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Theoretical and kinetic modelling study of chloromethane (CH₃Cl) pyrolysis and oxidation.

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Abstract

This work presents a comprehensive kinetic modeling study of the pyrolysis and oxidation of chloromethane. Theoretical calculations were performed for the decomposition reaction $\text{CH}_3\text{Cl} + \text{M} = \text{CH}_3 + \text{Cl} + \text{M}$ and for a set of relevant H-abstraction reactions ($\text{CH}_3\text{Cl} + \text{R}$, $\text{R} = \text{Cl}, \text{H}, \text{OH}, \text{HO}_2, \text{O}_2, \text{O}, \dot{\text{C}}\text{H}_3, \dot{\text{C}}_2\text{H}_3, \dot{\text{C}}_2\text{H}_5$; $\text{CH}_4 + \text{Cl}$, $\text{C}_2\text{H}_6 + \text{Cl}$, $\text{C}_2\text{H}_4 + \text{Cl}$, $\text{C}_2\text{H}_2 + \text{Cl}$). Comparison with previous experimental or theoretical determinations, when available, proved the appropriateness of the adopted protocols and the accuracy of the calculated rate constants. Previously developed subsets for CH_3Cl and HCl/Cl_2 were updated with the theoretical rate constants and combined with the CRECK C₁-C₃ mechanism, yielding a kinetic mechanism consisting of 143 species and 2347 reactions. The validation was performed through comparison with all the pyrolysis and oxidation measurements available for pure CH_3Cl and its mixtures with CH_4 , H_2 and $\text{CO}/\text{H}_2\text{O}$. The kinetic discussion highlights the role of key reaction steps that have been theoretically investigated in this work and in our previous efforts (Singla et al., *Phys. Chem. Chem. Phys.* 2018), and shades light on additional reaction pathways needing better assessments.

Keywords

Chloromethane

Kinetic modeling

Theoretical kinetics

Flame inhibition

Ignition

Supplementary Material contents:

1. Kinetic model (*kinetics.CHEMKIN.CKI*) with thermodynamic properties (*thermo.CHEMKIN.CKT*)
2. Additional details on theoretical methods, comparison of calculated rate constants with experimental measurements and additional targets for model validation
3. Master Equation input for H-abstraction reactions computed in this study.

1. Introduction

Chlorine chemistry in pyrolysis, gasification and combustion of solid fuels is a concern due to the considerable amount of chlorine impurities often contained in biomass and waste fractions [1-3]. Under pyrolysis conditions, chlorine is released as hydrogen chloride (HCl), chlorinated hydrocarbons (e.g. chloromethane, CH_3Cl) or alkali chloride (mainly KCl), while during combustion it is largely emitted as HCl. As summarized by Glarborg [1, 2], trace species such as chlorine can affect nitrogen oxides and CO release as well as soot formation[4-8]. A high chlorine content in a fuel **inhibits** ignition [9], **lowers** flame speeds [10], and **facilitates** flame quenching [11]. Pelucchi et al. [12] presented a state of the art kinetic model of the high-temperature chemistry of HCl and Cl_2 , and analyzed the effect of chlorine species on laminar, premixed hydrogen and syngas flames. The underlying HCl/ Cl_2 chemistry was adopted recently for the development of a preliminary CH_3Cl model for specific application to biomass gasification processes [13]. In this previous work the role of key reactions steps such as $\dot{\text{C}}\text{H}_2\text{Cl} + \text{O}_2$ and $\dot{\text{C}}\text{H}_2\text{Cl} + \text{C}_2\text{H}_4$ was highlighted, and rate coefficients determined with ab initio methods.

The aim of the present paper is to extend the understanding of chloromethane (CH_3Cl) pyrolysis and oxidation chemistry further, developing a comprehensively validated model. Accurate rate constants were obtained theoretically for the highly sensitive, unimolecular dissociation reaction $\text{CH}_3\text{Cl} + \text{M} = \text{CH}_3 + \text{Cl} + \text{M}$ as well as for 13 H-abstraction reactions. Concerning the unimolecular initiation step, we determined temperature and pressure dependent rate coefficients ($T=800\text{-}2500\text{ K}$, $0.1\text{-}50\text{ bar}$). The present theoretical analysis differs from other studies by the inclusion of the spin-orbit energy in the estimation of the interaction potential, which was considered only in an approximate way by Parker et al. [14]. This shortcoming was explicitly acknowledged by the authors, correctly addressing this aspect in a following study by Jasper et al. [15]. However, this second paper was focused on the determination of high pressure limit rate constants, and did not provide pressure dependent expressions to be used in kinetic models. Results from theoretical calculations are compared with experimental measurements [16] and with previous evaluation of the reverse reaction at lower temperatures [14].

The H-abstraction reactions were computed using ab initio transition state theory based master equation (AI-TST-ME) [17, 18], as implemented in the automatic EStokTp routines [19]. EStokTp has previously been successfully adopted for selected fuels and reaction classes of interest for pyrolysis, gasification and combustion processes [20, 21]. Rate constants were determined for the temperature range $T=500-2500$ K.

The CH_3Cl subset of reactions previously developed [13] was then updated based on these new theoretical determinations. Reaction rate coefficients not assessed theoretically have been assigned based on previous experimental or theoretical estimates, as already discussed by Singla et al. [13] for the major pathways. The CH_3Cl submodel thus obtained was coupled with the CRECK kinetic framework, and with the HCl/Cl_2 module recently presented [12]. The resulting model was validated by means of comparison with the entirety of pyrolysis and oxidation measurements available for pure CH_3Cl and its mixtures with CH_4 , H_2 and $\text{CO}/\text{H}_2\text{O}$. Sensitivity and rate of production analyses were exploited to interpret the observed phenomena and to highlight possible needs for further revisions based on additional theoretical and experimental estimates of key rate constants.

Beside the direct application to CH_3Cl pyrolysis and oxidation, this model constitutes a solid basis for better assessing the influence of the chlorinated function and for further extension to higher molecular weight molecules [22, 23] or to molecules with multiple chlorine substitution. Indeed, the increasing interest in biomass utilization for energy production, the likely perspective of chemical recycling of solid plastic wastes containing polyvinylchloride PVC [24], as well as the interest in reducing the environmental impact of chlorinated composite solid materials for rocket propulsion [25], further motivates the present work.

