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Combustion and Pyrolysis Kinetics of Chloropicrin

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Abstract

Chloropicrin (CCl_3NO_2) is widely used in agriculture as a pesticide, weed-killer, fungicide or nematicide. It has also been used as chemical agent during World War I. The precise understanding of its combustion chemistry for destruction processes or in the event of accidental fire of stored reserves is a major safety issue. A detailed chemical kinetic model for the combustion and pyrolysis of chloropicrin is proposed for the first time. A large number of thermo-kinetic parameters were calculated using quantum chemistry and reaction rate theory. The model was validated against experimental pyrolysis data available in the literature. It was shown that the degradation of chloropicrin is ruled by the breaking of the C-N bond followed by the oxidation of the trichloromethyl radical by NO_2 through the formation of the adduct CCl_3ONO , which can decompose to NO , chlorine atom and phosgene. Phosgene is much more stable than chloropicrin and its decomposition starts at much higher temperatures. Combustion and pyrolysis simulations were also compared and demonstrated that the addition of oxygen has very little effect on the reactivity or product distribution due to the absence of hydrogen atoms in chloropicrin.

Introduction

Chloropicrin (CCl_3NO_2) is a nitroaliphatic compound, also known as trichloronitromethane. It is a colorless liquid which volatilizes slowly at room temperature and atmospheric pressure. Chloropicrin has been widely used as herbicide, repellent, fumigant, insecticide, nematicide and disinfectant^{1,2}. It was also found to be an efficient chemical agent during World War, as a tear and a vomiting gas, also known as acquinite, G-25, S-1 or PS^{3,4}. Despite its little prevalence in environment, its high toxicity and environmental concerns have led to the prohibition of agricultural uses in Europe, but chloropicrin is still involved in many treatments in other countries, including the US for soil fumigation⁵. The evaluation of danger in case of accidental fire and the destruction by thermal treatments of excess quantities of pesticides as well as stockpiles or unexploded ammunitions still found every year on old battlefields, requires the development of highly safe processes⁶. The yields of toxic emissions from incinerations or other thermal destruction processes are mostly controlled by chemical kinetics.

Few quantitative experimental studies have been devoted to chloropicrin thermal decomposition⁷⁻¹¹. High toxicity of this compound induces a high level of complexity for any experiments. Consequently, there is a considerable lack of knowledge on the behavior of this chemical under high-temperature conditions with or without oxygen. Chloropicrin is an active chemical species, which manifests low bond dissociation energies (BDE) compared to hydrocarbons. Our calculations at the CBS-QB3 level of theory show that the BDE of the C—Cl and C—N bonds are 68.9 and 42.1 kcal mol⁻¹ respectively (Fig. 1). Note that chloropicrin, which does not contain any H-atom, is known as non-combustible, but enhances the reactivity of combustible mixtures and broaden the flammability limits of gas mixtures thanks to the oxidant role of the NO_2 function^{12,13}.

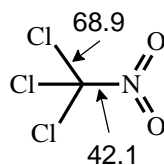


Figure 1. Bond dissociation energies at 298 K in chloropicrin computed at the CBS-QB3 level of theory (in kcal mol⁻¹).

