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Kinetic Modeling of the Decomposition of Carbon Tetrachloride in Thermal Plasma

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Decomposition of carbon tetrachloride in a RF thermal plasma reactor was investigated in argon atmosphere. The net conversion of CCl_4 *and the main products of its decomposition were determined from the mass spectrometric analysis of outlet gases. Flow and temperature profiles in the reactor were calculated and concentration profiles of the species along the axis of the reactor were estimated using a newly developed chemical kinetic mechanism, containing 12 species and 34 reaction steps. The simulations indicated that all carbon tetrachloride decomposed within a few microseconds. However,* CCl_4 *was partly recombined from its decomposition products. The calculations predicted 70% net conversion of* CCl_4*, which was close to the experimentally determined value of 60%. A thermodynamic equilibrium model also simulated the decomposition. Results of the kinetic and thermodynamic simulations agreed well above 2000 K. However, below 2000 K the thermodynamic equilibrium model gave wrong predictions. Therefore, application of detailed kinetic mechanisms is recommended for modeling* $CC1_4$ *decomposition under thermal plasma conditions.*

KEY WORDS: Carbon tetrachloride; thermal plasma; decomposition.

1. INTRODUCTION

In the 1960s, halogenated hydrocarbons, such as chloroform and carbon tetrachloride, were frequently used solvents in the chemical industry. Freons were also applied in many industrial and other fields because of their advantageous properties like being non-toxic, cheap, and easy to produce. In the last decades, it became clear that these materials are directly responsible for the global warming and the depletion of stratospheric ozone. Therefore, international treaties have banned their applications. However, large quantities are still being stored waiting for a

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safe decomposition technology. Traditional technologies like incineration or catalytic decomposition are not efficient enough on one hand and sometimes they generate products that are even more dangerous for the environment and the human health on the other.

Decomposition under thermal plasma conditions represents a safe and environmental friendly technology for processing halogenated hydrocarbons. In the last few years, extensive experimental work has been done and many papers have been published that show the research interest in this technology. However, only few papers are available on the modeling of the decomposition of halogenated hydrocarbons in thermal plasmas.

2. DESCRIPTION OF THE EXPERIMENTAL CONDITIONS AND THE KINETIC MODEL

Föglein *et al.*(1) investigated the decomposition of carbon tetrachloride in an inductively coupled, RF thermal plasma reactor. This reactor had a length of 150 mm and a diameter of 26 mm and operating with a plate power of 2.1 kW Argon was used as plasma gas (8 $1 \cdot \mathrm{min}^{-1}$ (STP)) and sheath gas (21 $1 \cdot \mathrm{min}^{-1}$ (STP)), respectively. Atmospheric pressure was maintained in the whole system. The gas mixture to be decomposed consisted of 0.93 m% CCl_4 and 99.07 m% Ar. Conversion (i.e. extent of decomposition) of CCl_4 and the main decomposition products were determined from the GC-MS analysis of outlet gases. At experimental conditions as above, a CCl_4 conversion of 60% was achieved and the main C-atom containing compounds in the outlet gas were C_2Cl_4 (68%), C_2Cl_6 (14%), and CCl_4 (18%).

Using the 2D plasma model of Proulx and Bilodeau(2) that was developed for RF thermal plasmas, we have calculated the temperature and the velocity profiles within the reactor. Temperature pattern for conditions used in this work is shown in Fig. 1. Using the temperature and flow velocity profiles, the approximate temperature of the gas phase as a function of time was determined along the axis of the reactor (Fig. 2). The linear gas velocity in the centerline of the reactor varied from 30 to 60 $\mathrm{cm \cdot s^{-1}}$. Thus, diffusion could be neglected and spatially homogeneous plug-flow simulations were carried out with the SENKIN code(3) of the CHEMKIN-II gas kinetics simulation program package.(4) Systems with inhomogeneous concentration, temperature and flow fields can be modeled based on either the Euler or the Lagrange approach. In the former, the system is covered with a grid and the concentration changes in all grid points are simulated simultaneously. The Euler approach usually requires considerably computer time. According to the Lagrange approach, concentration-time changes are calculated in air parcels, and