The manuscript is organized as follows: Section 2 discusses the theoretical methods for the determination of the temperature and pressure dependent rate constants for the unimolecular decomposition reaction $\text{CH}_3\text{Cl}+\text{M}=\text{CH}_3+\text{Cl}+\text{M}$ (Section 2.1), and briefly reiterates the protocols used to investigate the H-abstraction reactions. The theoretical approach was indeed already presented and widely applied by Cavallotti and co-workers [19-21]. The kinetic model is presented and discussed in Section 3. The kinetic model validation is presented in Section 4. Rate of production and sensitivity analyses highlight peculiar features of the chemistry

involved in the pyrolysis and combustion of pure CH_3Cl and of its mixtures with hydrogen (H_2), carbon monoxide (CO) and methane (CH_4).

2. Theoretical methods

2.1 Unimolecular decomposition rate constant $\text{CH}_3\text{Cl}+\text{M}=\text{CH}_3+\text{Cl}+\text{M}$

The rate constant for the decomposition of CH_3Cl was determined from detailed balance integrating stochastically the 1D master equation [26] for the recombination reaction calculating its rate constant using microvariational E,J resolved transition state theory [27]. Microcanonical rate constants were determined in the rigid rotor harmonic oscillator approximation using RRKM theory on a potential energy surface (PES) studied at the CASPT2 level [28]. Energies, structures, and vibrational frequencies were determined using an active space consisting of 6 electrons in 4 orbitals, which comprised the σ and σ^* C-Cl bonding and antibonding orbitals and the two valence p orbitals of chlorine. The CH_3Cl PES was scanned performing constrained geometry optimization at steps of 0.1 Å, for C-Cl distances comprised between 3.0 and 4.5 Å. Spin-orbit energy splittings were determined for each optimized structure increasing the active space up to 14 electrons in 11 orbitals (that is the full valence space) using CI wave functions, the aug-cc-pVDZ basis set, and a Breit-Pauli Hamiltonian. CI calculations were performed using CASSCF wave functions [29] determined considering three singlet and three triplet states. Twelve spin-orbit contributions were thus determined, the lowest of which is attractive [15]. The spin-orbit splitting calculated for a 10 Å separation of the fragments is 820 cm^{-1} , in good agreement with the experimental value of 881 cm^{-1} [30]. The reaction energy calculated at this level of theory is 76.6 kcal/mol, considerably below the experimental 0K reaction energy of 82.2 kcal/mol [31]. The CASPT2 PES was therefore rescaled over the CCSD(T)/CBS reaction energy, which is in good agreement with the experimental value (82.05 kcal/mol, inclusive of spin-orbit corrections, determined using an aug-cc-pVTZ - aug-cc-pVQZ extrapolation). The $\text{CH}_3\text{-Cl}$ interaction energy so determined is reported in the Supplementary Material (Figure S1). All ab initio calculations were performed using Molpro 2010 [32, 33].

Master equation simulations were performed in an argon bath considering CH_3 and Cl as reactants, determining stochastically the entrance energy level in the PES as described by Polino and Cavallotti [27].

The electronic degeneracy of chlorine was determined accounting explicitly for the fourfold degeneracy of its ground state and for the existence of two low lying degenerate excited states with an energy of 820 cm⁻¹. Two possible reaction channels were considered: decomposition to reactants and collisional stabilization. A reacting system was assumed to get collisionally stabilized when its rovibrational energy became equal or smaller than that at which the Maxwell-Boltzmann population of the well is maximum. The rate constant for the decomposition reaction was successively determined from detailed balance. Simulations were performed using the same collisional energy transfer parameter that was used with success to study the low temperature recombination kinetics of CH₃ and Cl by Parker et al. [14]: $\Delta E_{\text{down}} = 387 \times (T/298)^{0.4} \text{ cm}^{-1}$. Simulations were performed determining K(E,J) rate constants at steps of 1 cm⁻¹, which were then averaged first over J and then over bins of sizes of 100 cm⁻¹ [26]. The investigated temperature and pressure ranges are comprised between 800 and 2500 K and between 0.1 and 50 bar, respectively. The total number of reactive events considered for each simulation is 200000. Table 1 reports rate coefficients in the modified Arrhenius form for the investigated pressures.

Table 1: Kinetic constants for $\text{CH}_3\text{Cl} = \dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{l}$ interpolated between 800 and 2500 K.

P [bar]	A [s ⁻¹]	n	E _a [cal mol ⁻¹]
HPL	1.72E+19	-0.985	85903.3
0.1	1.22E+44	-9.175	94303.5
1.0	3.28E+44	-9.011	95477.8
2.0	2.53E+44	-8.887	95909.6
5.0	4.22E+44	-8.837	96706.9
10.0	1.02E+44	-8.58	96837.0
20.0	1.33E+43	-8.246	96882.5
50.0	1.27E+42	-7.857	97025.6

Figure 1a and b compare the decomposition rate constant from this study with experimental data [16, 34]. Figure 1c reports the recombination rate constants as measured (symbols) and calculated (dashed lines) in Parker et al. [14] with results from this study (solid lines). At the low temperatures investigated in Figure 1c, the recombination reaction is in the fall off regime. As the fall off extent increases with temperature at parity

of pressure and the high pressure recombination rate constant is almost temperature independent between 200 K and 300 K, it follows that the rate constant increases with a decrease of the temperature. Results from our calculations generally agree with the experimental measurements within a factor of ≈ 2 . Larger deviations (i.e. factor of ≈ 4) are observed for the 0.3 torr case at $T=298$ K.

Figure 1: Comparison between the calculated (lines) and experimental (symbols) rate constants for CH_3Cl decomposition (a, b) [16, 34] and backward recombination (c) [14]. Dotted lines in Figure 1c are calculations from Parker et al. [14]

2.2 H-abstraction reactions

The rate constants for relevant H-abstraction pathways (Table 2) were computed with ab initio transition state theory based master equation simulations (AI-TST-ME) [17, 18]. The ab initio investigation of the PES was performed with EStokTP (available at <https://github.com/PACChem/EStokTP>)[19], an automatized software program for the calculation of temperature and pressure dependent rate constants, jointly

developed by Politecnico di Milano and Argonne National Laboratories. EStokTP relies on external codes such as Gaussian G09 [35] and Molpro 2010 [32, 33] for electronic structure calculations, and MESS for Master Equation simulations (available at <https://github.com/PACChem/MESS>) [36].