The first analytical attempts demonstrated that the decomposition of chloropicrin starts at its boiling temperature (~112°C) and that the main products of decomposition are phosgene (COCl₂) and nitrosyl chloride (ClNO)⁷. Radulescu and Zemfirecu⁸ later measured the global rate of decomposition in the temperature range 130-160°C and found an activation energy around 40 kcal mol⁻¹, which is consistent with a reaction occurring mainly by the unimolecular breaking of the C—N bond, which BDE equals 42.1 kcal mol⁻¹ (Fig. 1). In 1938, Steacie and Smith⁹ pyrolyzed chloropicrin between 138 and 170°C. Their study confirmed that the reaction occurs by a unimolecular decomposition producing phosgene and nitrosyl chloride. The authors obtained a high pressure limit rate constant of $4.90 \times 10^{15} \exp^{-18958/T} \text{ s}^{-1}$. They also observed that, under these temperature conditions, ClNO decomposed slowly to NO and Cl and concluded that the main products of chloropicrin decomposition are COCl₂ and an equilibrium mixture of ClNO, NO and Cl₂. Experimental work by Dubikhin et al.¹⁰ in 1971 on the same temperature range led to rate constant of $2.24 \times 10^{15} \exp^{-18837/T} \text{ s}^{-1}$, in very good agreement with previous data^{8,9}. The authors observed that the reaction depends on pressure below 300 Torr. A more recent experimental work was carried out by Battin-Leclerc *et al.*¹¹. In this work, the decomposition of chloropicrin under pyrolysis conditions was studied for temperatures ranging from 100 to 530°C in an isothermal closed reactor at an initial pressure of 25 Torr (0.033 bar) and for reaction times ranging between 10 and 120 min. According to this work, phosgene is the main carbon containing reaction product; the other quantified products are majorly NO and Cl₂ and the less important are CO and CCl₄.

These studies show potential conditions for the destruction of chloropicrin, however to our knowledge there is no detailed kinetic model for the description of chloropicrin chemistry. Following a methodology used for other chemical agents such as yperite (sulfur mustard) and HN-3 (nitrogen mustard)^{14,15} and more recently phosgene and diphosgene¹⁶, a comprehensive detailed kinetic model for the thermal decomposition and the combustion of chloropicrin has been developed in this work and validated against available experimental data.

Computational methods

Calculations from quantum chemistry were used to evaluate the high-pressure kinetic constants and thermodynamic data ($\Delta_f H^\circ_{298\text{ K}}$, $S^\circ_{298\text{ K}}$, $C^\circ_P(T)$) associated with elementary processes involved in the primary mechanism of chloropicrin thermal decomposition, that are not available in the literature. Note that barrierless reactions, such as unimolecular initiations and radical combinations, which do not involve a defined transition state, were not treated theoretically. The calculations of the electronic structure of the reactants, products and transition states have been computed at the CBS-QB3 level of theory. This composite method involves a geometry optimization at the B3LYP/6-311G(2d,d,p) level of calculation and energy computations using several levels of theory. A basis set extrapolation allows to estimate a “complete basis set” (CBS) energy^{17,18}. In addition, an analysis of vibrational frequencies was systematically performed to confirm the nature of the transition states (TS). In the cases where the imaginary frequency is not non-ambiguously related to the reaction coordinate, the Intrinsic Reaction Coordinate (IRC) approach¹⁹ has been used to ensure the correct connection between a given transition state structure and the reactant and product. In this study, all the calculations have been performed using the GAUSSIAN 09 Rev. B.01 software²⁰. For all the studied molecules, the enthalpies of formation have been evaluated using atomization reaction energies²¹. The references for atomization energies of atoms were taken from the CODATA database²². Spin-orbit corrections have been taken into account²³.

This methodology has proven its precision with molecules containing hetero-atoms^{15,16,24}. In addition, the low frequency vibration modes, corresponding to internal rotations, were treated as hindered rotors instead of harmonic oscillators, using THERMROT²⁵. This in-house code allows a one-dimensional hindered rotor (1D-HR) treatment of internal rotations and avoids the coupling of torsional modes encountered in the frequency analysis made by Gaussian09, using the method proposed by Vansteenkiste et al.²⁶. 1D-HR treatment was used with torsional potential calculated from relaxed scans computed at the B3LYP/6-311G(2d,d,p) level of theory. Rate constants were eventually calculated as a function of temperature thanks to the Transition State Theory. The high pressure limit kinetic rate constants were fitted using the three parameter modified Arrhenius equation ($A \times T^n \times \exp(-E_a/RT)$) over the temperature range 300-2000 K.

Chemical kinetic model development

The detailed kinetic model for the thermal decomposition of chloropicrin is composed of three sub-mechanisms: a first part corresponding to the decomposition of nitrogen species, another one dedicated to chlorinated species, and a mechanism specific to the decomposition and oxidation of chloropicrin and derived products.