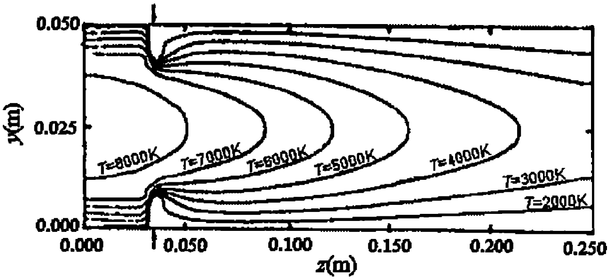

Fig. 1. Temperature profiles calculated by 2D plasma model; Feeding of CCl_4 into the tail flame region is indicated by arrows; Plasma gas: Ar 8 l·min^{-1} (STP), sheath gas: Ar 21 l·min^{-1} (STP), plate power: 2.1 kW.

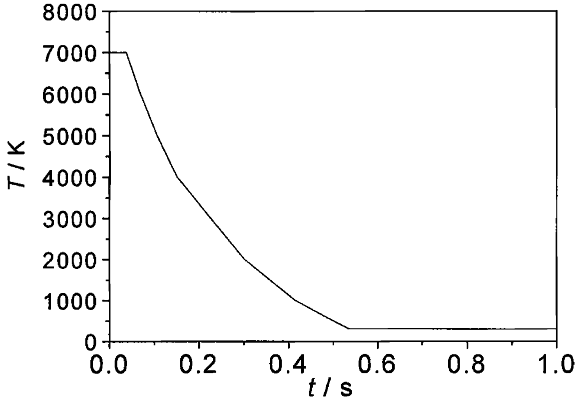

Fig. 2. The estimated temperature–time profile along the axis of the reactor.

the temperature-time history of the parcels is determined from the temperature and flow fields. The Lagrange approach can handle systems with diffusion. However, if diffusion is neglected, the concentration changes in each air parcel can be calculated separately. The concentration changes are calculated using a plug-flow model, while the modeled air parcel actually is moving according to inhomogeneous temperature and flow fields.

A detailed reaction mechanism was constructed for describing the decomposition of CCl_4 in argon gas at high temperatures. The reaction mechanism (Table I) contains 12 species and 34 reactions. The thermodynamic data for the species and the kinetic parameters of reactions were obtained from the Burcat's Thermodynamic Database⁽⁵⁾ and the NIST Chemical Kinetics Database,⁽⁶⁾ respectively. Arrhenius parameters were not found for reaction steps 3 and 7. Particular Arrhenius parameters were

Table I. The Detailed Mechanism for the Decomposition of CCl_4 in Argon Atmosphere