The structure of the reactants and products were determined with density functional theory (DFT) using M06-2X/6-31+G-(d,p) [37]. The absolute minimum energy structure was determined using Monte Carlo sampling of torsional dihedral angles. A guess structure of the transition state was searched through a one-dimensional grid scan of the atomic distance between the atom of the abstracting radical carrying the unpaired electron and the H atom to be abstracted. A conformational search was thus performed for the transition state, retaining the lowest energy conformer for the following calculations. The M06-2X/aug-cc-pVTZ was used to calculate electronic energies, geometries, vibrational frequencies of all the stationary points (reactants, products, transition state). The same method is used to determine the above properties for the van der Waals entrance and exit complexes, according to the three transition state model (3TS) described in Cavallotti et al. [19]. Intrinsic reaction coordinate (IRC) calculations were performed at the same level of theory to investigate the molecular evolution along the reaction path, and to verify the location of saddle points. Hindered rotor scans and symmetry calculations were performed using M06-2X/6-311+G(d,p). High-level calculations for single point energies were performed at the CCSD(T)/aug-cc-pVTZ level [38] with CBS basis set correction given by $\text{DF-MP2/aug-cc-pVQZ} - \text{DF-MP2/augcc-pVTZ}$ [39]. TS searches were performed in internal coordinates, computing the Hessians only for the first structure. All DFT calculations were performed using G09 [35], and all CCSD(T) and DF-MP2 calculations were performed with Molpro 2010 [32, 33, 40]. In the 3TS model, the rate constant for the full H-abstraction process is computed by solving the master equation for the three channels: entrance, exit, and H-abstraction. The explicit consideration of van der Waals wells to describe the reaction kinetics for the computationally investigated reactions is minor, as it affects the calculated rate constants by less than 5%. The hydrogen bonding interactions range from -0.5 kcal/mol ($\text{CH}_3\text{Cl}+\text{CH}_3$, $\text{CH}_3\text{Cl}+\text{O}_2$) up to -4.9 kcal/mol for OOH. The collisional stabilization of the van der Waals well is significant only at room temperature, also when pressure increase up to 100 bar.

Rate parameters for the modified Arrhenius expression of the 13 H-abstraction reaction rate constants are reported in Table 2.

Table 2: Arrhenius fits in the 300-2500 K temperature range of the calculated rate constants for H-abstraction reactions. Units are cm³, mol, s, cal. Fitting errors are <10%.

Reaction	A	n	Ea
CH ₄ +Cl=CH ₃ +HCl	3.22E+08	1.658	2591.9
C ₂ H ₆ +Cl=C ₂ H ₅ +HCl	1.96E+10	1.003	-533.9
C ₂ H ₄ +Cl=C ₂ H ₃ +HCl	1.52E+07	2.191	4986.3
C ₂ H ₂ +Cl=C ₂ H+HCl	2.33E+12	0.680	31858.9
CH ₃ Cl+Cl=CH ₂ Cl+HCl	2.81E+07	1.759	767.8
CH ₃ Cl+O ₂ =CH ₂ Cl+HO ₂	4.82E+05	2.491	48787.4
CH ₃ Cl+C ₂ H ₅ =CH ₂ Cl+C ₂ H ₆	3.10E+01	3.346	10711.6
CH ₃ Cl+C ₂ H ₃ =CH ₂ Cl+C ₂ H ₄	7.39E+00	3.501	4426.7
CH ₃ Cl+O=CH ₂ Cl+OH	6.47E+02	3.280	4718.4
CH ₃ Cl+CH ₃ =CH ₂ Cl+CH ₄	1.49E+02	3.278	9640.9
CH ₃ Cl+HO ₂ =CH ₂ Cl+H ₂ O ₂	1.52E+00	3.800	16549.9
CH ₃ Cl+OH=CH ₂ Cl+H ₂ O	1.63E+05	2.418	913.2
CH ₃ Cl+H=CH ₂ Cl+H ₂	1.02E+04	2.981	6055.0

Following the work of Corchado et al. [40] the spin-orbit coupling was accounted for by lowering the energy barrier of 0.8 kcal/mol. The best fits reported in Table 2 already include these corrections. The calculated rate constants agree with experimental determinations [41-53] within a factor of 2.5, as highlighted in the Supplementary Material (Figure S2). All the input data for the Master Equation simulations

used to determine the H-abstraction rate constants reported in this work have been reported in the Supplementary Material. Notably, these data include the optimized geometries, together with many other important parameters, such as vibrational frequencies and symmetry factors, that make it possible to reproduce the simulations results.

H-abstraction reactions by chlorinated radical species ($\dot{\text{C}}\text{H}_2\text{Cl}$, $\dot{\text{C}}\text{HCl}_2$, $\dot{\text{C}}\text{Cl}_3$, $\text{CH}_2\text{Cl}\dot{\text{C}}\text{H}_2$, $\text{CH}_3\dot{\text{C}}\text{HCl}$) on CH_3Cl and other relevant intermediates (CH_2Cl_2 , $\text{CH}_2\text{ClCH}_2\text{Cl}$, etc.) for which no accurate assessment were found in the literature, have been automatically generated according to Ranzi et al. [54, 55]. In such approach, corrections in C-H bond dissociation energies for chlorinated species have been taken according to McGivern et al. [56].

3. Kinetic model

The kinetic model presented here is obtained by coupling the core chemistry of the CRECK kinetic framework, with the HCl/Cl_2 subset previously developed [12]. The core chemistry is largely constituted by the AramcoMech1.3 $\text{C}_0\text{--C}_2$ mechanism [57, 58], and by the C_3 subset from Burke et al. [59] and Ranzi et al. [60] for higher molecular weight species. Minor updates were recently implemented in the $\text{C}_0\text{--C}_1$ chemistry [61]. On top of the subsets above we implemented the CH_3Cl model presented by Singla et al. [13], and introduced the new kinetic rate constants from the theoretical calculations described in Section 2.

