ORIGINAL ARTICLE

Modelling of Carbon Tetrachloride Decomposition in Oxidative RF Thermal Plasma

Tamás Kovács · Tamás Turányi · Katalin Főglein · János Szépvölgyi

Abstract   Decomposition of carbon tetrachloride in a RF thermal plasma reactor was investigated in oxygen–argon atmosphere. The net conversion of CCl_4 and the main products of decomposition were determined by GC–MS (Gas Chromatographic Mass Spectroscopy) analysis of the exhaust gas. Temperature and flow profiles had been determined in computer simulations and were used for concentration calculations. Concentration profiles of the species along the axis of the reactor were calculated using a newly developed chemical kinetic mechanism, containing 34 species and 134 irreversible reaction steps. Simulations showed that all carbon tetrachloride decomposed within a few microseconds. However, CCl_4 was partly recombined from its decomposition products. Calculations predicted 97.9% net conversion of carbon tetrachloride, which was close to the experimentally determined value of 92.5%. This means that in RF thermal plasma reactor much less CCl_4 was reconstructed in oxidative environment than using an oxygen-free mixture, where the net conversion had been determined to be 61%. The kinetic mechanism could be reduced to 55 irreversible reaction steps of 26 species, while the simulated concentrations of the important species were within 0.1% identical compared to that of the complete mechanism.

Keywords   Carbon tetrachloride · Oxygen · Thermal plasma · Decomposition · Modelling

1. Introduction

Halogenated hydrocarbons had been frequently used solvents in industrial areas because of their advantageous properties like being non-toxic and cheap. However, their chemical stability causes several environmental problems like global warming or stratospheric ozone depletion [1]. Having this fact realized—only in the last decades—, international treaties

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banned their applications. On the other hand, large quantities are still being stored in many countries waiting for a safe decomposition technology. According to previous studies, there are only few incineration techniques, which are efficient enough and not generating dangerous products in large quantities. Decomposition in plasma offers a safe and environmental friendly technology. In the last few years, extensive experimental work has been done on both thermal and cold plasmas [2, 3], however, only few papers are available on modelling related to such systems [4, 5, 6].

2. Description of the experimental conditions and the kinetic model

Főglein et al. [4] investigated the decomposition of carbon tetrachloride in an inductively coupled, RF thermal plasma reactor. The reactor had a length of 150 mm, a diameter of 26 mm and operated with a specific energy of 2.1 kW. Argon was used both as the plasma gas (8 dm^3 min^{-1} (STP)) and the sheath gas (21 dm^3 min^{-1} (STP)). Atmospheric pressure was maintained in the whole system.

The inlet gas mixture consisted of 3.50 m/m% CCl_4, 0.57 m/m% O_2 and 95.93 m/m% Ar (m/m% denotes mass percentage). Re-formation of CCl_4 and the main decomposition products were determined from the GC–MS (Gas Chromatographic Mass Spectroscopy) analysis of the exhaust gas, while a FT–IR technique was used for the calibration. The carrier gas containing the model compound was sampled by an IR cell of KBr windows on its ends. The exhaust gas was also sampled by this cell. The FTIR measurements were performed by a Perkin–Elmer 1750 FT–IR Spectrometer with an MCT detector. For quantitative evaluation, calibration curves of relevant materials were determined in particular concentration ranges.

$CCl_4/O_2/Ar$ experiments were carried out at 0.022 kWh·g^{-1} specific energy, while CCl_4/Ar experiments (0.93 m/m% CCl_4, 99.07 m/m% Ar) were done at several specific energies in the range 0.022 kWh g^{-1} to 0.089 kWh g^{-1}. Table 1 contains the experimentally measured re-formation ratio of carbon tetrachloride as the function of specific energy. It is clear that the net conversion of carbon tetrachloride is higher in oxidative environment: 39% of the initial CCl_4 was re-formed in the CCl_4/Ar mixture and only 7.5% in $CCl_4/O_2/Ar$ mixture, using the same specific energy. Net conversion of carbon tetrachloride in the CCl_4/Ar system increased with the specific energy and only 10% was re-formed at 0.089 kWh g^{-1}. In the case of $CCl_4/O_2/Ar$ mixture increasing the specific energy, the concentration of CO and Cl_2 in the exhaust gas also increased [4]. Even this increased net conversion is lower than the one obtained in oxidative environment, showing the importance of such systems. In the computer simulations reported here all experimental parameters are in agreement with oxygen–argon atmosphere thermal plasma reactor studies of Főglein et al. [4].

Cylindrically symmetric, 2D temperature and flow velocity profiles within the plasma reactor were used in our simulations, based on the 2D plasma model of Proulx and Bilodeau [5]. In [6] the methods, which could be used to calculate the temperature and flow velocity

Table 1 The experimentally measured re-formation ratio of carbon tetrachloride as the function of specific energy

System	Specific energy/kW g^{-1}	CCl_4 re-formation/%
CCl_4/Ar	0.089	10.4
CCl_4/Ar	0.072	17.3
CCl_4/Ar	0.061	22.9
CCl_4/Ar	0.022	39.4
$CCl_4/O_2/Ar$	0.022	7.5

profiles, were also discussed. The same profiles had been used in our previous study [6] and the temperature profiles of the reactor had been reported there. Using these temperature and flow velocity profiles, the temperature of the gas phase as a function of reaction time was determined along the axis of the reactor (see Fig. 1 and Table 2). The linear gas velocity in the centreline of the reactor varied from 30 to 60 cm s^{-1}. Diffusion could be neglected and spatially homogeneous plug-flow simulations were carried out with the SENKIN code [7] of the CHEMKIN-II gas kinetics simulation program package [8].

A detailed reaction mechanism was constructed for describing the decomposition of CCl$_4$ in the presence of oxygen and argon gases at high temperature. This reaction mechanism contains 26 species and 134 irreversible reactions and it is available from the Web [9] and in Appendix A. The thermodynamic data for the species and the kinetic parameters of the reactions were obtained from the Burcat's Thermodynamic Database [10] and the NIST Chemical Kinetics Database [11], respectively. Temperature dependence of the rate parameters was described by an extended Arrhenius expression in the form of $k = BT^n \exp(-C/RT)$. Arrhenius parameters were not found for some reaction steps and for these reactions the Arrhenius parameters were estimated from the rate parameters of analogous reactions or from other steps, containing similar species. Reference to the origin of the rate parameters is given in the comments to the mechanism [9]. For the reverse reaction steps, the rate parameters were calculated in accordance with the principle of detailed balancing using the
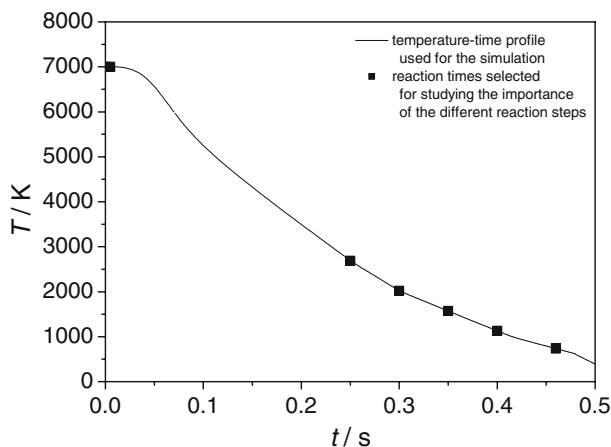

Fig. 1 The estimated temperature–time profile along the axis of the reactor

Table 2 Reaction times selected for the investigation of the importance of the reactions steps

No.	t /s	T / K
1.	5.00×10^{-8}	7000
2.	5.00×10^{-7}	7000
3.	5.00×10^{-6}	7000
4.	5.00×10^{-4}	7000
5.	2.50×10^{-2}	2686
6.	3.00×10^{-2}	2020
7.	3.50×10^{-2}	1570
8.	4.00×10^{-2}	1128
9.	4.65×10^{-2}	704

kinetic parameters of the forward reaction steps and the equilibrium constant determined from the thermodynamic data using code MECHMOD [12]. The mechanism contains thermal reactions only, and no ionic species are present. This is a reasonable approximation, because at atmospheric pressure the concentrations of ionic species and electrons are low, therefore the rates of ionic reactions are smaller than that of non-ionic ones. On the other hand, the rate constants of ionic and electron impact reactions are usually much smaller compared to non-ionic ones [6, 13].