Reactions of nitrogen species are taken from the mechanism proposed by Konnov *et al.*²⁷. Since chloropicrin just involves C, N, and Cl atoms, the species containing hydrogen atoms in their chemical structure have been removed. In the same way, the sub-mechanism for chlorinated species has been adapted from the mechanism of Leylegian *et al.*²⁸ for the reactions of chloromethanes where hydrogen containing species have been removed. Recently, a new mechanism for HCl combustion has been proposed by Pelucchi *et al.*²⁹ which notably updates the reactions of light chlorinated compounds and re-examines the mechanism of flame inhibition involving the HCl/Cl₂ system. Thus, we added to the mechanism of Leylegian *et al.* all the missing reactions and updated some kinetic data of reactions that

appeared in both mechanisms. Some reactions of polychloromethanes not included in the previous mechanisms were also taken into account from the kinetic model proposed by Drakon and Eremin³⁰.

A mechanism specific to chloropicrin has been developed in this work, in which were included unimolecular initiations, chlorine-atom abstractions, decomposition of the radicals formed, chlorine-nitrogen coupling reactions, as well as some oxidation reactions not included in kinetic models of chlorinated and nitrogenous species. The thermochemical properties were taken from the literature in the case of light species involved in the nitrogen and chlorine sub-mechanisms^{27–29}, and theoretically calculated for chloropicrin and related products. Main species theoretically studied are presented in Table 1. The kinetic constants were either taken from the literature or theoretically obtained using the CBS-QB3 level of theory or estimated by analogy with similar reactions of the chlorinated species. The details of this mechanism will be presented in the following.

Table 1: Thermochemical properties of chloropicrin and related species determined at the CBS-QB3 level of theory.

	$\Delta_f H_{298}^\circ$ (kcal mol ⁻¹)	S_{298}° (calmol ⁻¹ K ⁻¹)	$C_p^\circ(T)$ (calmol ⁻¹ K ⁻¹)						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CCl ₃ NO ₂	-19.81	88.11	24.29	27.45	29.72	31.31	33.19	34.22	34.39
Cl ₂ CNO ₂	19.30	82.42	20.72	23.24	25.17	26.61	28.47	29.47	29.59
Cl ₃ CONO	-28.79	91.99	27.60	30.08	31.75	32.83	34.00	34.69	34.89
Cl ₂ C(ONO)NO ₂	-23.93	99.17	33.42	37.84	40.99	43.16	45.56	46.57	46.74
CCl ₃ O	-10.36	75.88	20.01	21.80	22.94	23.66	24.50	24.94	25.40
CCl ₃ OO	-7.60	84.70	23.35	25.77	27.34	28.31	29.21	29.63	29.79
CINO	12.88	62.64	10.62	11.20	11.65	11.99	12.47	12.82	12.88
CIONO	14.32	68.43	14.29	15.82	17.05	18.01	19.35	20.10	20.24
CIONO ₂	3.86	74.07	16.64	18.82	20.46	21.67	23.20	24.01	24.13
COCINO ₂	-40.68	78.94	19.14	21.48	23.30	24.69	26.60	27.78	27.91

Mechanism specific to chloropicrin

Possible unimolecular initiation reactions involve the rupture of the C—N and C—Cl bonds, with the first being the easiest (BDE 42.1 vs. 68.9 kcal mol⁻¹, Fig. 1). Reactions were written in the reverse direction as barrierless radical combinations (reactions (1) and (2) in Table 2).

The kinetic constant of the first reaction was estimated from the correlations involved in the EXGAS software³¹ and that of the second one by analogy with the reaction $\text{CCl}_3 + \text{Cl}$ ³² which produces a C—Cl bond with a close BDE. Decomposition reactions of the produced radicals were included, based on analogies with species featuring similar chemical structures, like CH_3NO_2 ³³, CHCl_2NO_2 ³⁴ and $\text{C}_2\text{Cl}_3\text{NO}_2$ ³⁵. The authors showed that NO_2 and the carbon radicals (CH_3 , CHCl_2 or C_2Cl_3) react by combination to form either the reactant (addition of the N side of NO_2) or a R—ONO species (addition of the O side of NO_2). These combinations are barrierless. To better understand this behavior, the potential energy surface for the primary decomposition of chloropicrin was calculated (Fig. 2).