Overall, the kinetic mechanism includes 143 species and 2347 reactions. Thermochemistry parameters for CH_3Cl related species were taken from the Burcat thermodynamic database [62]. The Transport Data Estimator package of the Reaction Mechanism Generator software was used to calculate transport properties [63]. The kinetic mechanism, thermodynamic and transport properties in CHEMKIN format are attached in the Supplementary Material. Detailed references [10, 55, 64-91] to the source of the kinetic parameters that have not been determined in the current nor in our previous study on CH_3Cl [13] are provided alongside the kinetic mechanism.

4. Results and discussion

Available experimental targets to validate the kinetic model cover a wide range of operating conditions ($T=1000\text{--}2500\text{ K}$, $p=0.5\text{--}18\text{ atm}$, $\phi=0.5\text{--}\infty$) for both pure CH_3Cl and its mixtures with H_2 , CO and CH_4 .

Specifically we have considered speciation measurements in plug flow reactors [5, 6, 65, 92-95], laminar flame speciation [73], laminar flame speed measurements [96-98] and ignition delay time data from shock tube experiments [99-101]. For sake of brevity, only a representative subset of these targets will be shown and discussed in the manuscript: additional comparisons are reported and briefly discussed in the Supplementary Material (Figure S3-S11). Model simulations, including sensitivity and reaction flux analyses, were performed with the OpenSMOKE++ code by Cuoci et al. [102]. To the authors knowledge this work presents the most comprehensively validated kinetic model for CH₃Cl pyrolysis and oxidation available in the literature.

4.1 Pyrolysis, Oxidative Pyrolysis and Combustion in Plug Flow Reactor

In 1980, Benson proposed a single step process for converting methane gas into C₂ and higher hydrocarbons by using chlorine as a catalyst [103]. Later Senkan [104] proposed a chlorine catalyzed oxidative pyrolysis process. The kinetics of pyrolysis and oxidative pyrolysis of CH₃Cl and its mixtures with CH₄ and H₂ was studied by Granada et al. [92] in an adiabatic flow reactor at 1253 K and 0.68 atm. Figure 2 shows a comparison between experimental and predicted profiles of major species. To account for possible deviations from the ideal plug flow conditions, **species profiles** have been shifted so as to reproduce fuel conversion profiles. The addition of oxygen (2.05 mol % O₂, $\phi=5.1$) does not significantly affect ethylene and acetylene yields, mainly produced by recombination reactions of chloro-methyl ($\dot{\text{C}}\text{H}_2\text{Cl}$) and $\dot{\text{C}}\text{H}_3$ radicals ($\dot{\text{C}}\text{H}_2\text{Cl} + \dot{\text{C}}\text{H}_3 = \text{C}_2\text{H}_4 + \text{HCl}$) and by the molecular elimination of HCl from vinyl chloride ($\text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_2 + \text{HCl}$).

Figure 2: Comparison of experimental (symbols) [92] and calculated (lines) species profiles at 1253 K and 0.68 atm in an adiabatic flow reactor. Open symbols and dashed lines: pyrolysis (7.47% CH₃Cl /92.53% Ar); full symbols and solid lines: oxidative pyrolysis (7.32%CH₃Cl/2.05%O₂/90.63%Ar). Time shift = 0.12 s.

Figure 3 shows a rate of production analysis for both mixtures. Grey arrows and italics refer to specific reaction channels of relevance in the case of oxygen addition. Chain radical initiation occurs through the unimolecular decomposition reaction discussed in Section 2, overall contributing ~20% of fuel consumption. CH₃Cl mainly undergoes H-abstraction reaction by $\dot{\text{C}}\text{l}$ (~60% fuel consumption) to form HCl and $\dot{\text{C}}\text{H}_2\text{Cl}$. The subsequent step is the chemically activated recombination of two $\dot{\text{C}}\text{H}_2\text{Cl}$ to form energized complexes that, at $T > 1000$ K, are rapidly decomposed to lower energy products before stabilization [21]. The main products of such decomposition are vinyl chloride (~30% of $\dot{\text{C}}\text{H}_2\text{Cl}$) followed by chloro-ethyl radical ($\text{CH}_2\text{Cl}\dot{\text{C}}\text{H}_2$) and 1,2-dichloro-ethane.

Figure 3: Rate of production analysis at 20% fuel consumption and conditions of Figure 2. The size of the arrows is proportional to the relative importance of a reaction channel. Grey arrows refer to specific reaction channels of relevance in presence of 2.05% oxygen.

In the case of pyrolysis, chloromethane is mostly consumed by H-abstraction by $\dot{\text{Cl}}$ ($\text{CH}_3\text{Cl} + \dot{\text{Cl}} = \dot{\text{C}}\text{H}_2\text{Cl} + \text{HCl}$), followed by the unimolecular decomposition ($\text{CH}_3\text{Cl} + \text{M} = \dot{\text{C}}\text{H}_3 + \dot{\text{Cl}} + \text{M}$), for which we theoretically computed the rate constants. A large amount of $\dot{\text{C}}\text{H}_2\text{Cl}$ is converted back to CH_3Cl through the reverse H-abstraction on HCl ($\text{CH}_3\text{Cl} + \dot{\text{Cl}} \rightarrow \dot{\text{C}}\text{H}_2\text{Cl} + \text{HCl}$). Methane and HCl production is largely controlled by the backward reaction $\dot{\text{Cl}} + \text{CH}_4 = \dot{\text{C}}\text{H}_3 + \text{HCl}$ rapidly converting HCl to $\dot{\text{Cl}}$. We calculated the rate of H-abstraction as described in Section 2.1 (Table 2). An alternative route for $\dot{\text{C}}\text{H}_2\text{Cl}$ is the self-recombination discussed above ($\dot{\text{C}}\text{H}_2\text{Cl} + \dot{\text{C}}\text{H}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$), for which we adopted the rate parameters from Roussel et al. [105]. Ethylene is produced by the recombination reaction $\dot{\text{C}}\text{H}_2\text{Cl} + \dot{\text{C}}\text{H}_3 = \text{C}_2\text{H}_4 + \text{HCl}$, whose parameters have been taken from [67], as discussed in [13].