3. Results of simulations

Up to now, thermal plasma decomposition of CCl_4 in oxidative environment had been modelled only by thermodynamic calculations[4]. In our previous study for the plasma decomposition of CCl_4/Ar mixtures [6], it had been shown that below 2000 K the chemical reactions are relatively slow and the concentrations determined by a kinetic model are not close to the thermodynamic equilibrium values, therefore kinetic and thermodynamic models give different results. To check if the same is true for the oxidative environment, kinetic and thermodynamic simulations for the $CCl_4/O_2/Ar$ mixture are compared over the temperature range 1000–7000 K.

Above 2000 K, the two methods gave identical results, similarly to the CCl_4/Ar case [6]. However, below about 2000 K the results obtained by the kinetic and the thermodynamic models are different. Therefore, chemical kinetic simulations based on detailed mechanisms are vital for a realistic simulation of the low temperature zone of plasma reactors, where recombination reactions take place.

Using the newly developed reaction mechanism, mass fraction profiles as a function of reaction time were calculated for all species. The basic feature of this incineration reaction is that carbon tetrachloride is almost completely decomposed within a few milliseconds (see Fig. 2a). However, after 4×10^{-3} s (approximately at 6550 K) CCl_4 started to recombine with a rapid rate and after 0.04 s (1130 K) its mass fraction was already 7.75×10^{-3}. The initial value was mass fraction 0.350, which means that only 2.1% of carbon tetrachloride was reformed. This result should be compared to the 39% reformation ratio obtained for CCl_4/Ar system, which means that the CCl_4 reformation is clearly lower in oxidative environment.

The most important and also the most hazardous products are CO, Cl_2, $COCl_2$ and the reformed CCl_4. Concentration–time profiles of these species are shown in Fig. 2a–d. Concentration of CO increases sharply at the beginning of the reaction when temperature is still 7000 K, and then CO reaches a constant mass fraction of 8×10^{-4}. $COCl_2$ appears as a product after 0.03 s when the temperature is 2000 K. After a peak at 0.038 s its concentration is reaching a steady-state value of mass fraction of 2.7×10^{-6}. Cl_2 has a much larger concentration in the fume gas (mass fraction of 8.3×10^{-2}). Its presence is not significant below 0.025 s (2700 K), but then the mass fraction of Cl_2 rises and reaches a plateau after 0.038 s (1300 K). Comparing the $COCl_2$ and Cl_2 concentration curves, the strong coupling between these two species is obvious. Rapid decrease of the mass fractions of Cl and COCl occurs after 0.03 s as it can be seen in Fig. 2e and f. The Cl concentration increases rapidly in the first 0.001 s (till 7000 K) where Cl is mainly formed from CCl_4 and its fragments, CCl_3, CCl_2 and CCl. Therefore, it is not surprising that during this period CCl_4 is simultaneously decomposed in a process, which is as rapid as the Cl formation. Then, Cl has a steady-state concentration and after 0.02 s conversion to Cl_2 occurs.

It is important to study the concentration evolution of C2-molecules such as C_2Cl_2, C_2Cl_4 and C_2Cl_6 (Fig. 3a–b). Below 0.02 s (above 3350 K), these products are not present in signifi-

Fig. 2 (**a–f**) Concentration profiles of the most important products containing one carbon-atom (CCl_4, $COCl_2$, CO, Cl_2) and of two of the most important intermediates, Cl and COCl
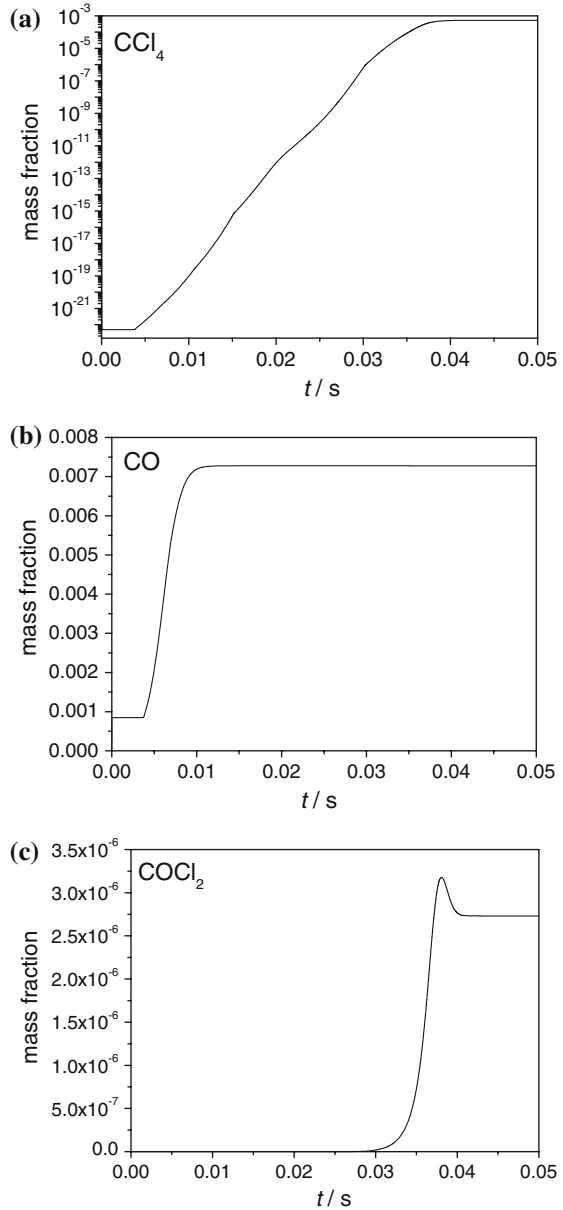
cant quantity, which is due to their rapid consumption rate at high temperature. After 0.02 s C_2Cl_2 is formed in rapid process and its mass fraction increases until 0.024 s when Cl_2 formation also starts to consume the Cl-atoms. Hence, C_2Cl_2 reaches a steady-state concentration, until 0.035 s (1570 K). Then, C_2Cl_2 is transformed to C_2Cl_4, also producing C_2Cl_6 in a four orders of magnitude smaller quantity.