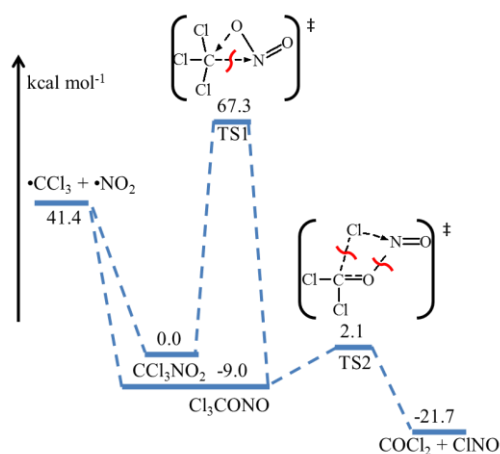


Figure 2. Energy profile at 0 K of the primary decomposition of chloropicrin, computed at the CBS-QB3 level of theory (in kcal mol⁻¹).

In Fig. 2, the combination of CCl_3 with NO_2 on the O—NO side produced Cl_3CONO , which lies about 9 kcal mol⁻¹ below chloropicrin (CCl_3NO_2). The latter can directly interconvert into Cl_3CONO (TS1 and reaction 3 in Table 2) but the energy barrier is high (67.3 kcal mol⁻¹) and remains much above the exit channel yielding trichloromethyl and NO_2 . Meanwhile, Cl_3CONO decomposes easily through a cyclic transition state (TS2 and reaction 4 in Table 2), in which a Cl-atom is transferred on the N-atom, while the O—N bond breaks to produce

CINO and phosgene COCl_2 . The geometry of TS2 is displayed in Fig. 3. The energy barrier is only $11.1 \text{ kcal mol}^{-1}$ at 0 K. To verify the connection between the reactant and the products, an IRC calculation at the B3LYP/6-311G(2d,d,p) level of calculation was performed. Chloropicrin will then readily react by an initial C—N bond breaking and the combination of produced radicals will further produce Cl_3CONO (reaction 5). The latter can decompose by reaction 4 through TS2, or by the O—NO bond breaking (bond dissociation energy $40.1 \text{ kcal mol}^{-1}$) yielding CCl_3O radicals and NO (reaction 6), which rate constant was set equals to that of CH_3ONO ³⁶. The rate parameter of the decomposition of CCl_3O to phosgene and Cl-atom was calculated theoretically (reaction 7).

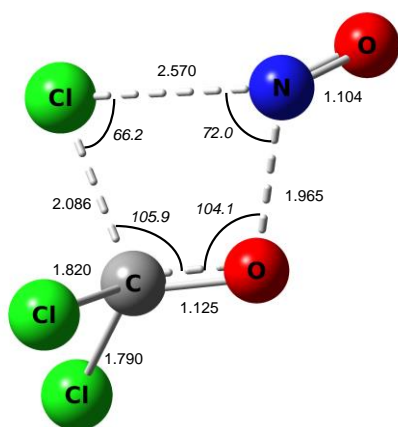


Figure 3. CBS-QB3 geometry of chloropicrin transition state TS2. Bond length in Å, angle in degree. CONO dihedral angle is 101.2° .

Table 2. Reactions of decomposition of chloropicrin and its primary products. Units are cm^3 , mol, s, cal with $k = A T^n \exp(-E/RT)$.

