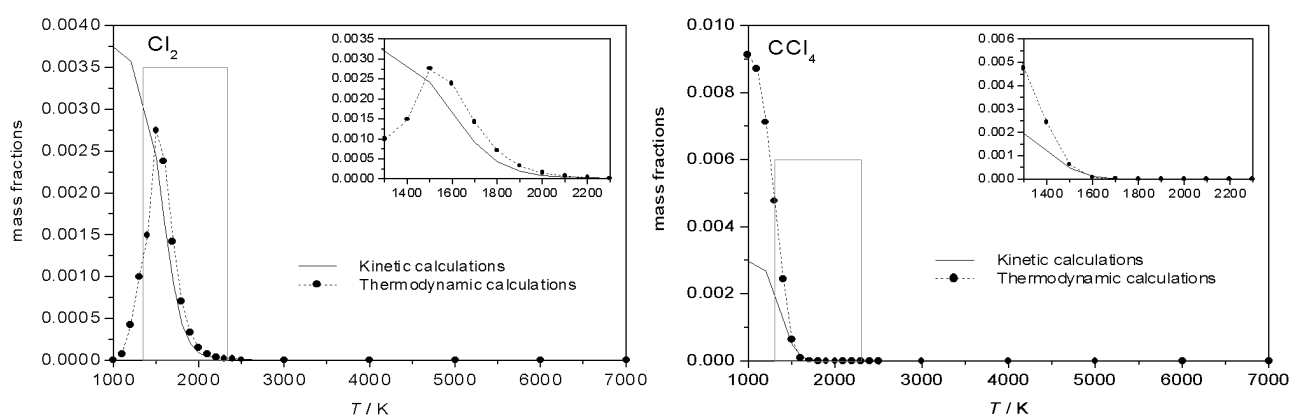

Figure 3.a-b. The results of kinetic and thermodynamic calculations for the concentrations of Cl_2 and CCl_4, respectively

After an inspection of the concentration profiles, time points were selected that cover all regions were the mass fraction of one or more species change significantly. A kinetic analysis was carried out at these times. Using the KINALC [8] program package, we examined which are the most important consuming and producing reaction steps of the various species. We used the net flux for C and Cl atoms in order to describe it. The flux of atoms is the sum of the rates of all reaction steps that convert one species to another multiplied by the change of the number of the atom investigated. These fluxes were determined at each time point studied. Figure 4 shows the fluxes of C and Cl atoms at five time points. The widths of the arrows in this Figure are proportional to the relative values of the fluxes.
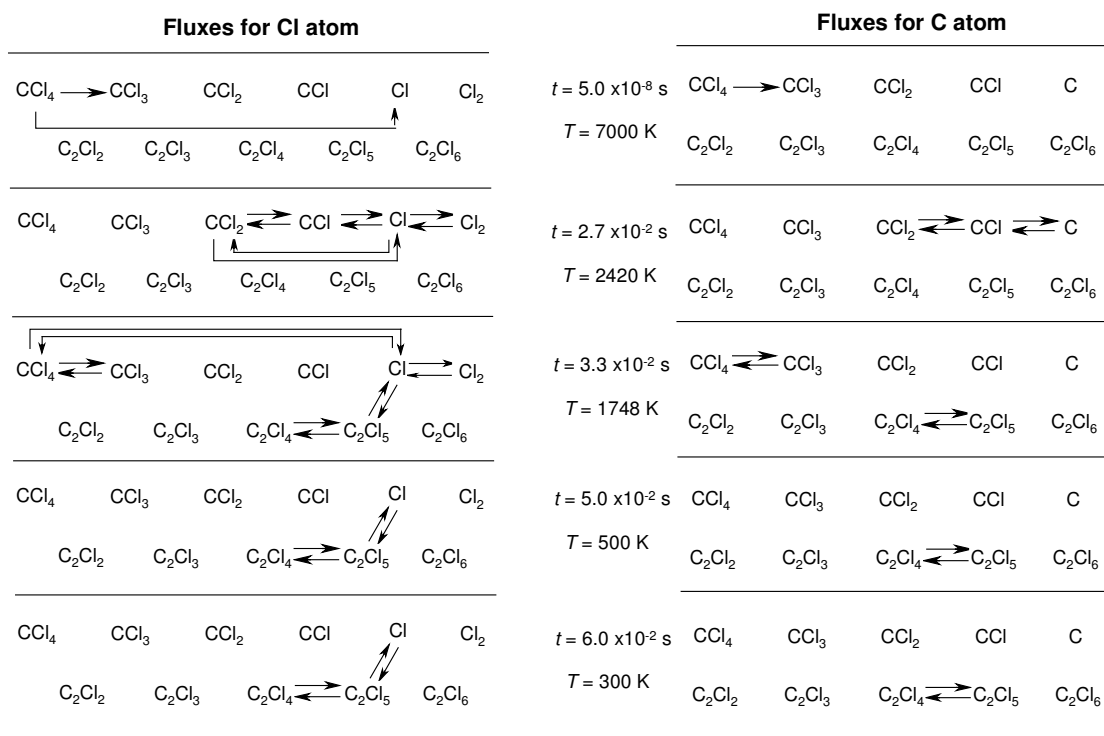