Fig. 2 continued

(d) Cl_2

(e) Cl

(f) COCl
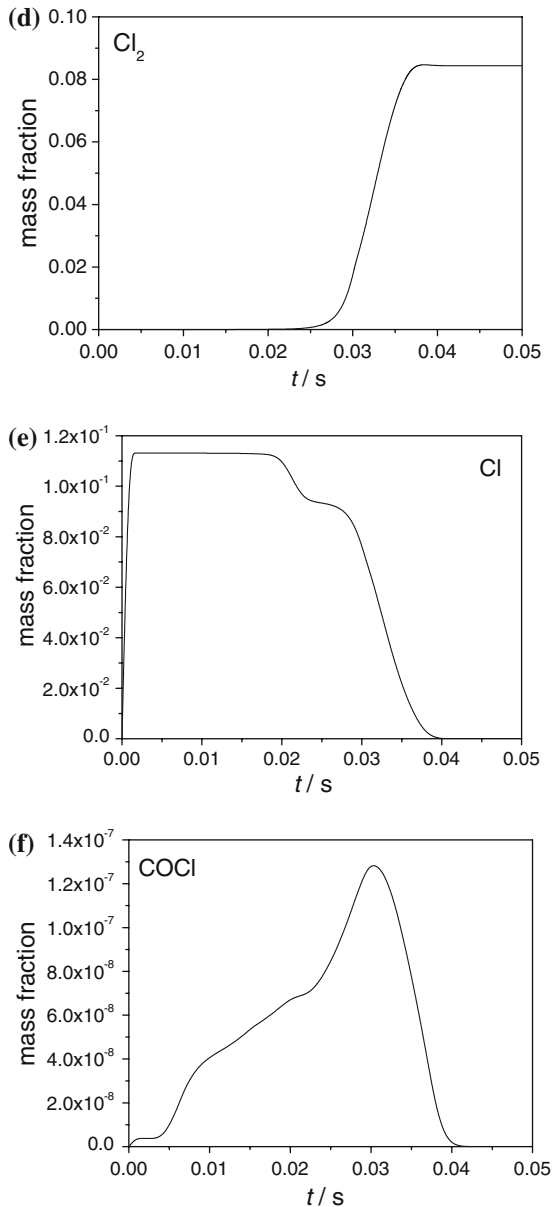
Note that according to the simulations, CO_2 is not an important species in this process and its mass fraction is never larger than 1.75×10^{-8}. On the contrary, CO has relatively large concentration at the end of the reaction (a mass fraction of 8×10^{-4} at 0.05 s).

Mass fractions of reactive radicals like C_2Cl_3 or C_2Cl_5 are smaller than that of the molecules above. The one carbon containing CCl_x radicals have a significant role at mid temperatures. Figure 4 shows that the concentration of each CCl_x radical has a peak, but at different temperature. The O-atoms, formed from O_2 molecules, play an important role in the

oxidation steps of CCl_4 fragments. The concentration profile of O-atom is seen in Fig. 5. If the temperature is above 3000 K (up to 0.20 s), Cl radical has almost steady-state concentration (Fig. 2e). Also, there is a plateau in the C concentration profile (Fig. 3c) between 0.005 and 0.008 s. On the other hand, almost all O atoms are consumed till 0.01 s.

Cl_2O is the most stable species in the Cl_2O–$OClO$–$ClOO$ series (see Fig. 6), which is due to their molecular structure (i.e. $ClOO$ is peroxide). Molecules Cl_2O_2 and CCl_3O_2 never reach high concentration, either, which can be explained by their peroxy character.
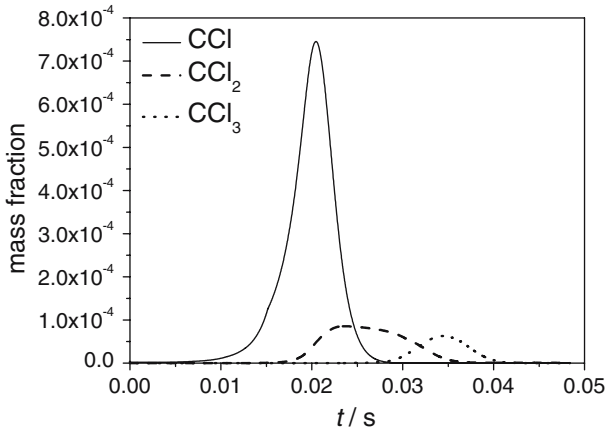
Fig. 4 Concentration profiles of direct fragments of carbon tetrachloride, CCl_3, CCl_2 and CCl
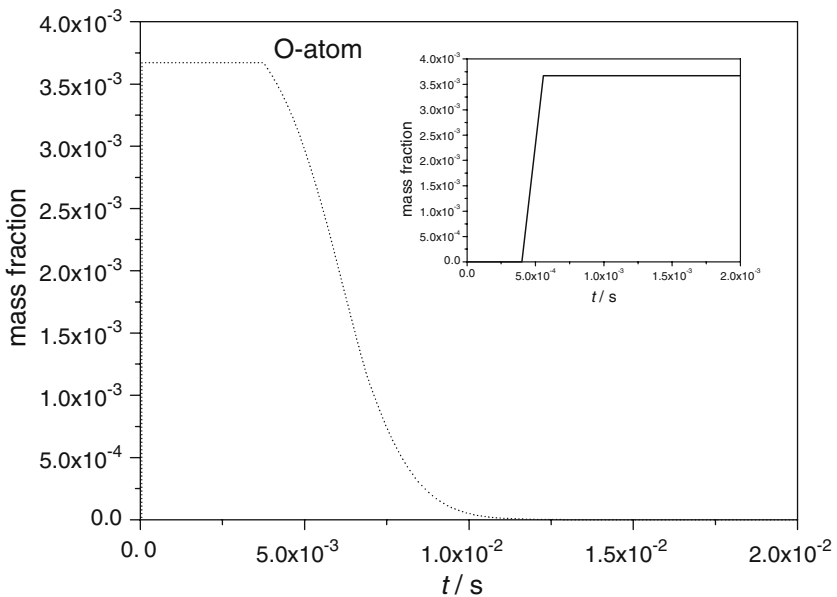
Fig. 5 Concentration profiles of O-atom

Note that the less diluted the initial $CCl_4/O_2/Ar$ mixture is, the smaller are the possibilities of the third order and thermal dissociation steps (where Ar plays an important role as collider). Therefore, by decreasing the argon concentration in the inlet mixture, the time of decomposition is most probably increases. It would mean that the more complex molecules like C_2Cl_4 or C_2Cl_6 may have chance to be stabilised and the exhaust gas mixture may be more rich in these molecules.
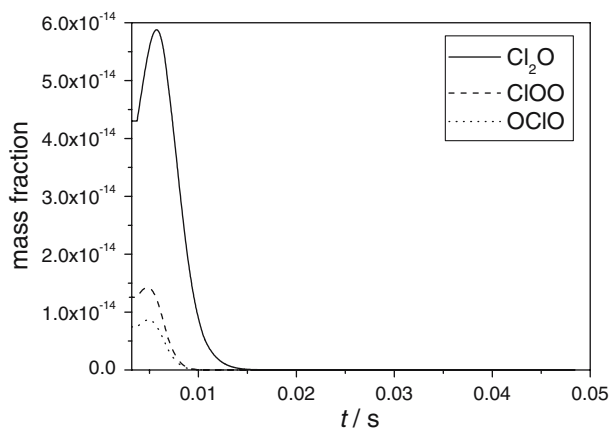
Fig. 6 Concentration profiles of three important three atom containing species, Cl_2O, ClOO and OClO

4. Analysis of the atom fluxes and the importance of reactions

Based on the shape of the concentration profiles, reaction times corresponding to significant changes of the mass fractions of one or more species were selected for further kinetic analysis. Fluxes of C-, Cl- and O-atoms were calculated by the KINALC [14] code. 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 [15]. Element fluxes were calculated at reaction times given in Table 2, too but the results were plotted only (see Fig. 7a–c) at times 5.0×10^{-7}, 5.0×10^{-6}, 0.025 and 0.037 s. Widths of the arrows are proportional to the extent of the atom fluxes. A dotted arrow means that the corresponding flux is one order of magnitude smaller than the flux represented by the thinnest solid arrow.