Reactions	A/s^{-1}	n	C/KJ mol^{-1}	References
$CCl_4 + Ar \rightarrow CCl_3 + Cl + Ar$	8.33×10^{54}	-10.6	313	(12)
$CCl_3+Cl+Ar\rightarrow CCl_4+Ar$	1.71×10^{47}	-9.1	19.8	a
$CCl_3+Ar\rightarrow CCl_2+Cl+Ar$	1.57×10^{49}	-9.0	386	(13), b
$CCl_2+Cl+Ar\rightarrow CCl_3+Ar$	8.63×10^{43}	-8.1	90.0	a
$CCl_2 + Ar \rightarrow CCl + Cl + Ar$	4.40×10^{15}	0.0	283	(14)
$CCl+Cl+Ar\rightarrow CCl_2+Ar$	1.91×10^{10}	1.2	-99.6	a
$CCl+Ar\rightarrow C+Cl+Ar$	4.32×10^{15}	0.0	290	(15), b
$C+Cl+Ar\rightarrow CCl+Ar$	2.30×10^{13}	0.5	-56.3	a
$CCl_2+C\rightarrow 2CCl$	1.62×10^{12}	0.0	196	(14)
$2CCl\rightarrow CCl_2+C$	1.34×10^{9}	0.7	153	a
$CCl_4+Cl\rightarrow CCl_3+2Cl$	5.75×10^{13}	0.0	65.8	(16)
$CCl_3+2Cl\rightarrow CCl_4+Cl$	1.18×10^{6}	1.5	-227	a
$CCl_4+C\rightarrow CCl_3+CCl$	9.04×10^{12}	0.0	0.0	(17)
$CCl_3+CCl\rightarrow CCl_4+C$	3.54×10^{7}	0.9	46.6	a
$2CCl_3\rightarrow C_2Cl_6$	4.55×10^{12}	-1.6	1.5	(18)
$C_2Cl_6 \rightarrow 2CCl_3$	3.83×10^{26}	-4.5	288	a
$C_2Cl_6+CCl_3\rightarrow CCl_4+C_2Cl_5$	7.94×10^{11}	0.0	59.9	(19)
$C_2Cl_5+CCl_4 \rightarrow CCl_3+C_2Cl_6$	2.95×10^{8}	0.8	39.5	a
$C_2Cl_5+Cl_2 \rightarrow C_2Cl_6+Cl$	2.04×10^{11}	0.0	9.9	(19)
$C_2Cl_6+Cl\rightarrow C_2Cl_5+Cl_2$	3.51×10^{17}	-1.1	64.7	a
$C_2l_5 \rightarrow C_2Cl_4+Cl$	1.12×10^{16}	0.0	62.4	(18)
$C_2Cl_4+Cl\rightarrow C_2Cl_5$	3.82×10^{13}	0.7	-0.61	a
$C_2l_5+Cl\rightarrow C_2Cl_4+Cl_2$	2.45×10^{11}	0.0	0.00	(18)
$C_2Cl_4+Cl_2 \rightarrow C_2Cl_5+Cl$	6.37×10^{15}	-0.4	195	a
$2Cl+Ar\rightarrow Cl_2+Ar$	2.00×10^{15}	0.0	0.00	(20)
$Cl_2+Ar\rightarrow 2Cl+Ar$	1.52×10^{20}	-1.1	258	a
$2CCl+Ar\rightarrow C_2Cl_2+Ar$	5.40×10^{14}	0.0	63.5	(14)
$C_2Cl_2+Ar\rightarrow 2CCl+Ar$	4.56×10^{24}	-1.9	858	a
$2CCl_2+Ar\rightarrow C_2Cl_4+Ar$	5.70×10^{15}	0.0	24.9	(14)
$C_2Cl_4+Ar\rightarrow 2CCl_2+Ar$	4.14×10^{26}	-1.9	527	a
$C_2Cl_2+Cl+Ar\rightarrow C_2Cl_3+Ar$	3.55×10^{7}	0.9	46.6	(14), b
$C_2Cl_3+Ar\rightarrow C_2Cl_2+Cl+Ar$	6.59×10^{11}	-0.1	192	a
$C_2Cl_3+Cl\rightarrow C_2Cl_4$	2.45×10^{13}	0.0	0.00	(18), b
$C_2Cl_4 \rightarrow C_2Cl_3+Cl$	6.03×10^{20}	-1.4	327	a

[a]calculated from the rate parameters of the previous reaction and the thermodynamic data.
[b]estimated on the basis of the analogous reactions of fluorine species.

estimated from the rate parameters of analogous fluorine reactions. 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 in accordance with the principle of detailed balancing using the kinetic parameters of the preceding ("forward") reaction steps and the equilibrium constant determined from the thermodynamic data using code MECHMOD.$^{(7)}$

We would like to emphasize that the mechanism contains thermal reactions only, and no ionic species are present. It seems to be a good approximation, since at atmospheric pressure the ionization rate of the plasma and the concentration of electrons are low. In addition, the rate constants of the ionic reaction steps are much smaller than that of non-ionic ones. Orlandini and Riedel(8) studied the reactions of NO in thermal plasma at atmospheric pressure. They found that the ionic reactions under such conditions were slow as compared to the thermal, non-ionic reactions. Therefore, they also neglected the ionic reactions from the reaction mechanism.