The presence of oxygen increases the concentration of $\dot{\text{C}}\text{H}_2\text{Cl}$, due to the contribution of the H-abstraction by $\dot{\text{O}}\text{H}$ ($\text{CH}_3\text{Cl} + \dot{\text{O}}\text{H} = \dot{\text{C}}\text{H}_2\text{Cl} + \text{H}_2\text{O}$), whose equilibrium is much more shifted toward the products. The oxidation of $\dot{\text{C}}\text{H}_2\text{Cl}$ through the reaction $\dot{\text{C}}\text{H}_2\text{Cl} + \text{HO}_2 = \dot{\text{O}}\text{H} + \text{CH}_2\text{ClO}$ [65] produces $\dot{\text{O}}\text{H}$ and additional $\dot{\text{Cl}}$ from the decomposition of CH_2ClO [10] to formaldehyde (CH_2O). Clearly, considering the high equivalence ratio ($\phi=5.1$) the contribution of the branching pathway is limited. Overall, in the presence of oxygen, the reactivity is promoted, as well as the rate of self-recombination ($\dot{\text{C}}\text{H}_2\text{Cl} + \dot{\text{C}}\text{H}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$). This justifies the slightly higher amount of HCl, methane ($\dot{\text{C}}\text{H}_3 + \text{HCl} \rightarrow \dot{\text{Cl}} + \text{CH}_4$) and acetylene ($\text{C}_2\text{H}_3\text{Cl} + \text{M} = \text{C}_2\text{H}_2 + \text{HCl} + \text{M}$). For the

decomposition of $\text{C}_2\text{H}_3\text{Cl}$ we adopt the values of Zabel et al. [106]. From a thermal energy perspective in the adiabatic flow reactor, the low amount of oxygen does not significantly affect the temperature increase. This is due to the limited exothermicity of the system at the residence times of the measurements ($\tau < 0.25$ s), with the ignition event, defined as the maximum temperature increase, is predicted to occur at $\tau=0.4$ s.

Ho et al. [65] reported additional species measurements for rich mixtures of $\text{CH}_3\text{Cl}/\text{H}_2/\text{O}_2$ in 96% argon in an isothermal flow reactor, at atmospheric pressure. Temperatures between 1098 and 1273 K and residence times of 0.2-2.0 s were investigated. Figure 4a and 4b show comparisons between experimental data and simulations at 1173 K. Figure 4c reports CH_3Cl conversion at different reactor temperatures.

Figure 4: a,b) CH_3Cl decomposition at 1173K and 1 atm in isothermal flow reactors. Product yields expressed as fractions of the initial methyl chloride concentration. c) CH_3Cl conversion at different reactor temperatures. Mixture composition is 2% CH_3Cl , 1% H_2 , 1% O_2 , 96% Ar. Experimental data (symbols) [65] and simulation results (lines).

Similarly to what was observed by Wang et al. [10], the kinetic mechanism correctly predicts fuel conversion at lower temperatures ($T \leq 1123$ K), and underestimates fuel conversion at the higher temperatures ($T > 1123$ K). Additional results for the outlet concentrations as a function of the reactor temperature are reported in the Supplementary Material (Figure S6), confirming a ~ 20 K delay in reactivity for the higher temperature

cases. To highlight reasons for such deviations, we performed a sensitivity analysis at 20% fuel conversion for $T=1173$ K and $T=1098$ K. Results are reported in Figure 5.

Figure 5: Sensitivity analysis of rate constants to CH_3Cl consumption at 1 atm and $\tau=2.0$ s (5% fuel conversion).

The reactivity is determined by the chain initiation reaction (Section 2.1). To obtain a more significant comparison we normalized the sensitivity coefficients over that of this reaction. Beside the branching reaction $\dot{H} + O_2 = \ddot{O} + \dot{OH}$, no direct interactions with oxygen or oxygenated radicals emerge as being dominant, as expected in the early pyrolytic decomposition steps. Only a minor contribution to reactivity is provided by the reaction of $O_2 + \dot{C}H_2Cl = \dot{OH} + ClCHO$ whose rate constants have been theoretically determined Singla et al. [13]. Radical recombination reactions such as $\dot{C}H_2Cl + \dot{C}H_2Cl$ and $\dot{C}H_2Cl + \dot{C}H_3$, as expected, decrease fuel conversion, in particular for the lower temperature case. At higher conversions (50 %), the reactivity is triggered by the reaction sequence $HO_2 + \dot{Cl} = \dot{OH} + Cl\dot{O}$, $Cl\dot{O} + HCl = HOCl + \dot{Cl}$, $HOCl + H = HCl + OH$, restoring the amount of chlorine atoms and HCl, and producing two $\dot{OH}$ radicals. The rate constants for these pathways have been already discussed in our previous study on HCl/Cl_2 [12].

In general, the performances of the model for pyrolysis and rich oxidation systems in atmospheric flow reactors could be improved by a better evaluation of the rates of self-recombination and recombination of $\dot{C}H_2Cl$ with other relatively stable radicals such as $H\dot{O}_2$ and $\dot{C}H_3$. The recombination disproportionation reaction between $\dot{C}H_2Cl$ and $\dot{C}H_3$ is the major pathway producing C_2H_4 , followed by the β -decomposition of reaction of $CH_2Cl\dot{C}H_2$. Ethylene is mostly consumed by the H-abstraction reaction $C_2H_4 + \dot{Cl} = \dot{C}_2H_3 + HCl$ for

which the rate constant was theoretically determined in this study (Section 2.2). C_2H_2 is mostly produced by the molecular decomposition reaction of C_2H_3Cl ($C_2H_3Cl+M=C_2H_2+HCl+M$) and consumed by reactions belonging to the core mechanism (e.g. $O_2+C_2H_2=CO+CH_2O$, $O_2+C_2H_2=\dot{H}+H\dot{C}CO$) whose assessment is outside the scope of this study.

Indeed, the experimental studies [67, 105] from which we adopted the rate constants were performed at relatively low temperatures ($T<700$ K and $T<900$ K) compared to the targets of Figure 2 and Figure 4. A theoretical assessment beyond the QRRK analysis of Ho et al. [65] could be helpful for further model developments.