At the beginning of the reaction (at reaction time 5.0×10^{-7} s) when the temperature is 7000 K, inter-conversions $C \rightleftarrows CO$ and $CO \rightleftarrows CO_2$ are fast and in equilibrium. The C-atom fluxes show that thermal decomposition of CCl_4 occurs via reaction $CCl_4 \rightarrow CCl_3 + Cl$. This is also clear from the Cl fluxes, since one of the most important sources of Cl atoms is the thermal decomposition of CCl_4. However, there are other steps, which are also significant in Cl formation, like conversion $ClO \rightarrow Cl$. On the other hand, temperature is high enough for inter-conversions $ClO \rightleftarrows Cl$ and $CCl_3 \rightleftarrows C_2Cl_6$ being in equilibrium. It is seen from the O-atom fluxes that there is a very complicated coupling between the formation and consumption of different species at 5.0×10^{-7} s. Molecule O_2 is in equilibrium both with O-atom and ClO radical at each reaction time investigated. However, the most significant O_2 product is the O-atom, which oxidizes other species, forming mainly CO_2 and ClO at high temperature. Note that neither CO nor CO_2 are stable species at this temperature. There is a rapid formation and decomposition of ClOO at the beginning of the reaction, but its concentration remains low.

At the next examined reaction time (5.0×10^{-6} s, when the temperature is still 7000 K) there are much less steps to be considered. By this time CCl_4 has been totally consumed and therefore there is no possible channel for $COCl_2$ formation. The most important inter-conversions are still in equilibrium, like $C \rightleftarrows CO$, $CO \rightleftarrows CO_2$ and $CO \rightleftarrows COCl$. Inter-conversion $ClO \rightleftarrows Cl$ is still as dominant as at the beginning, however, COCl formation is less significant and $COCl_2$ is not a source for COCl any longer. At this time, no

(a) **C-atom fluxes**

$t = 5.00\times10^{-7}$ s	$T= 7000$ K

$t = 5.00\times10^{-6}$ s	$T= 7000$ K

$t = 2.50\times10^{-2}$ s	$T= 2687$ K

$t = 3.70\times10^{-2}$ s	$T= 1394$ K

(b) **Cl-atom fluxes**

$t = 5.00\times10^{-7}$ s	$T= 7000$ K

$t = 5.00\times10^{-6}$ s	$T= 7000$ K

$t = 2.50\times10^{-2}$ s	$T= 2687$ K

$t = 3.70\times10^{-2}$ s	$T= 1394$ K
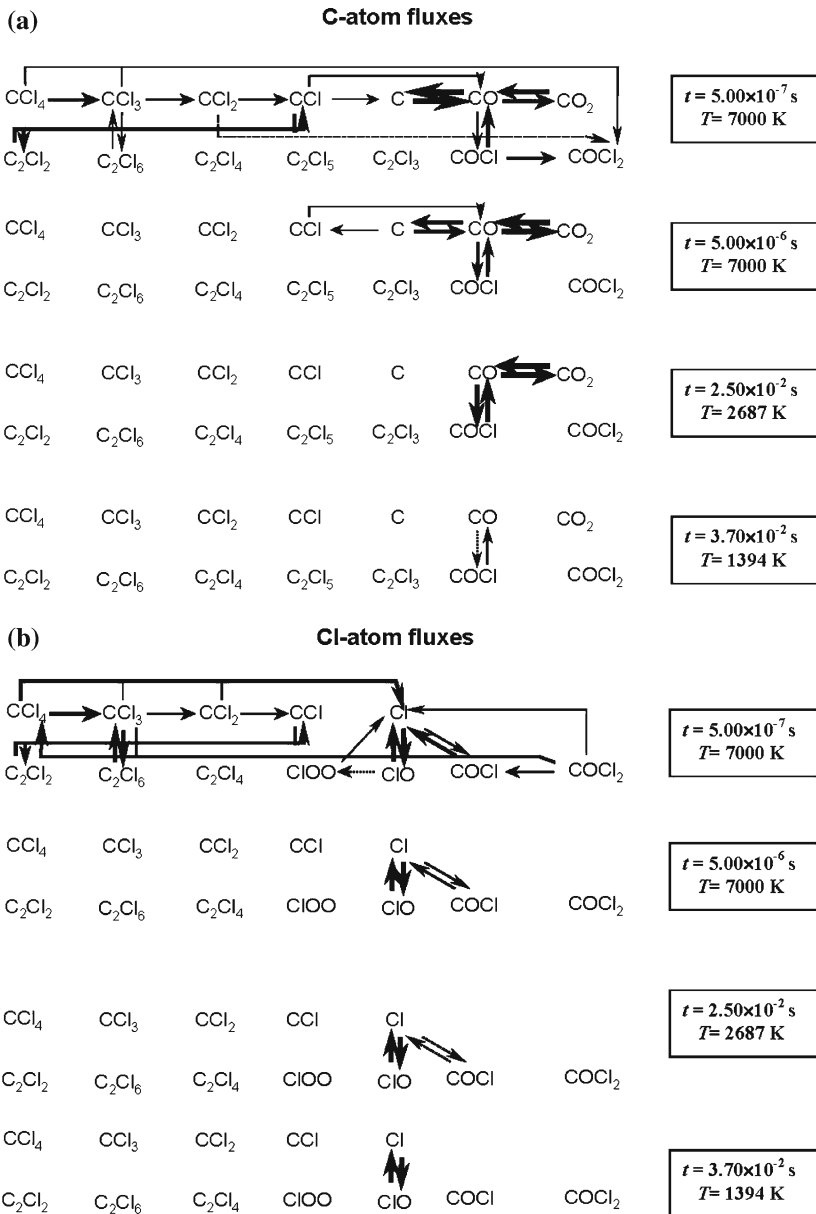
Fig. 7 **(a–c)** Fluxes of C-, Cl- and O-atoms

phosgene and ClOO must be considered because of the lack of their sources. However, apart from this, the scheme of O-atom fluxes is still complicated because O_2 is in excess, therefore most inter-conversions that involve O_2 are still significant. After 0.025 s, the temperature is much lower (2687 K), and all inter-conversions of CO, CO_2, COCl, Cl, ClO, O_2 and O are in equilibrium. O_2 is still in excess therefore, $O_2 \rightleftarrows O$ equilibrium can take place. The only source of ClO is Cl. However, temperature is low enough for the rapid Cl $\rightarrow$ Cl_2 conversion.