Figure 4. The net fluxes of Cl and C atoms

Inspection of the change of the fluxes provides information which are the most important reaction steps at various stages of the reaction. At the beginning of the reaction (at 7000 K), the most important consuming step of CCl_4 is its thermal decomposition (step 1). After 2.7×10^{-2} s the temperature is low enough (2420 K) for the decomposition reactions to reach the equilibrium. After 3.3×10^{-2} s, the temperature is below 1748 K, allowing the generation of the C_2-species even if their quantity remains low. Note, that other species like C_2Cl_2 or C_2Cl_3 also play role in the kinetics but the rate of their reactions are much slower than the steps showed, therefore their fluxes were not plotted. There are no changes in the fluxes below 500 K (after 5×10^{-2} s).

We have also examined the importance of all reaction steps in the mechanism. A reaction is important if its elimination causes a large change in the calculated values. In this work, we considered a reaction step important if its contribution to the producing rate of any species is larger than 5% of the contribution of the most effective reaction step. In Figure 5, cross shows if the reaction step is important at the investigated time point. The numbering of the time points and the corresponding temperatures can be identified in Table 2.

num-ber	Reactions	1	2	3	4	5	6	7	8	9	10	11	12	13
1.	$CCl_4 + Ar \rightarrow CCl_3 + Cl + Ar$	x	x	x	x	x	x	x	x	x				
2.	$CCl_3 + Cl + Ar \rightarrow CCl_4 + Ar$			x	x	x	x	x	x	x				
3.	$CCl_3 + Ar \rightarrow CCl_2 + Cl + Ar$	x	x	x	x	x	x	x	x	x				
4.	$CCl_2 + Cl + Ar \rightarrow CCl_3 + Ar$			x	x	x	x	x	x	x	x	x		
5.	$CCl_2 + Ar \rightarrow CCl + Cl + Ar$	x	x	x	x	x	x	x	x	x	x	x	x	x
6.	$CCl + Cl + Ar \rightarrow CCl_2 + Ar$			x	x	x	x	x	x	x	x	x	x	x
7.	$CCl + Ar \rightarrow C + Cl + Ar$	x	x	x	x	x	x	x	x	x				
8.	$C + Cl + Ar \rightarrow CCl + Ar$			x	x	x	x	x	x	x	x	x	x	x
9.	$CCl_2 + C \rightarrow 2CCl$													
10.	$2CCl \rightarrow CCl_2 + C$													
11.	$CCl_4 + Cl \rightarrow CCl_3 + 2Cl$										x	x		
12.	$CCl_3 + 2Cl \rightarrow CCl_4 + Cl$										x	x	x	x
13.	$CCl_4 + C \rightarrow CCl_3 + CCl$								x	x				
14.	$CCl_3 + CCl \rightarrow CCl_4 + C$								x	x				
15.	$2\,CCl_3 \rightarrow C_2Cl_6$	x	x	x	x	x	x	x	x	x				
16.	$C_2Cl_6 \rightarrow 2\,CCl_3$	x	x	x	x	x	x	x						
17.	$C_2Cl_6 + CCl_3 \rightarrow CCl_4 + C_2Cl_5$													
18.	$C_2Cl_5 + CCl_4 \rightarrow CCl_3 + C_2Cl_6$											x	x	x
19.	$C_2Cl_5 + Cl_2 \rightarrow C_2Cl_6 + Cl$									x	x	x	x	x
20.	$C_2Cl_6 + Cl \rightarrow C_2Cl_5 + Cl_2$	x	x	x	x	x	x	x	x					
21.	$C_2Cl_5 \rightarrow C_2Cl_4 + Cl$	x	x	x	x	x	x	x	x	x	x	x	x	x
22.	$C_2Cl_4 + Cl \rightarrow C_2Cl_5$			x	x	x	x	x	x	x	x	x	x	x
23.	$C_2Cl_5 + Cl \rightarrow C_2Cl_4 + Cl_2$											x	x	x
24.	$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_5 + Cl$													
25.	$2Cl + Ar \rightarrow Cl_2 + Ar$	x	x	x	x	x	x	x	x	x	x			
26.	$Cl_2 + Ar \rightarrow 2\,Cl + Ar$	x	x	x	x	x	x	x	x	x				
27.	$2\,CCl + Ar \rightarrow C_2Cl_2 + Ar$			x	x									
28.	$C_2Cl_2 + Ar \rightarrow 2CCl + Ar$			x										
29.	$2\,CCl_2 + Ar \rightarrow C_2Cl_4 + Ar$	x	x	x	x	x	x	x	x	x	x	x	x	x
30.	$C_2Cl_4 + Ar \rightarrow 2\,CCl_2 + Ar$													
31.	$C_2Cl_2 + Cl + Ar \rightarrow C_2Cl_3 + Ar$			x	x	x	x	x	x	x	x	x	x	x
32.	$C_2Cl_3 + Ar \rightarrow C_2Cl_2 + Cl + Ar$	x	x	x	x	x	x	x	x	x				
33.	$C_2Cl_3 + Cl \rightarrow C_2Cl_4$				x	x	x	x	x	x	x	x	x	x
34.	$C_2Cl_4 \rightarrow C_2Cl_3 + Cl$	x	x	x	x	x	x	x	x	x				