4.2 Ignition of $CH_3Cl/O_2/Ar$ mixtures

Miller et al. [99] measured ignition delay times of stoichiometric mixtures of 10% CH_3Cl in argon also with the addition of hydrogen (1%). The experiments were carried out in a shock tube at 2 atm and temperatures between 1300 K and 1600 K. Figure 6 shows a comparison with model predictions performed assuming a constant volume batch reactor.

Figure 6: Ignition delay times of $CH_3Cl/O_2/Ar$ mixtures at 2 atm. Comparison of experimental (symbols) [99] and calculated (lines). Diamonds and black line: 10% $CH_3Cl/15\%O_2/75\%Ar$, open circles and green line: 10% $CH_3Cl/1\%H_2/15.5\%O_2/73.5\%Ar$.

The mechanism predicts the ignition delays for the stoichiometric CH_3Cl mixture within the experimental uncertainty ($\sim 15\%$). The promoting effect of hydrogen addition is accurately captured by the model. Figure 7 reports the results of a sensitivity analysis carried for the two mixtures at $T=1450$ K. A positive sensitivity

coefficient stands for a reaction promoting ignition and vice versa. The unimolecular initiation $\text{CH}_3\text{Cl} = \dot{\text{C}}\text{H}_3 + \dot{\text{Cl}}$ is once again the most sensitive in promoting ignition. The competition between the self-recombination reactions of $\dot{\text{C}}\text{H}_2\text{Cl}$ terminating ($\dot{\text{C}}\text{H}_2\text{Cl} + \dot{\text{C}}\text{H}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$) or propagating ($\dot{\text{C}}\text{H}_2\text{Cl} + \dot{\text{C}}\text{H}_2\text{Cl} = \dot{\text{Cl}} + \text{CH}_2\text{Cl}\dot{\text{C}}\text{H}_2$) the radical chain mechanism respectively inhibit and promote the ignition. The successive decomposition of $\text{CH}_2\text{Cl}\dot{\text{C}}\text{H}_2$ ($\text{CH}_2\text{Cl}\dot{\text{C}}\text{H}_2 = \text{C}_2\text{H}_4 + \dot{\text{Cl}}$) produces an additional chlorine atom. For this reaction we adopted the values of Knyazev et al. [89]. The higher concentration of $\dot{\text{H}}$ radicals in the case of H_2 addition promotes the branching reaction $\dot{\text{H}} + \text{O}_2 = \ddot{\text{O}} + \dot{\text{O}}\text{H}$ and therefore the reactivity by enhancing fuel consumption through H-abstraction by $\dot{\text{O}}\text{H}$ and $\dot{\text{Cl}}$.

Figure 7: Sensitivity analysis of rate constants to ignition delay times for $\text{CH}_3\text{Cl}/\text{O}_2/\text{Ar}$ (black) and $\text{CH}_3\text{Cl}/\text{H}_2/\text{O}_2/\text{Ar}$ (red) mixtures 2 atm.

4.3 Effect of CH_3Cl addition on CH_4 ignition at high temperatures

Shin et al. [100] investigated the effect of the addition of small quantities of CH_3Cl on the ignition of stoichiometric $\text{CH}_4/\text{O}_2/\text{Ar}$ mixtures between 1580 and 1920 K at atmospheric pressure. Figure 8 shows a comparison of measured and calculated ignition delay times in shock tubes. The lower dissociation energy of the $\text{CH}_3\text{-Cl}$ bond (~ 82 kcal/mol) compared to $\text{CH}_3\text{-H}$ (~ 103 kcal/mol) results in a faster production of $\dot{\text{C}}\text{H}_3$ and $\dot{\text{Cl}}$ through $\text{CH}_3\text{Cl} = \dot{\text{C}}\text{H}_3 + \dot{\text{Cl}}$. Therefore, both the H-abstraction by chlorine and the enhanced sequence $\dot{\text{C}}\text{H}_3 \rightarrow \text{CH}_3\dot{\text{O}} \rightarrow \text{CH}_2\text{O} + \dot{\text{H}}$ sustaining the branching reaction $\dot{\text{H}} + \text{O}_2 = \ddot{\text{O}} + \dot{\text{O}}\text{H}$ explain the faster fuel consumption and the faster ignition. The mechanism predicts lower CH_3Cl concentration dependence compared to the

measurements where the promoting effect is pronounced only for 0.35% CH₃Cl addition. Compared to the comparisons of Section 4.2, the lower amount of CH₃Cl in the reactive mixture justifies the lower importance of self-recombination reactions of $\dot{\text{C}}\text{H}_2\text{Cl}$.

Figure 8: Ignition delay times of stoichiometric CH₄/O₂/Ar mixtures with different CH₃Cl addition. Comparison of experimental data (symbols) [100] and model predictions (lines).

Shi et al. [101] recently measured ignition delay times for a number of CH₄/CH₃Cl/O₂/Ar mixtures using a shock tube. The conditions investigated cover temperatures between 1350 and 1950 K, pressures between 4 and 18 atm and equivalence ratios of $\phi=0.5$ and 1.0. The reader is referred to Section 4.4 for the definition of the equivalence ratio ϕ in the case of CH₄/CH₃Cl mixtures [96].

The ignition of pure methane (M100) and pure CH₃Cl (M0) were investigated together with intermediate mixtures (M50, M80 and M90) resulting in a very large number of experimental data that are useful for validation of the model here presented. Comparisons between experimental data and model results are reported in Figure 9. Once again, the model reproduces the enhancing effect of CH₃Cl methane ignition, showing an excellent agreement with the experimental data. Additional comparisons are reported in the Supplementary Material (Figure S9).

Figure 9: Ignition delay times of different mixtures of CH_4 and CH_3Cl in $4\%\text{O}_2/\text{Ar}$. M0=100 mol% CH_3Cl , M100=100 mol% CH_4 . Lines: model predictions, symbols: experimental data [101].