(c) **O-atom fluxes**
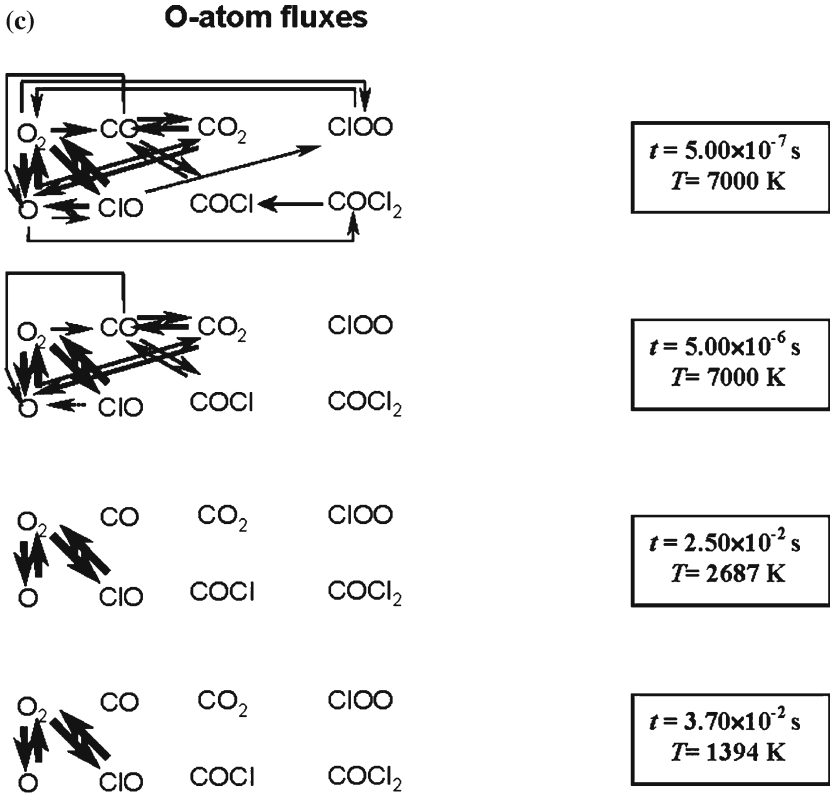
Fig. 7 continued

Further decrease in temperature initiates further channels for the production of stable molecules. After 0.037 s, temperature is only 1394 K and COCl is rapidly consumed, forming CO molecule. At this temperature COCl does not play a significant role in further steps except for CO formation, therefore its concentration is decreasing considerably. This low temperature also allows the formation of C_2-species in low quantities. It is important to mention that other species such as C_2Cl_2, C_2Cl_3 or OClO also play some role in the kinetics of the decomposition. However, the rates of their reactions are much lower than those of the other reaction steps shown in Fig. 7a–c. Therefore, the corresponding fluxes were not plotted. There are no significant changes in the fluxes and in the concentrations after 0.04 s below 1100 K.

KINALC [14] was used to determine also the most important reaction steps. In general, a reaction can be regarded as an important one, if its elimination results in great changes in the simulated concentration values [16]. In this study, the importance of reactions was examined by the principle component analysis of matrix **F** (method PCAF) [16, 17, 18]. Matrix **F** contains the partial derivatives of the production rates of species with respect to the rate parameters.

The normalized Jacobian was used to determine the kinetic connections among the species i.e. the effectiveness of small changes in the concentration of each species on the rates of production rates of a group of species. Species CCl_4, Cl_2, CO and CO_2 were defined as the important ones, giving the initial group. Then, the most closely connected species were added to this group and the strengths of connections of each species to this group of species

were recalculated. After a few iterations (usually 5–6) a large gap appeared in the list of the strengths of connections. The species below the gap were not necessary ones in a mechanism that describes the kinetic behaviour of the important species. It was concluded that 8 species, namely ClOO, Cl_2O_2, CCl_3O_2, CCl_3O, OClO, Cl_2O, C_2Cl_5, C_2Cl_6 can be eliminated from the mechanism. After eliminating the reactions of these species from the 134-step full mechanism, a 64-step reduced mechanism was obtained. Then, the importance of reactions was examined by PCAF at the nine time steps given in Table 2, where significant changes were identified in the concentration profiles. Nine more reactions, mainly the reactions of CCl_4 fragments and of CO, appeared to be unimportant in any reaction time, therefore the finally reduced mechanism contains only 55 steps. The final reduced mechanism and the list of important reactions at these reaction times are available from the Web.

At temperatures close to 7000 K, the dominating steps are the thermal decomposition reactions like $CCl_4 + Ar \rightarrow CCl_3 + Cl + Ar$ or $C_2Cl_2 + Ar \rightarrow 2 CCl + Ar$. At lower temperatures, the backward reactions like $CCl_3 + Cl + Ar \rightarrow CCl_4 + Ar$ compete with forward steps and become also important. Note that six reactions ($C + Cl + Ar \rightarrow CCl + Ar$, $O_2 + Ar \rightarrow 2O + Ar$, $CO + O \rightarrow CO_2$, $COCl_2 + Cl \rightarrow CCl_3 + O$, $CCl + O \rightarrow C + ClO$ and $CO + Cl \rightarrow CCl + O$) in this reduced mechanism are important only in a short time interval, however the elimination of them gave significant deviation from the concentrations obtained by the full mechanism.

Only one CO_2 forming reaction, $CO + O \rightarrow CO_2$ is significant at each reaction time while the other CO_2 forming step, $CO + O_2 \rightarrow CO_2 + O$ is not important at all. On the other hand, there are three CO forming reactions, which seem to be important at least in two time points, namely $C + O \rightarrow CO$, $CO_2 \rightarrow CO + O$, $C + O_2 \rightarrow CO + O$. Most CO formation steps are important only at high temperatures and only one of them, $CO_2 \rightarrow CO + O$, is important almost in each time point.

Note that there are 21 important reactions at the beginning at 7000 K but there are already 24 ones at 700 K [9]. On the other hand, there are only nine reactions that are important in each reaction time investigated. It is also seen that the importance of reactions is strongly related to the atom fluxes, i.e. species which take place in the most important reactions do have significant atom fluxes and that steps generating radicals like C, Cl or O slow down with decreasing temperature. Reformation of CCl_4 becomes significant quite early, after 0.004 s when the temperature is still around 5200 K.

It is important to note that here, in the case of oxidative environment the mechanism could be reduced much more significantly than in the case of CCl_4/Ar mixture. In the CCl_4/Ar system only five reactions could be eliminated from the 34-step long full mechanism, while here the 134-step long full mechanism could be reduced to a much smaller, 55-step long one. Note that 21, only CCl_x ($x=0$–4) containing steps remained in the 55-step long reduced mechanism. This means that CCl_x only reactions seem to be more important than the reactions of oxygen containing species. However, the reduced CCl_4/Ar model contained 29 steps while here less, namely 21 CCl_x only steps remained after the reduction. This is because the C_2Cl_5 and C_2Cl_6 species are unimportant in the CCl_4/O_2/Ar model, therefore their reactions could be eliminated.

5. Conclusions

Decomposition of carbon tetrachloride was investigated in an RF inductively coupled thermal plasma reactor at oxidative conditions. The exhaust gas mixture was cooled to room temperature, and was subsequently analyzed by GC–MS. The kinetics of CCl_4 decomposition at
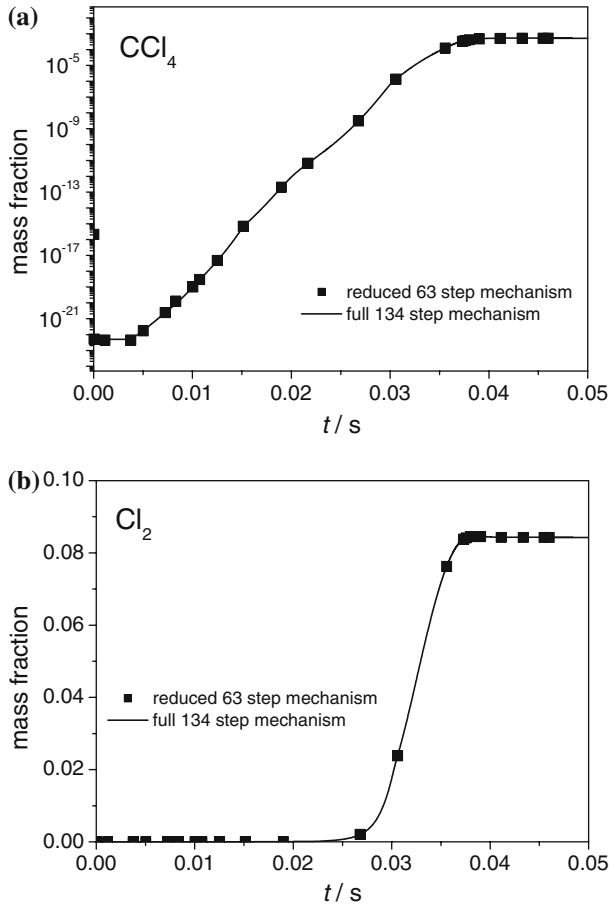
Fig. 8 (**a–d**) Comparison of the concentrations of important species obtained with the full and the reduced mechanisms

