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High-temperature chemistry of HCl and Cl_2

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ABSTRACT

The high temperature chlorine chemistry was updated and the inhibition mechanisms involving HCl and Cl_2 were re-examined. The thermochemistry was obtained using the Active Thermochemical Tables (ATcT) approach, resulting in improved data for chlorine-containing species of interest. The HCl/Cl_2 chemistry discussed in the paper was based on reference and experimental measurements of rate constants available in the literature. By coupling the new HCl/Cl_2 subset with the Politecnico di Milano (POLIMI) syngas mechanism a kinetic mechanism consisting of 25 species and 102 reactions was obtained. The validation was carried out on selected experimental data from laminar flames, shock tubes and plug flow reactors. Systems containing Cl_2 showed high sensitivity to $Cl_2 + M \rightleftharpoons Cl + Cl + M$; the rate constant for this reaction has a significant uncertainty and there is a need for an accurate high-temperature determination. The importance of the chain propagating steps such as $Cl + H_2 \rightleftharpoons HCl + H$ and $Cl_2 + H \rightleftharpoons HCl + Cl$ competing with the branching reaction $H + O_2 \rightleftharpoons OH + O$ and the termination reaction $H + Cl + M \rightleftharpoons HCl + M$ is also pointed out by the kinetic analysis. Other relevant reactions in HCl containing systems are the chain propagation reactions $HCl + O \rightleftharpoons Cl + OH$, $HCl + OH \rightleftharpoons Cl + H_2O$ and $Cl + HO_2 \rightleftharpoons ClO + OH$, together with the termination reaction $Cl + HO_2 \rightleftharpoons HCl + O_2$. With the present thermochemistry and rate constants, reaction cycles involving HOCl and ClCO were found not to be important under the investigated conditions.

1. Introduction

The chlorine chemistry in combustion and gasification of solid fuels is a concern, partly due to the possibility of pollutant emissions and partly due to the corrosive potential of chlorine. In particular annual biomass and certain waste fractions may contain chlorine in significant quantities [1]. Chlorine is typically released during pyrolysis as chlorinated hydrocarbons (e.g., chloromethane, CH_3Cl), hydrogen chloride (HCl) or alkali chloride (mainly KCl). During combustion the chlorine will largely be oxidized and emitted as HCl. Hydrogen chloride is typically the desired chlorine containing product in combustion, because it can easily be removed from the flue gas by a scrubbing process. However, chlorine is known to participate also in dioxin/furan formation through mechanisms that may involve high-temperature gas phase reactions as well as low-temperature reactions catalyzed by fly ash [2–4].

The presence of chlorine may affect the overall combustion process as well as the fate of other pollutants [1]. Chlorine species is known to inhibit fuel oxidation [5–9], even though the effect is less pronounced than for other halogens such as bromine [10]. The content of chlorine in a fuel may also have an impact on NO_x-emissions [11] and on the formation of PAH and soot [12,13]. In addition, chlorine may affect the partitioning of trace metals such as Cd, Cu, Mn, Zn, Cr, As, Hg, and lead salts [14,15]. In particular the effect of chlorine on mercury speciation has received attention [16–18]. Other examples include interaction between chlorine and potassium in biomass combustion, leading to formation of aerosols and/or corrosive deposits [19–23].

A high chlorine content in a fuel may act to inhibit ignition [24], lower flame speeds [25], and facilitate flame quenching [26]. The presence of HCl [5,6,8] or chlorinated hydrocarbons [7,9,27] is also known to inhibit oxidation of CO to CO_2 under reactor conditions. The interaction of HCl with the O/H radical pool is quite complex, and even though the overall mechanism of inhibition is known [1,6], details are still under investigation. Presumably, the inhibition takes place through simple cycles, initiated by chain propagating steps such as

$$HCl + H \rightleftharpoons Cl + H_2 \qquad \text{(R2b)}$$

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$$HCl + OH \rightleftharpoons Cl + H_2O \tag{R4}$$

and completed by terminating reactions like

$$Cl + H + M \rightleftharpoons HCl + M \tag{R1}$$

$$Cl + HO_2 \rightleftharpoons HCl + O_2 \tag{R6}$$

As the Cl atom concentration builds up in the post flame region, reactions (R2) and (R4) may become partially equilibrated and even driven in the reverse direction. Under these conditions inhibition is significantly reduced [6]. The inhibiting cycles compete with a chain propagating cycle [28],

$$Cl + HO_2 \rightleftharpoons ClO + OH \tag{R7}$$

$$ClO + CO \rightleftharpoons Cl + CO_2 \tag{R48}$$

which corresponds to the overall reaction $CO + HO_2 \rightarrow CO_2 + OH$. The competition between these cycles determines whether the chlorine has an overall promoting or inhibiting effect on the fuel oxidation. The inhibition process is sensitive to the branching ratio of the $Cl + HO_2$ reaction, which is well established only at low temperatures [29].

Evaluations of the elementary reactions involved in chlorine chemistry at combustion conditions have been reported by Baulch et al. [30] and more recently by Senkan [31]. Kinetic modeling studies have mostly focused on chloromethane [9,25,32,33], but also studies of chlorine inhibition of CO oxidation in flow reactors [5] and in flames [34] have been reported.