Reaction	A	n	E	$k_{500\text{K}}$	
(1) $\text{CCl}_3 + \text{NO}_2 \rightleftharpoons \text{CCl}_3\text{NO}_2$	2.0×10^{12}	0.0	0.0	2.0×10^{12}	Est. ³¹
(2) $\text{Cl}_2\text{CNO}_2 + \text{Cl} \rightleftharpoons \text{CCl}_3\text{NO}_2$	3.52×10^{13}	0.0	0.0	3.5×10^{13}	Est. ³²
(3) $\text{CCl}_3\text{NO}_2 \rightleftharpoons \text{Cl}_3\text{CONO}$	3.86×10^{11}	0.924	67728	3.0×10^{-16}	theory
(4) $\text{Cl}_3\text{CONO} \rightleftharpoons \text{COCl}_2 + \text{CINO}$	8.51×10^{11}	0.343	11362	7.7×10^7	theory

(5)	$\text{CCl}_3 + \text{NO}_2 \rightleftharpoons \text{Cl}_3\text{CONO}$	2.0×10^{13}	0.0	0.0	2.0×10^{13}	Est. ³¹
(6)	$\text{Cl}_3\text{CONO} \rightleftharpoons \text{CCl}_3\text{O} + \text{NO}$	1.06×10^{15}	0.0	35970	2.0×10^{-1}	Est. ³⁶
(7)	$\text{CCl}_3\text{O} \rightleftharpoons \text{COCl}_2 + \text{Cl}$	1.52×10^{13}	0.201	17797	8.8×10^5	theory
(8)	$\text{CCl}_3\text{NO}_2 + \text{Cl} \rightleftharpoons \text{Cl}_2\text{CNO}_2 + \text{Cl}_2$	9.37×10^{08}	1.784	17556	1.3×10^6	Est. ³⁷
(9)	$\text{Cl}_2\text{CNO}_2 \rightleftharpoons \text{COCl}_2 + \text{NO}$	2.46×10^{12}	0.485	61558	6.2×10^{-14}	theory
(10)	$\text{Cl}_2\text{CNO}_2 + \text{NO}_2 \rightleftharpoons \text{Cl}_2\text{C}(\text{ONO})\text{NO}_2$	2.0×10^{12}	0.0	0.0	2.0×10^{12}	Est. ³¹
(11)	$\text{Cl}_2\text{C}(\text{ONO})\text{NO}_2 \rightleftharpoons \text{COCINO}_2 + \text{ClNO}$	9.17×10^{13}	-0.350	11189	1.3×10^8	theory
(12)	$\text{Cl}_2\text{C}(\text{ONO})\text{NO}_2 \rightleftharpoons \text{COCl}_2 + \text{N}_2\text{O}_3$	1.12×10^{14}	-0.104	23850	2.2×10^3	theory

The chlorine atom abstraction reaction was also considered (reactions 8). The kinetic parameters were estimated by analogy with the Cl-atom abstraction from CCl_4 calculated theoretically by Brudnik *et al.* ³⁷. The values were recalculated from the high-pressure limit rate constant given in the paper. The radical Cl_2CNO_2 can decompose by a rearrangement reaction, in which an oxygen atom from the nitro group is transferred to the carbon atom (reaction 9). The C—N and N—O bonds break simultaneously forming COCl_2 and NO as products (Fig. 4). The combination of Cl_2CNO_2 with NO_2 to yield $\text{Cl}_2\text{C}(\text{ONO})\text{NO}_2$ (reaction 10) and the subsequent decompositions were also written by analogy with Cl_3CONO and the rate of the subsequent decompositions calculated theoretically (reactions 11-12).

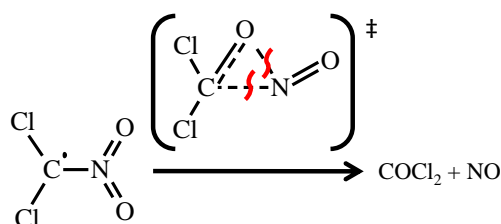


Figure 4. Reaction of rearrangement-elimination of radical CCl_2NO_2 .

The decomposition reactions of the primary products were also included. Reactions of phosgene COCl_2 were taken from a previous study ¹⁶. Reactions of nitrosyl chloride ClNO , and reactions of coupling between light chlorine and nitrogen containing species were taken from the literature or by analogy with equivalent reactions ³⁸⁻⁴⁰.