the experimental conditions was modelled in the temperature range from 7000 to 600 K. A detailed reaction mechanism was created that contains 134 irreversible reaction steps of 26 species. Kinetic calculations provided mass fraction–time profiles for each species based on simulated flow velocity and temperature profiles of the reactor. CCl_4 was totally decomposed within a few milliseconds and later it was partly recombined from the decomposition products at lower temperatures. Our simulations predicted 97.9% net conversion of CCl_4, which is close to the experimentally determined value of 92.5%. This can be considered a very good agreement, since the model described the processes in the centreline of the reactor only.

Kinetic analysis was carried out by investigating the fluxes of C-, Cl- and O-atoms. Flux analysis revealed the change of inter-conversion rates among species during the process. Redundant species in the detailed mechanism were identified via the analysis of the Jacobian [17]. Only 26 species are needed to describe quantitatively the concentration changes of CCl_4, Cl_2, CO and CO_2. Using the PCAF method [16, 18], the kinetic mechanism could be reduced to 55 irreversible reaction steps, while the simulated concentration profiles of the important species were within 0.1% identical compared to that of the complete mechanism.
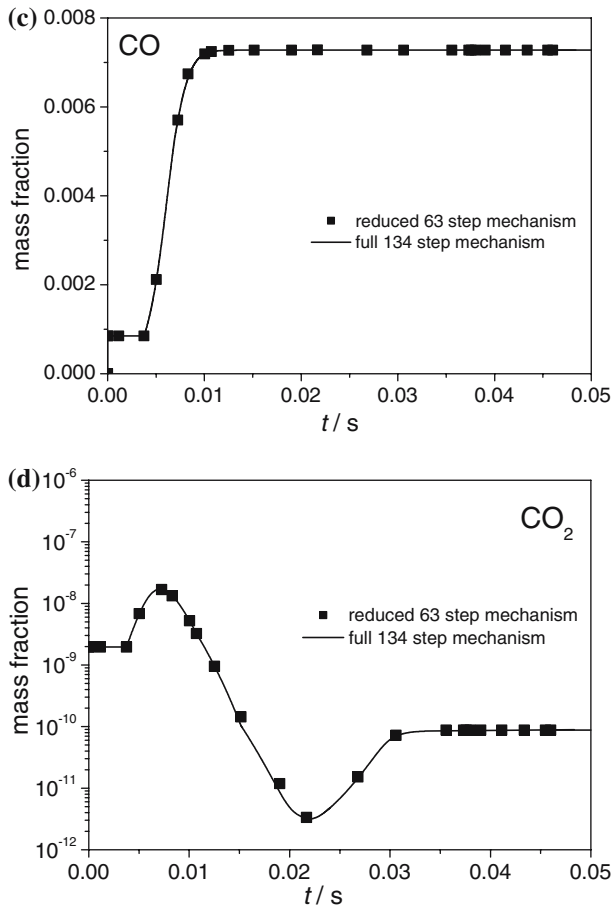
Fig. 8 continued

Appendix A

Appendix A.1. CCl_4/O_2 reaction mechanism and results of mechanism reduction

REACTIONS	MOLES		kJ/mole
1			
CCL4+AR => CCL3+CL+AR	8.326E+54	−10.6000	313.00
[19]			
2 R			
CCL3+CL+AR => CCL4+AR	1.709E+47	−9.1210	20.24
MECHMOD			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
3			
CCL3+AR => CCL2+CL+AR adopted from CF3+AR => CF2+F+AR, [20]	1.571E+49	−9.0400	386.00
4 R			
CCL2+CL+AR => CCL3+AR MECHMOD	8.630E+43	−8.0758	90.05
5			
CCL2+AR => CCL+CL+AR [21]	5.400E+14	.0000	62.53
6 R			
CCL+CL+AR => CCL2+AR MECHMOD	1.908E+10	1.2026	−99.57
7			
CCL+CL => C+CL2 [22]	8.490E+13	.0000	103.00
8 R			
C+CL2 => CCL+CL MECHMOD	3.384E+16	−.5484	21.99
9			
CCL+AR => C+CL+AR adopted from CH+M => C+H+M, [23]	1.900E+14	.0000	280.00
10 R			
C+CL+AR => CCL+AR MECHMOD	9.945E+11	.5465	−59.32
11			
2CCL => CCL2+C adopted from CCL+CL => C+CL2 (reaction 7)	8.490E+13	.0000	103.00
12 R			
CCL2+C => 2CCL MECHMOD	1.025E+17	−.6561	146.24
13			
CCL4+CL => CCL3+CL2 [24]	5.750E+13	.0000	64.85
14 R			
CCL3+CL2 => CCL4+CL MECHMOD	8.988E+10	.3842	30.41
15			
CCL4+C => CCL3+CCL [25]	9.040E+12	.0000	.00
16 R			
CCL3+CCL => CCL4+C MECHMOD	3.545E+07	.9325	46.57