3. RESULTS OF SIMULATIONS

Using the reaction mechanism as above along with the SENKIN code,(3) the mass fraction profiles as a function of reaction time were calculated for all species. Figure 3a–e show the profiles of mass fractions up to a reaction time of 0.1 s. Carbon tetrachloride almost completely decomposed within 5×10^{-5} s (Fig. 3a). However, after 0.03 s CCl_4 was recombined in a considerable extent from its fragments (Fig. 3d). If the temperature is above 3000 K (up to 2×10^{-2} s), the C and Cl radicals have almost stationary concentrations (Fig. 2b). According to our calculations, the stationary values are reached within 10^{-4} s. The mass fraction of CCl_2 radical has a maximum at 3×10^{-2} s (2050 K), and it decreases to a mass fraction of 5×10^{-4} after 0.1 second.

Our calculations provided the simulated composition of the outlet gas, as well. The most important products in the outlet gas were Cl_2, CCl_4, C_2Cl_2, C_2Cl_4 and C_2Cl_6. A net CCl_4 conversion of 70% was calculated, which was close to the experimentally determined value of 60%.

Up to now, thermal decomposition of CCl_4 was modeled by thermodynamic calculations only.(1) In order to compare the kinetic modeling as above with the thermodynamic simulation, we also performed thermodynamic equilibrium calculations for the same reacting mixture, between 1000 K and 7000 K. In Fig. 4a and b, the results of kinetic and thermodynamic equilibrium calculations are compared in terms of simulated mass fractions of Cl_2 and CCl_4. Above 2000 K, the two methods gave actually similar results. However, below 2000 K results obtained by the two models are different. In this temperature region, 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 modeling the decomposition of carbon tetrachloride in thermal plasmas.

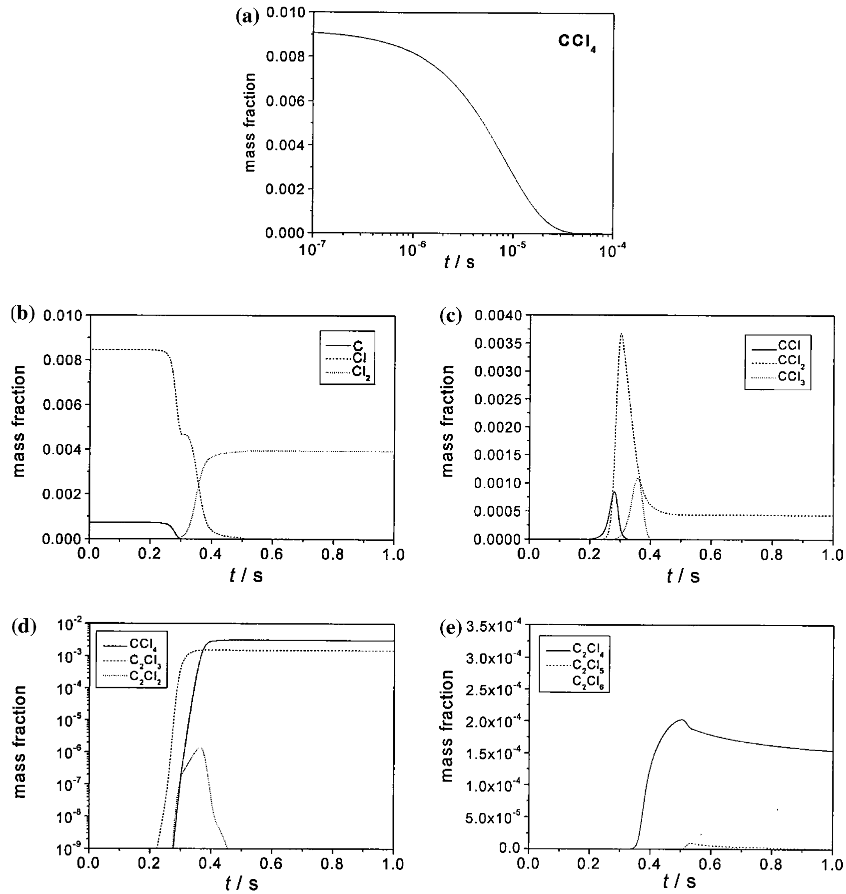

Fig 3a–e. Concentration profiles of the most important species.