Figure 5.The importance of the reaction steps

When the temperature is high (near 7000 K), reactions 1, 3, 5, and 7 dominate. Later, the temperature is lower and the backward reaction steps (2, 4, 6, and 8) become also important. At lower temperatures the C and Cl generating steps are slower but the generation of larger radicals (CCl, CCl_2 , CCl_3) and that of the C_2-species (C_2Cl_3 , C_2Cl_5) are faster as can be seen in Figure 2c-2e. The course of the reaction can be divided to two regimes, separated approximately by time point 4×10^{-2} s (1400 K). Below that time the reactions of the C_1-species have larger importance, and above it the reactions of C_2-species are important. Regeneration of CCl_4 is dominant in the second regime. Five reactions (reaction steps 9, 10, 17, 24 and 34) can be eliminated from the mechanism, because these are not important at any of the thirteen times.

Table 2. The times at which the importance of the reactions steps were examined

number	t / s	T / K
1.	$5,0 \times 10^{-8}$	7000
2.	$5,0 \times 10^{-6}$	7000
3.	$2,5 \times 10^{-2}$	2686
4.	$2,7 \times 10^{-2}$	2420
5.	$2,9 \times 10^{-2}$	2153
6.	$3,1 \times 10^{-2}$	1925
7.	$3,3 \times 10^{-2}$	1748
8.	$3,5 \times 10^{-2}$	1571
9.	$3,7 \times 10^{-2}$	1394
10.	$5,0 \times 10^{-2}$	500
11.	$5,2 \times 10^{-2}$	389
12.	$5,4 \times 10^{-2}$	300
13.	$6,0 \times 10^{-2}$	300

Conclusions

Only few papers were found in the literature that deal with the modelling of plasma incineration of halogenated hydrocarbons, and the most of these papers included thermodynamic equilibrium calculations. We have modelled the kinetics of the decomposition of carbon tetrachloride in thermal plasma in argon bulk gas in the temperature range of 300 K to 7000 K. A reaction mechanism was created that contained 34 irreversible reaction steps of 12 species. The conditions of the modelling were in accordance with that used in a recent experimental paper to allow the comparison of the modelling and the experimental results. The modelled reactor was an inductively coupled plasma (ICP) reactor. The modelled temperature and velocity profile was in accordance with that of the laboratory reactor. In the experiments, the gas mixture, cooled to room temperature, was analysed by GC-MS. The kinetic calculations provided the concentration–time profiles for each species. All initial carbon tetrachloride was consumed within 10^{-5} s, but a part of the CCl_4 was regenerated from the decomposition products. Our calculations predicted 70% net conversion of CCl_4, which is close to the experimentally determined 60%. Apart from the regenerated CCl_4, other main products of the incineration were C_2Cl_2 and Cl_2. The simulations were also repeated by a thermodynamic equilibrium model. Results of the kinetic and thermodynamic modelling were in good accordance above 2000 K, but our calculations showed that below 2000 K the thermodynamic equilibrium model gave wrong predictions. We have done also a kinetic analysis and examined the importance of the individual elementary reaction steps. Only 5 reactions from the total 34 ones were not important at any of the examined times.

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