Results and discussion

The detailed kinetic model for the thermal decomposition of chloropicrin is composed of 54 species and 207 reactions and is available as Supplemental material. The Senkin program of Chemkin II ⁴¹ was used to perform simulations of the decomposition of chloropicrin under pyrolysis conditions in a close vessel. The simulations were done for temperatures ranging from 100 to 500°C, the reactor volume was 350 cm³, the initial pressure was set at 25 Torr (0.033 bar) and the residence time up to 10 minutes. These conditions correspond to the experimental study on the thermal decomposition of chloropicrin carried out by Battin-Leclerc *et al.* ¹¹.

Figure 5 shows the total pressure profiles as a function of residence time at different temperatures. Simulations are in very good agreement with the experimental results, without any fitting of rate constants, considering the experimental uncertainties due to the initial injection of the liquid reactant¹¹. The constant pressure observed at 100°C implies that liquid chloropicrin is quickly vaporized after its injection into the reactor (the saturating vapor pressure of chloropicrin at 20°C is 20.25 Torr) and that no further reaction occurs thereafter. The increase of pressure with time at 200°C indicates the onset of a slow chloropicrin decomposition. At 400°C, the pressure increases almost instantly after injection up to 66 Torr experimentally indicating that the chloropicrin is completely decomposed, but the very little change of the pressure over the next 10 min denotes a little reactivity of first reaction products at this temperature. The further increase in pressure at 500°C implies the occurrence of secondary decomposition reactions of the primary products. The model reproduces well these different behaviors at the different temperatures.

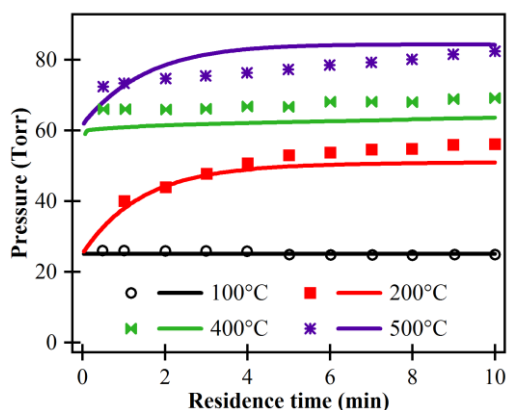


Figure 5. Profiles of pressure vs. residence time for the thermal decomposition of chloropicrin. Initial pressure, 25 Torr. Symbols: experimental results ¹¹; lines: simulation.

The experimental conversion of chloropicrin presented in Figure 6 as a function of temperature, for a fixed residence time of 10 min, is well predicted by the simulations. Under these conditions, chloropicrin begins to decompose below 150°C and is totally destroyed around 200°C.

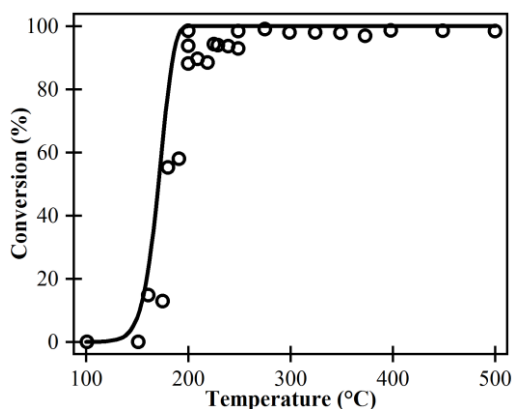


Figure 6. Conversion of chloropicrin vs. temperature. Initial pressure, 25 Torr; residence time, 10 min. Symbols: experimental results ¹¹; lines: simulation.

Figure 7 shows the evolution of the partial pressures of experimentally quantified products as a function of the temperature, for a residence time of 10 min. Results of simulations agree well for the main products, i.e. NO and phosgene. For CCl₄, model predictions are correct for