The enhancing effect of CH_3Cl saturates at about 20 mol% (M80), according to both our model and to the experimental measurements of Shi et al. [101]. This behavior seems to disagree with the experimental observations by Shin et al. [100] reported in Figure 8, where the saturation occurred for the 3.5 mol% CH_4 , 0.18 mol% CH_3Cl mixture, that is comparable to a M95 mixture in the nomenclature adopted by Shi et al. [101]. Results from our model predicted quite similar ignition delay times for the two $\text{CH}_4/\text{CH}_3\text{Cl}$ mixtures investigated by Shin et al. [100], consistent with the more recent measurements showed in the top left panel of Figure 9.

To unravel the reasons for this discrepancy, we performed a sensitivity analysis at $T=1650\text{ K}$ for the two mixtures M80 [101] and M95 [100]. The different pressure conditions (4 atm [101] and 1 atm [100]) are counterbalanced by different amounts of fuel (1 mol% [101] and 3.7 mol% [100] in terms of total carbon)

resulting in similar partial pressures of fuel. Sensitivity coefficients of the most sensitive reactions are reported in Figure 10.

Figure 10: Sensitivity analysis of rate constants to ignition delay times for $\text{CH}_3\text{Cl}/\text{CH}_4/\text{O}_2/\text{Ar}$ mixtures at $T=1650\text{ K}$. Red: M80 [101], black: M95 [100]. Sensitivity coefficients are normalized over the most sensitive reaction $\text{H}+\text{O}_2=\text{O}+\text{OH}$ that has been omitted for clarity.

The sensitivity analysis clearly shows that the same CH_3Cl specific reactions are responsible for the observed behaviors, thus supporting the experimental measurements of Shi et al. [101]. In particular, the initiation reaction strongly promotes the reactivity, producing methyl radical and $\dot{\text{Cl}}$. H-abstraction by $\dot{\text{C}}\text{H}_3$ from chloromethane dominates its consumption, leading to $\dot{\text{C}}\text{H}_2\text{Cl}$ that recombines with $\dot{\text{C}}\text{H}_3$ forming ethylene and HCl. Ethylene and methane are largely consumed by H-abstraction by $\cdot\dot{\text{Cl}}$, together with other radicals such as $\dot{\text{H}}$ and $\dot{\text{O}}\text{H}$, producing vinyl ($\dot{\text{C}}_2\text{H}_3$) and methyl radicals. The ignition is governed by the competition between interactions of methyl and vinyl radicals with O_2 , propagating the radical chain mechanism, and recombination reactions such as $\dot{\text{C}}\text{H}_3+\dot{\text{C}}\text{H}_3$ and $\dot{\text{C}}\text{H}_3+\dot{\text{C}}\text{H}_2\text{Cl}$ inhibiting ignition.

4.4 Laminar Flame speed of CH_3Cl and $\text{CH}_3\text{Cl}/\text{CH}_4$

Chelliah et al. [97] measured laminar burning velocities of premixed flames and the extinction stretch rates of non-premixed flames for $\text{CH}_3\text{Cl}/\text{O}_2/\text{N}_2$ and $\text{CH}_3\text{Cl}/\text{CH}_4/\text{O}_2/\text{N}_2$ mixtures in a counterflow configuration. Recently Shin et al. [98] studied the effect of CH_3Cl addition and O_2 enrichment on atmospheric laminar premixed flame of $\text{CH}_3\text{Cl}/\text{CH}_4/\text{O}_2/\text{N}_2$ at room temperature using the Bunsen nozzle. As previously reported [96], the complete oxidation of CH_3Cl involves 1.5 moles of O_2 to give CO_2 , H_2O and one mole of HCl. Therefore, defining R as the molar ratio between CH_3Cl and CH_4 (e.g., $R=1$ for equimolar mixtures), the

equivalence ratio ϕ is defined as the ratio between $(2/R + 1.5)$ and the actual moles of O_2 . Ω is defined as the oxygen mole fraction in the oxidizer mixture [98] ($\Omega=0.21$ for synthetic air).

Figure 11a summarizes the comparisons between experiments [97, 98] and model predictions. For both the case of pure methane ($R=0$), where the experimental data for pure methane of Dirrenberger et al. [107] are also reported, and for the CH_3Cl/CH_4 mixture ($R=1$) very good agreement is observed for the $\Omega=0.21$ case. Figure S11 of the Supplementary Material shows a clearer view of this specific condition, for $R=0$, $R=1$ and $R=\infty$.

For higher oxygen levels ($\Omega=0.30$ and 0.35), the model under-predicts the experimental measurements [98] by $\sim 5\text{-}20$ cm/s, while there is a shift towards richer conditions with respect to Dirrenberger data [33]. As pointed out by Dirrenberger et al. [107] some distortions of the flame due to the high burning velocity ($100\text{-}120$ cm/s) may introduce additional uncertainties. The recent validation of our methane subset for MILD and oxy-flame conditions [61] showed good agreement over a range of oxygen levels. The discrepancies observed in the present work for the case of pure methane ($R=0$) are indeed surprising. Similar disagreement was obtained using the recent methane mechanism from Hashemi et al. [108], pointing to possible shortcomings in the experimental measurements.

Very good agreement is observed for the pure CH_3Cl case ($R=\infty$) [30], where the model accurately captures flame speed throughout the investigated range of equivalence ratios (see also Figure S11).

Figure 11b shows the inhibiting effect of CH_3Cl at different oxygen enrichment levels. As already shown in Figure 11a, the model coherently predicts the inhibiting effect on methane flame propagation of CH_3Cl . This effect increases for higher oxygen contents.

Figure 11: a) Laminar flame speeds of CH₃Cl/CH₄/O₂/N₂ mixtures at atmospheric pressure. $T_u=298-300$ K, $R=1.0$ (open symbols, dashed lines), $R=0$ (full symbols and crosses [107], solid lines), $R=\infty$ (pure CH₃Cl: green open diamonds and lines). b) [98] Effect of CH₃Cl addition Comparison of measured (symbols) [97, 98] and calculated (lines). Blue dotted line: predictions with the model of Hashemi et al. [108] for pure methane ($R=0$) and $\Omega=0.35$.