Based on the shape of concentration profiles, reaction times corresponding to significant changes of the mass fractions of one or more species were selected (Table II). Kinetic analysis of CCl_4 decomposition was carried out at these reaction times; net fluxes of C and Cl atoms were calculated by the KINALC(9) code. The flux of an atom is the sum of the rates of all reaction steps that convert the given species to another, multiplied by the change of the number of atom investigated. Revel *et al.*(10) have demonstrated usefulness of atom flux calculations in kinetic analysis. Changes in fluxes provide information on the fastest reaction steps at different reaction stages.

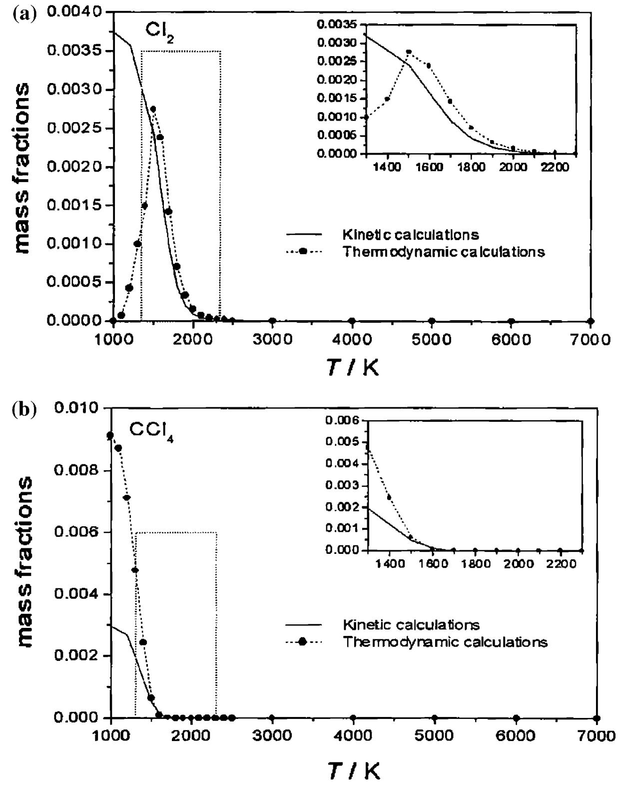

Fig. 4a–b. Results of kinetic and thermodynamic calculations for the mass fractions of Cl_2 and CCl_4, respectively.

In this work, the atom fluxes were determined at each reaction time listed in Table II. Figure 5 summarizes the fluxes of C and Cl atoms at five points of time corresponding to five different reaction temperatures. At a reaction time of 2.7×10^{-2} s when the temperature is 7000 K, the most important reaction step is the thermal decomposition of CCl_4 (reaction No. 1). After 2.7×10^{-2} s, the temperature is much lower (2420 K), and the fast forward and backward reaction steps are in equilibrium. After 3.3×10^{-2} s the temperature is 1748 K, and it allows the formation of C_2-species in low quantities. It is worth mentioning that other species such as C_2Cl_2 or C_2Cl_3 also play some role in the kinetics of the decomposition. However, the rates of their reactions are much lower than that of the other reaction steps showed in Fig. 5. Therefore, their corresponding fluxes were not plotted. There are no changes in the fluxes after 5×10^{-2} s, i.e. below 500 K.