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
17			
C2CL5 => C2CL4+CL	1.120E+16	.0000	62.36
[24]			
18 R			
C2CL4+CL => C2CL5	3.824E+13	.7215	−.61
MECHMOD			
19			
C2CL5+CL => C2CL4+CL2	2.450E+13	.0000	.00
[24]			
20 R			
C2CL4+CL2 => C2CL5+CL	6.370E+15	−.3733	195.35
MECHMOD			
21			
CL2+AR => 2CL+AR	2.320E+13	.0000	196.00
1981BAU/DUXSuppl, NIST			
22 R			
2CL+AR => CL2+AR	3.046E+08	1.0948	−62.32
MECHMOD			
23			
C2CL2 => 2CCL adopted from C2CL2 => C2+2CL,	9.290E+15	.0000	284.00
[21]			
24 R			
2CCL => C2CL2	1.099E+06	1.8623	−510.89
MECHMOD			
25			
C2CL4 => C2CL3+CL adopted from C2CL5 => C2CL4+CL (reaction 17)	1.120E+16	.0000	62.36
26 R			
C2CL3+CL => C2CL4	4.552E+08	1.3804	−264.43
MECHMOD			
27			
C2CL3 => C2CL2+CL adopted from C2CL5 => C2CL4+CL (reaction 17)	1.120E+16	.0000	62.36
28 R			
C2CL2+CL => C2CL3	6.025E+11	1.0269	−83.00
MECHMOD			
29			
C2CL6+CL => C2CL5+CL2	1.320E+14	.0000	72.34
[24]			
30 R			
C2CL5+CL2 => C2CL6+CL	7.673E+07	1.1457	17.51
MECHMOD			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
31			
C2CL6+CCL3 => CCL4+C2CL5	8.130E+11	.0000	59.03
[24]			
32 R			
CCL4+C2CL5 => C2CL6+CCL3	3.023E+08	.7615	38.63
MECHMOD			
33			
C2CL6 => 2CCL3	3.980E+17	.0000	287.00
[24]			
34 R			
2CCL3 => C2CL6	4.731E+03	2.8981	.88
MECHMOD			
35			
C2CL6 => C2CL5+CL	1.000E+16	.0000	289.00
[26]			
36 R			
C2CL5+CL => C2CL6	7.633E+04	2.2405	−24.15
MECHMOD			
37			
C2CL6 => C2CL4+CL2	5.010E+13	.0000	226.00
[26]			
38 R			
C2CL4+CL2 => C2CL6	9.942E+04	1.8672	108.20
MECHMOD			
39			
2CCL2+AR => C2CL4+AR	5.700E+15	.0000	−24.86
[21]			
40 R			
C2CL4+AR => 2CCL2+AR	4.140E+26	−1.8644	477.04
MECHMOD			
41			
O2+AR => 2O+AR	1.200E+14	.0000	451.00
[27]			
42 R			
2O+AR => O2+AR	4.128E+09	.8312	−57.91
MECHMOD			
43			
CL2+O => CL+CLO	4.460E+12	.0000	13.72
[28]			
44 R			
CL+CLO => CL2+O	5.225E+09	.7208	4.29
MECHMOD			
45			
CCL4+O => CCL3+CLO	3.000E+11	.0000	18.29
[29]			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
46 R			
CCL3+CLO => CCL4+O	5.494E+05	1.1050	−25.58
MECHMOD			
47			
CCL3+O => CCL2+CLO	1.400E+13	.0000	1.65
[30]			
48 R			
CCL2+CLO => CCL3+O	6.862E+09	.5902	−45.42
MECHMOD			
49			
CCL2+O => CCL+CLO adopted from CF2+O	5.000E+13	.0000	.00
=> CF+OF,			
[31]			
50 R			
CCL+CLO => CCL2+O	1.934E+10	.8286	−133.68
MECHMOD			
51			
CLO+AR => CL+O+AR adopted from COCL	2.470E+14	.0000	24.61
=> CO+CL (reaction 91)			
52 R			
CL+O+AR => CLO+AR	2.701E+13	.3740	167.11
MECHMOD			
53			
C+O => CO	7.260E+13	.0000	.00
[31]			
54 R			
CO => C+O	2.540E+16	−.2386	1077.23
MECHMOD			
55			
CO+O => CO2	3.000E+14	.0000	12.55
[32]			
56 R			
CO2 => CO+O	1.316E+22	−1.4538	553.23
MECHMOD			
57			
C+O2 => CO+O	1.200E+14	.0000	16.71
[33]			
58 R			
CO+O => C+O2	2.407E+12	.5927	585.03
MECHMOD			
59			
CO+O2 => CO2+O	2.530E+12	.0000	200.00
[34]			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
60 R			
CO2+O => CO+O2	3.818E+15	−.6226	231.77
MECHMOD			
61			
C2CL6+O => C2CL5+CLO	1.320E+14	.0000	72.34
adopted from C2CL6+CL => C2CL5+CL2			
(reaction 29)			
62 R			
C2CL5+CLO => C2CL6+O	8.990E+04	1.8665	8.07
MECHMOD			
63			
C2CL5+O => C2CL4+CLO	2.450E+13	.0000	.00
adopted from C2CL5+CL => C2CL4+CL2			
(reaction 19)			
64 R			
C2CL4+CLO => C2CL5+O	7.463E+12	.3475	185.92
MECHMOD			
65			
C2CL4+O => COCL2+CCL2	1.900E−01	.0000	.00
[35]			
66 R			
COCL2+CCL2 => C2CL4+O	3.471E−06	.8810	217.68
MECHMOD			
67			
C2CL4+O => C2CL3+CLO	3.610E+10	.0000	.00
[36]			
68 R			
C2CL3+CLO => C2CL4+O	1.309E+05	1.0064	−77.90
MECHMOD			
69			
CCL2+O2 => COCL+CLO	1.810E+09	.0000	.00
[37]			
70 R			
COCL+CLO => CCL2+O2	1.076E+05	.8992	138.29
MECHMOD			
71			
CCL+O2 => CO+CLO	1.750E+12	.0000	.00
[37]			
72 R			
CO+CLO => CCL+O2	9.837E+09	.7651	477.88
MECHMOD			
73			
C2CL3+O => C2CL2+CLO	3.010E+13	.0000	.00
adopted from C2H3+O => C2H2+HO, [38]			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
74 R			
C2CL2+CLO => C2CL3+O	1.445E+11	.6529	103.53
MECHMOD			
75			
CCL4+O => COCL2+2CL	1.400E+13	.0000	1.65
adopted from CCL3+O => CCL2+CLO (reaction 47)			
76 R			
COCL2+2CL => CCL4+O	2.095E+06	1.4597	132.53
MECHMOD			
77			
CCL3+O => COCL2+CL	1.400E+13	.0000	1.65
adopted from CCL3+O => CCL2+CLO (reaction 47)			
78 R			
COCL2+CL => CCL3+O	1.021E+14	−.0192	425.28
MECHMOD			
79			
COCL2+CL => COCL+CL2	8.690E+12	.0000	96.45
[39]			
80 R			
COCL+CL2 => COCL2+CL	1.165E+10	.3305	33.50
MECHMOD			
81			
COCL2 => CCL2+O	1.450E+14	.0000	345.00
adopted from COCL2 => CO+CL2, [40]			
82 R			
CCL2+O => COCL2	1.093E+08	.9834	−374.59
MECHMOD			
83			
COCL2 => CO+CL2	1.450E+14	.0000	345.00
[40]			
84 R			
CO+CL2 => COCL2	6.606E+07	1.3991	239.07
MECHMOD			
85			
2COCL => COCL2+CO	1.070E+09	.5000	−5.78
adopted from 2COF => COF2+CO, [41]			
86 R			
COCL2+CO => 2COCL	2.064E+13	.1432	272.50
MECHMOD			
87			
CCL+O => C+CLO	8.320E+13	.0000	133.00
[42]			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
88 R			
C+CLO => CCL+O	3.886E+13	.1725	42.56
MECHMOD			
89			
CCL+O => CO+CL	6.000E+13	.0000	.00
[43]			
90 R			
CO+CL => CCL+O	1.099E+14	.3079	737.91
MECHMOD			
91			
COCL => CO+CL	2.470E+14	.0000	24.61
[44]			
92 R			
CO+CL => COCL	8.391E+10	1.0686	−18.37
MECHMOD			
93			
CL2O+CLO => O2+CL2+CL	6.500E+08	.0000	.00
[45]			
94 R			
O2+CL2+CL => CL2O+CLO	3.796E+09	−.1960	104.11
MECHMOD			
95			
CL2O+CLO => CL2+CLOO	2.600E+08	.0000	.00
[45]			
96 R			
CL2+CLOO => CL2O+CLO	7.976E+10	−.6611	77.03
MECHMOD			
97			
CL2O+O => 2CLO	1.630E+13	.0000	4.41
[44]			
98 R			
2CLO => CL2O+O	3.055E+10	.6080	87.95
MECHMOD			
99			
CL2O+CL => CL2+CLO	3.730E+13	.0000	−1.08
[44]			
100 R			
CL2+CLO => CL2O+CL	5.966E+13	−.1128	91.89
MECHMOD			
101			
CLOO+CL => CL2+O2	1.390E+14	.0000	.00
[46]			
102 R			
CL2+O2 => CLOO+CL	2.015E+17	−.6297	285.40
MECHMOD			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
103			
2CLO => O2+CL2	6.030E+11	.0000	13.22
[46]			
104 R			
O2+CL2 => 2CLO	1.677E+17	−1.1781	282.68
MECHMOD			
105			
CLOO+CL => 2CLO	7.230E+12	.0000	.00
[46]			
106 R			
2CLO => CLOO+CL	3.770E+10	.5483	15.94
MECHMOD			
107			
CLOO+O => O2+CLO	3.000E+13	.0000	.00
[45]			
108 R			
O2+CLO => CLOO+O	5.096E+13	.0911	275.97
MECHMOD			
109			
CLOO+AR => CL+O2+AR	1.690E+14	.0000	15.13
[47]			
110 R			
CL+O2+AR => CLOO+AR	3.217E+12	.4651	42.21
MECHMOD			
111			
CL2O2+CL => CL2+CLOO	6.030E+13	.0000	.00
[46]			
112 R			
CL2+CLOO => CL2O2+CL	3.911E+13	−.0460	140.16
MECHMOD			
113			
CL2O2+AR => 2CLO+AR	6.030E+17	.0000	66.52
[47]			
114 R			
2CLO+AR => CL2O2+AR	2.678E+10	1.5972	−35.70
MECHMOD			
115			
COCL2 => COCL+CL	5.710E+15	.0000	303.00
[40]			
116 R			
COCL+CL => COCL2	1.006E+08	1.4253	−18.26
MECHMOD			
117			
COCL+CL => CO+CL2	1.300E+15	.0000	13.89
1981BAU/DUXSuppl, NIST			