Despite the considerable interest in high-temperature chlorine reactions, details of the chemistry remain uncertain. The thermodynamic properties of oxygenated chlorine species have been in question and most chlorine reactions have only been characterized experimentally at low temperatures, if at all. Furthermore, no reported chlorine reaction mechanisms have been validated over a wider range of conditions. The objective of the present work is to update our knowledge of the high-temperature chlorine chemistry, emphasizing reactions of HCl and Cl_2 deserving investigation or better assessment. The thermochemistry of the chlorine species is re-examined and the hydrogen/chlorine/oxygen reaction mechanism is updated. The resulting model is validated against selected experimental data from literature and used to analyze the effect of HCl and Cl_2 on laminar, premixed hydrogen and syngas flames.

2. Thermochemistry

The thermochemistry of the chlorine-containing species of interest, given in Table 1, was obtained using the Active Thermochemical Tables (ATcT) approach [35,36], which, in contrast to the traditional "sequential" approach, derives accurate, reliable, and internally consistent thermochemical values by analyzing and simultaneously solving [37–40] the underlying Thermochemical Network (TN). A TN is constructed from the available thermochemical interdependencies relevant to the targeted species, such as measured reaction enthalpies, bond dissociation energies, constants of equilibria, ionization energies, electron affinities, etc. [41,42]. One of the advantages of the ATcT TN is that it allows commingling of experimental and computational results, the latter typically obtained from state-of-the-art electronic structure methods. The most recent previous version of the ATcT TN [40], has been updated to accommodate, inter alia, the targeted chlorine-containing species. Overall, the current ATcT TN (ver. 1.122) [43] contains over 1180 chemical species of interest to combustion and atmospheric chemistry, interconnected by more than 19,000 determinations.

ATcT outputs, in form of tables of enthalpies of formation, heat capacities, entropies, and enthalpy increments, covering the range 298–6000 K, were fitted to 7-term polynomials using the NASA program of McBride and Gordon [44]. Table 1 lists the current ATcT thermochemistry for the chlorine-containing species of interest. The respective NASA polynomials are given in the Supplementary Material. Note that Table 1 lists the values as obtained directly from the current version of ATcT. The polynomials, which are subject to inherent fitting errors because of the 7-term limitation, produce very slightly different values.

3. Reaction mechanism

The chemical kinetic model used in the present study consists of a H_2/CO oxidation scheme together with a subset for the Cl/H/O system. The H_2/CO oxidation mechanism was adopted from the work by Frassoldati et al. [45] and by Cuoci et al. [46] and has been validated over a broad range of conditions. The complete mechanism is available in Chemkin format with thermo and transport properties on the CreckModeling web site (http://creckmodeling.chem.polimi.it), and also reported as Supplementary Material to this paper.

The chlorine subset of the reaction mechanism is listed in Table 2. The key steps in the H_2/Cl_2 system, i.e.,

$$H + Cl + M \rightleftharpoons HCl + M \tag{R1}$$

$$Cl + H_2 \rightleftharpoons HCl + H \tag{R2}$$

$$Cl + Cl + M \rightleftharpoons Cl_2 + M \tag{R9}$$

$$H + Cl_2 \rightleftharpoons HCl + Cl, \tag{R10}$$

are among the few chlorine reactions that have been characterized over a wider temperature range. The thermal dissociation of HCl (R1b) has been measured at high temperatures in shock tube studies [47,73–77]. The early work was evaluated by Baulch et al. [30] who made a recommendation for k_{1b} for the temperature range

Table 1
Thermodynamic properties for selected chlorine species. Units are kcal mol^{-1} and cal mol^{-1} K^{-1}.

Species	$H_{f,0}$	$H_{f,298}$	±	S_{298}	$C_{p,300}$	$C_{p,400}$	$C_{p,500}$	$C_{p,600}$	$C_{p,800}$	$C_{p,1000}$	$C_{p,1500}$	$C_{p,2000}$
HCl	–21.986	22.030	0.001	44.670	6.964	6.973	7.004	7.069	7.289	7.562	8.149	8.529
Cl_2	0.000	0.000	exact	53.317	8.122	8.436	8.620	8.735	8.870	8.949	9.073	9.194
Cl	28.590	28.992	0.000	39.482	5.223	5.370	5.436	5.445	5.389	5.314	5.175	5.101
ClO	24.169	24.311	0.008	53.800	8.243	8.436	8.587	8.699	8.847	8.941	9.094	9.217
HOCl	–17.655	–18.357	0.006	56.540	8.926	9.580	10.113	10.529	11.140	11.602	12.423	12.918
OClO	24.146	23.556	0.069	61.395	10.058	11.011	11.745	12.282	12.963	13.356	13.849	14.103
ClOO	24.814	24.552	0.086	65.759	11.329	11.811	12.206	12.527	12.979	13.256	13.589	13.723
ClCHO	–42.927	–43.693	0.217	61.919	10.707	12.067	13.210	14.155	15.591	16.599	18.052	18.746
ClCO	–5.242	–4.908	0.114	63.154	10.682	11.233	11.645	11.989	12.524	12.891	13.382	13.595
HOOCl	0.923	–0.339	0.231	64.070	12.694	14.033	14.975	15.658	16.589	17.227	18.242	18.805
ClOOCl	32.148	31.375	0.130	70.995	15.733	17.134	17.965	18.481	19.049	19.332	19.626	19.733