Table II. Reaction Times Selected for Studying the Importance of Different the Reactions Steps

t/S	T/K
5.0×10^{-7}	7000
5.0×10^{-5}	7000
2.5×10^{-1}	2686
2.7×10^{-1}	2420
2.9×10^{-1}	2153
3.1×10^{-1}	1925
3.3×10^{-1}	1748
3.5×10^{-1}	1571
3.7×10^{-1}	1394
5.0×10^{-1}	500
5.2×10^{-1}	389
5.4×10^{-1}	300
6.0×10^{-1}	300

KINALC(9) was also used to determine the most important decomposition and recombination steps at each reaction time. In general, a reaction can be regarded as an important one, if its elimination results in great changes in the simulated values.(11) In this work, we considered a reaction step as important, if its contribution to the formation rate of any

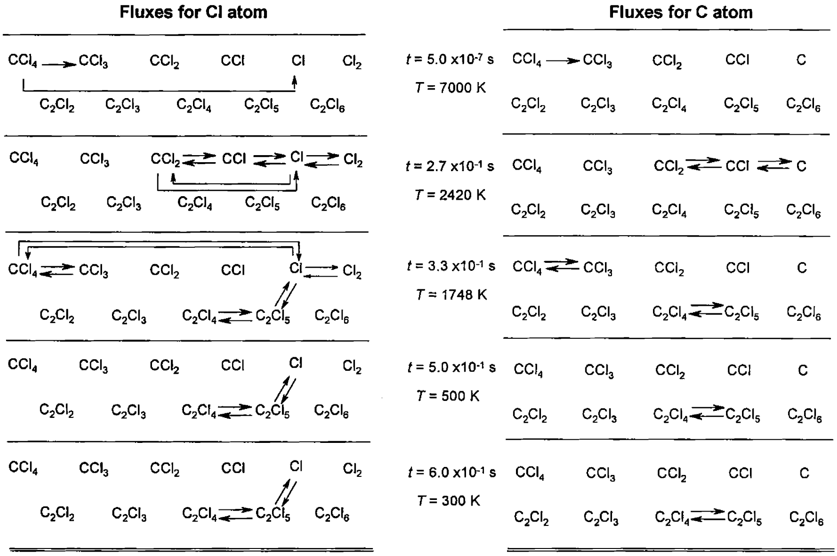

Fig. 5. The net fluxes of Cl- and C-atoms.

species is larger than 5% compared to the most effective reaction step. Reaction steps being important at reaction times selected for the investigations in this work are denoted by **x** in Table III. Numbering of reaction times corresponds to those listed in Table II. At temperatures close to 7000 K, the dominating ones steps are reactions 1, 3, 5, and 7. At lower