Figure 12 shows the effect of oxygen enrichment at three different equivalence ratios on a dimensionless basis, by assuming the reference value of the laminar flame speed for methane/air mixtures as measured by Dirrenberger et al. [107] at $\Omega=0.21$. CH₄ and CH₃Cl decomposition starts with H-abstraction by chlorine ($\dot{\text{Cl}}+\text{CH}_4=\dot{\text{C}}\text{H}_3+\text{HCl}$, $\dot{\text{Cl}}+\text{CH}_3\text{Cl}=\dot{\text{C}}\text{H}_2\text{Cl}+\text{HCl}$). C-H bond dissociation energy in CH₃Cl is ~ 5 kcal/mol lower than that of CH₄ [56], resulting in a higher rate of abstraction particularly at lower temperatures. A significant amount of CH₃Cl is also consumed via H-abstraction by methoxy radical (CH₃ $\dot{\text{O}}$) whose concentration builds up significantly due to the high amount of methyl radical.

Figure 12: Effect of oxygen enrichment for $CH_4/O_2/N_2$ (black triangles) and $CH_3Cl/CH_4/O_2/N_2$ mixtures (grey squares). Dirrenberger laminar flame speed for pure methane in air [107] is assumed as reference. Experimental (symbols) and calculated (lines).

The amount of chlorine ($\dot{Cl}$) consumed at the onset of the fuel decomposition is produced through the reaction cycle reported in Figure 13. The reactivity is promoted by $\dot{CH}_2Cl + O_2 = ClCHO + \dot{OH}$, thus explaining the dependence of the inhibiting effect on oxygen concentration. The successive decomposition of formyl chloride ($ClCHO$) and hypochlorous acid ($HOCl$) restores the amount of chlorine.

Figure 13: Reaction channels involved in the onset of the stoichiometric laminar flame. $T_u=298K$, $p=1atm$, $d=1.42$ cm, $R=1.0$, $\Omega=0.21$.

Figure 14 shows species profiles (a), formation rates of key radical species (b) and stable species (c) as a function of the domain length. At $d=1.5$ cm from the burner, CH_3Cl is mainly consumed via H-abstraction by

$\dot{\text{H}}$, $\dot{\text{OH}}$ and $\dot{\text{Cl}}$ to form $\dot{\text{CH}}_2\text{Cl}$. Recombination reactions of $\dot{\text{CH}}_3$ and $\dot{\text{CH}}_2\text{Cl}$ largely proceed towards termination to produce HCl, ethane and ethylene, inhibiting the flame propagation.

Figure 14: Species profiles (a) and formation rates of key radical (b) and stable species (c) in a CH_3Cl stoichiometric laminar flame, $T_u=298\text{K}$, $p=1\text{atm}$, $R=1$, $\Omega=0.21$.

Moving towards $d=1.51$ cm, methane consumption reaches its maximum, mainly due to the H-abstraction by $\dot{\text{Cl}}$ ($\dot{\text{Cl}}+\text{CH}_4 = \dot{\text{CH}}_3+\text{HCl}$). The onset of the chain branching reaction $\dot{\text{H}}+\text{O}_2 = \ddot{\text{O}}+\dot{\text{OH}}$ promotes the H-abstraction by $\dot{\text{OH}}$ from HCl, producing $\dot{\text{Cl}}$ and water. As the $\dot{\text{Cl}}$ concentration builds up, the recombination reaction $\dot{\text{CH}}_3+\dot{\text{Cl}} = \text{CH}_3\text{Cl}$ subtracts radicals from the system, thus inhibiting flame propagation. Moreover, the reaction $\text{HCl}+\dot{\text{H}} = \text{H}_2+\dot{\text{Cl}}$ consuming HCl at $d<1.52$ cm starts to proceed in the reverse direction.

5. Conclusions

The interest in chlorine species emissions from solid fuels combustion processes [1, 2] motivates this theoretical and kinetic modeling study of chloromethane pyrolysis and oxidation. An accurate theoretical assessment of temperature and pressure dependence of the key decomposition reaction $\dot{\text{CH}}_3\text{Cl}+\text{M} = \dot{\text{CH}}_3+\dot{\text{Cl}}+\text{M}$ is presented and discussed. Differently from previous theoretical studies, both spin-orbit corrections and pressure dependence were explicitly accounted for, allowing satisfactory agreement with fundamental rate constant measurements. In addition, the rate constants of 13 H-abstraction reactions that were highlighted to be relevant in our preliminary model [13] were computed using AI-TST-ME methods.

Even in this case our determinations agree very well with the available experimental data, with maximum deviations of a factor of 2.5.

By coupling the core mechanism of the CRECK kinetic framework, our previous HCl/Cl₂ submechanism [12] and the recent subset for CH₃Cl pyrolysis and combustion [13], we obtained a kinetic model to describe the pyrolysis and oxidation of chloromethane and its mixtures with hydrogen, methane and carbon monoxide. This subset was updated with the rate constants computed from theory. The mechanism thus obtained was tested against a wide set of experimental data, providing good agreement and improving the performances reported in [13]. The model was used to highlight the chemical reasons behind the promoting effect of CH₃Cl on methane ignition, and its inhibition effects on laminar flame speeds. The ignition is promoted substantially by the higher decomposition rate of CH₃Cl compared to that of methane, creating the radical pool. In flames instead the reactivity is inhibited by the reverse recombination reaction subtracting reactive radicals such as $\dot{\text{C}}\text{H}_3$ and $\dot{\text{C}}\text{I}$ from the system. Self-recombination reactions of $\dot{\text{C}}\text{H}_2\text{Cl}$ and recombination with stable radicals such as $\dot{\text{C}}\text{H}_3$ and $\text{H}\dot{\text{O}}_2$ play a major role in the description of kinetic effect of CH₃Cl on the combustion of methane, hydrogen and CO. The same reactions are responsible for the disagreement between measured and predicted profiles of C₂ species such as acetylene and ethylene in some of the flow reactor experiments reported in the main text and in the Supplementary Material. Large improvement could be obtained from a theoretical reassessment of the temperature and pressure dependence of these reactions, beyond the QRRK approach of Bozzelli and co-workers [65].

This work presents the first comprehensively validated model for CH₃Cl pyrolysis and combustion, providing a solid basis for further developments. The number of theoretical determination of rate constants reported here and in our previous efforts provide useful information for analogy based extension of this kinetic subset.

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