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
118 R CO+CL2 => COCL+CL MECHMOD	3.363E+16	−.0263	229.23
119 COCL+CL2O2 => COCL2+CLOO adopted from CL2O2+CL => CL2+CLOO (reaction 111)	6.030E+13	.0000	.00
120 R COCL2+CLOO => COCL+CL2O2 MECHMOD	2.916E+16	−.3765	203.10
121 CL+O2 => CLO+O 1981BAU/DUXSuppl, NIST	8.770E+14	.0000	.00
122 R CLO+O => CL+O2 MECHMOD	2.692E+12	.4572	−260.03
123 CCL3O2+CL => COCL2+CL2O [48]	1.260E+13	.0000	.00
124 R COCL2+CL2O => CCL3O2+CL MECHMOD	1.608E+09	.9453	265.25
125 OCLO+O => O2+CLO [46]	1.450E+12	.0000	7.98
126 R O2+CLO => OCLO+O MECHMOD	9.137E+10	.3241	242.91
127 CL+OCLO => 2CLO [49]	3.560E+13	.0000	.00
128 R 2CLO => CL+OCLO MECHMOD	6.886E+09	.7813	−25.10
129 CCL3+O2+AR => CCL3O2+AR [50]	4.680E+33	−6.4100	.00
130 R CCL3O2+AR => CCL3+O2+AR MECHMOD	3.907E+40	−7.8994	63.70
131 CCL3+CCL3O2 => 2CCL3O 1990RUS/SEE3277, NIST	6.030E+11	.0000	.00

Appendix A.1. continued

REACTIONS	MOLES		kJ/mole
132 R			
2CCL3O => CCL3+CCL3O2	2.007E+13	−.4961	108.07
MECHMOD			
133			
2CLO => O2+2CL	6.300E−01	.0000	.00
[51]			
134 R			
O2+2CL => 2CLO	2.300E+00	−.0832	11.14
MECHMOD			
END			

Reverse Arrhenius parameters of reactions denoted by "R" were calculated by program MECHMOD. Parameters A, n, and E were fitted at temperatures 2000.0 K, 4500.0 K, and 7000.0 K

Here MECHMOD code indicates that the Arrhenius parameters for the reverse reaction steps were calculated by the MECHMOD program and were based on the principle of the detailed balance.

Appendix A.2. Mechanism Reduction

Importance of reactions was examined at 9 time points.

1. 5.0E−8 7000 K
2. 5.0E−7 7000 K
3. 5.0E−6 7000 K
4. 5.0E−4 7000 K
5. 2.5E−2 2686 K
6. 3.0E−2 2020 K
7. 3.5E−2 1570 K
8. 4.0E−2 1128 K
9. 4.65E−2 704 K

Below, the importance of reactions is labelled with * reaction times

	S 123456789
1. CCL4+AR=>CCL3+CL+AR	* ** *****
2. CCL3+CL+AR=>CCL4+AR	* ****
3. CCL3+AR=>CCL2+CL+AR	* *******
4. CCL2+CL+AR=>CCL3+AR	* ******
5. CCL2+AR=>CCL+CL+AR	* ******
6. CCL+CL+AR=>CCL2+AR	* ***
7. CCL+CL=>C+CL2	* ********
8. C+CL2=>CCL+CL	* ********
9. CCL+AR=>C+CL+AR	* ****
10. C+CL+AR=>CCL+AR	* *
11. CCL4+CL=>CCL3+CL2	* **** *

12. CCL3+CL2=>CCL4+CL	* ** *
13. CL2+AR=>2CL+AR	* * ****
14. 2CL+AR=>CL2+AR	* ****
15. C2CL2=>2CCL	* *********
16. 2CCL=>C2CL2	* *********
17. C2CL4=>C2CL3+CL	* *********
18. C2CL3+CL=>C2CL4	* ******
19. C2CL3=>C2CL2+CL	* *********
20. C2CL2+CL=>C2CL3	* ******
21. 2CCL2+AR=>C2CL4+AR	* **
22. O2+AR=>2O+AR	* *
23. CL2+O=>CL+CLO	* ***
24. CL+CLO=>CL2+O	* *****
25. CCL3+O=>CCL2+CLO	* ***
26. CCL2+CLO=>CCL3+O	* * **
27. CCL2+O=>CCL+CLO	* *
28. CCL+CLO=>CCL2+O	* * *
29. CLO+AR=>CL+O+AR	* ** *
30. C+O=>CO	* **
31. CO=>C+O	* ****
32. CO+O=>CO2	* *********
33. CO2=>CO+O	* ******* **
34. C+O2=>CO+O	* ***
35. CO+O=>C+O2	* *
36. CCL4+O=>COCL2+2CL	* **
37. CCL3+O=>COCL2+CL	* ***
38. COCL2+CL=>CCL3+O	* *
39. COCL2=>CCL2+O	* * *****
40. CCL2+O=>COCL2	* * *****
41. CCL+O=>C+CLO	* *
42. C+CLO=>CCL+O	* **
43. CCL+O=>CO+CL	* **
44. CO+CL=>CCL+O	* *
45. COCL=>CO+CL	* *********
46 CO+CL=>COCL	* ********
47. CL2O+CLO=>O2+CL2+CL	* ******
48. O2+CL2+CL=>CL2O+CLO	* ****
49. O2+CL2=>2CLO	* ***
50. COCL2=>COCL+CL	* *********
51. COCL+CL=>COCL2	* *******
52. COCL+CL=>CO+CL2	* * *****
53. CO+CL2=>COCL+CL	* * ****
54. CL+O2=>CLO+O	* *********
55. CLO+O=>CL+O2	* *********

Results of the mechanism reduction:

Number of reactions in the original mechanism: 134
Number of the selected reactions: 55
Number of the eliminated reactions: 79

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