Table III. Importance of the Reaction Steps

Reactions	1	2	3	4	5	6	7	8	9	10	11	12	13
$CCl_4 + Ar \rightarrow CCl_3 + Cl + Ar$	X	X	X	X	X	X	X	X	X				
$CCl_3 + Cl + Ar \rightarrow CCl_4 + Ar$			X	X	X	X	X	X	X				
$CCl_3 + Ar \rightarrow CCl_2 + Cl + Ar$	X	X	X	X	X	X	X	X	X				
$CCl_2 + Cl + Ar \rightarrow CCl_3 + Ar$			X	X	X	X	X	X	X	X	X		
$CCl_2 + Ar \rightarrow CCl + Cl + Ar$	X	X	X	X	X	X	X	X	X	X	X	X	X
$CCl + Cl + Ar \rightarrow CCl_2 + Ar$			X	X	X	X	X	X	X	X	X	X	X
$CCl + Ar \rightarrow C + Cl + Ar$	X	X	X	X	X	X	X	X	X				
$C + Cl + Ar \rightarrow CCl + Ar$			X	X	X	X	X	X	X	X	X	X	X
$CCl_2 + C \rightarrow 2CCl$													
$2CCl \rightarrow CCl_2 + C$													
$CCl_4 + Cl \rightarrow CCl_3 + 2Cl$										X	X		
$CCl_3 + 2Cl \rightarrow CCl_4 + Cl$										X	X	X	X
$CCl_4 + C \rightarrow CCl_3 + CCl$								X	X				
$CCl_3 + CCl \rightarrow CCl_4 + C$								X	X				
$2CCl_3 \rightarrow C_2Cl_6$	X	X	X	X	X	X	X	X	X				
$C_2Cl_6 \rightarrow 2CCl_3$	X	X	X	X	X	X	X						
$C_2Cl_6 + CCl_3 \rightarrow CCl_4 + C_2Cl_5$													
$C_2Cl_5 + CCl_4 \rightarrow CCl_3 + C_2Cl_6$											X	X	X
$C_2Cl_5 + Cl_2 \rightarrow C_2Cl_6 + Cl$									X	X	X	X	X
$C_2Cl_6 + Cl \rightarrow C_2Cl_5 + Cl_2$	X	X	X	X	X	X	X	X					
$C_2Cl_5 \rightarrow C_2Cl_4 + Cl$	X	X	X	X	X	X	X	X	X	X	X	X	X
$C_2Cl_4 + Cl \rightarrow C_2Cl_5$			X	X	X	X	X	X	X	X	X	X	X
$C_2Cl_5 + Cl \rightarrow C_2Cl_4 + Cl_2$											X	X	X
$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_5 + Cl$													
$2Cl + Ar \rightarrow Cl_2 + Ar$	X	X	X	X	X	X	X	X	X	X			
$Cl_2 + Ar \rightarrow 2Cl + Ar$	X	X	X	X	X	X	X	X	X				
$2CCl + Ar \rightarrow C_2Cl_2 + Ar$			X	X									
$C_2Cl_2 + Ar \rightarrow 2CCl + Ar$			X										
$2CCl_2 + Ar \rightarrow C_2Cl_4 + Ar$	X	X	X	X	X	X	X	X	X	X	X	X	X
$C_2Cl_4 + Ar \rightarrow 2CCl_2 + Ar$													
$C_2Cl_2 + Cl + Ar \rightarrow C_2Cl_3 + Ar$			X	X	X	X	X	X	X	X	X	X	X
$C_2Cl_3 + Ar \rightarrow C_2Cl_2 + Cl + Ar$	X	X	X	X	X	X	X	X	X				
$C_2Cl_3 + Cl \rightarrow C_2Cl_4$					X	X	X	X	X	X	X	X	X
$C_2Cl_4 \rightarrow C_2Cl_3 + Cl$	X	X	X	X	X	X	X	X	X				

temperatures, the backward reactions (No. 2, 4, 6 and 8) are also important. Steps generating C and Cl slow down by decreasing the temperature further on. However, larger radicals (such as CCl, CCl_2, and CCl_3) and C_2-species (C_2Cl_3 and C_2Cl_5) are generated faster at lower temperatures as it can be seen in Fig. 2c–e. The reaction scheme can be divided to two regimes, separated approximately by time point of 4×10^{-2} s corresponding to the reaction temperature of 1400 K. At reaction times below 4×10^{-2} s reactions of C_1-species are dominating, while after it reactions of C_2-species are important. Recombination of CCl_4 becomes significant in the second regime. Five reactions (reactions No. 9, 10, 17, 24, and 34) can be eliminated from the mechanism, because they are not important at any reaction time. Simulations were repeated using the reduced mechanism. Identical results were obtained with the reduced mechanism as with the full 34-step mechanism.

4. CONCLUSIONS

Decomposition of CCl_4 was investigated in an RF inductively coupled thermal plasma reactor in argon atmosphere. The outlet gas mixture was cooled to room temperature, and was subsequently analyzed by GC-MS. The kinetics of CCl_4 decomposition at the actual experimental conditions was modeled in the temperature range from 300 to 7000 K. The created reaction mechanism contained 34 irreversible reaction steps of 12 species. Kinetic calculations provided concentration-time profiles for each species. The total carbon tetrachloride feed was decomposed within 5×10^{-5} s. However, it was partly recombined from the decomposition products. Our calculations predicted a 70% net conversion of CCl_4, which was close to the experimentally determined value of 60%. The kinetic mechanism was analyzed in two ways. Analysis of the fluxes of C- and Cl-atoms revealed the change of inter-conversion rates among species during the reaction. Importance of reaction steps was investigated by rate-of-production analysis. It revealed the significant change of the importance of reaction steps with reaction time. Only five reaction steps of the total 34 were found to be unimportant at any reaction time.

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