temperatures below 300°C, but underestimate them at higher temperatures. Note that wall-promoted combinations of CCl₃ radicals with Cl-atoms cannot be disregarded. In the case of NO, the simulated profile displayed in Fig. 7 is the sum of the calculated mole fraction of NO and NOCl. This latter was indeed not detected in the experiments by Battin-Leclerc et al.¹¹, whereas it was found to be the primary product of chloropicrin decomposition in previous experimental studies^{7,9,10}. The very low Cl—NO BDE (37.2 kcal mol⁻¹) makes almost impossible the quantification of the species by gas-phase chromatography, and we assumed that nitrosyl chloride decomposed completely into NO and Cl during the analytical process. The model slightly overestimates the formation of NOCl at 225°C. However, for temperatures above 300°C a good agreement is obtained. With regard to phosgene, model predictions are in good agreement with the experimental results. This compound is a primary product of chloropicrin decomposition, which shows a much stronger thermal stability than the parent molecule. The decomposition of the phosgene starts to be noticeable around 370°C in these conditions¹⁶.

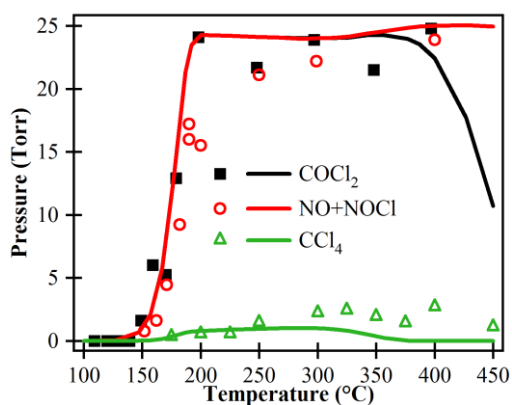


Figure 7. Products quantified during the thermal decomposition of chloropicrin. Initial pressure, 25 Torr; residence time, 10 min. Symbols: experimental results ¹¹; lines: simulation.

In conditions of Fig. 7, chloropicrin decomposes to CCl₃ and NO₂ over the entire temperature range, the Cl-atom abstraction remaining negligible. These products combine then together to

yield CCl_3ONO , which rapidly decomposes into phosgene and ClNO . Note that the global reaction $\text{CCl}_3\text{NO}_2 = \text{COCl}_2 + \text{ClNO}$ is strongly exothermic by 19.9 kcal/mol, as usual for the decomposition of NO_2 -containing species. Nitrosyl chloride reacts by Cl-atom abstractions by Cl atoms, NO_2 and in a lesser extent CCl_3 , producing NO and Cl_2 , ClNO_2 , and CCl_4 respectively. Reactions with Cl-atoms and CCl_3 are very exothermic (enthalpy of reaction of -20.3 and -35.5 kcal mol⁻¹, respectively), that with NO_2 slightly endothermic (3.7 kcal mol⁻¹). ClNO_2 easily decomposes to Cl and NO_2 . ClNO also reacts with itself to produce two NO and Cl_2 . Phosgene is more stable than other species and starts to react above 370°C. The main reactions of consumptions are Cl-atom abstractions by NO and Cl-atoms, and CCl_3 at the early stage of the reaction. The COCl radicals decompose then to Cl-atom and CO or react with NO_2 to form COCIONO , which decomposes to CO_2 and ClNO through a cyclic transition state. Tetrachloromethane is produced mainly at low temperature by the reaction of CCl_3 with ClNO . For temperature above 300°C, it is consumed by Cl-atom abstraction, to yield back CCl_3 . The reaction of the latter with NO_2 yields CCl_3O , which decomposes into phosgene and Cl-atom.

In order to compare pyrolysis and combustion behavior of chloropicrin in incineration or accidental fire conditions, simulations were performed in a perfectly stirred reactor for mixtures of 5% of chloropicrin in air and in nitrogen under atmospheric pressure from 400 K to 1500 K for a residence time of 1 s. Chloropicrin profiles are identical in both conditions since reactant consumption occurs uniquely by the initial bond breaking rather than any radical bimolecular reaction. Product distribution and consumption are very similar. Figure 8 depicts the reaction pathways in pyrolysis and combustion at 1000 K. Chloropicrin reacts via the same reaction paths under both conditions sets by decomposition to NO_2 and CCl_3 , followed by the combination to CCl_3ONO and the formation of phosgene and nitrosyl chloride. The main difference appears in the products reactions. In these high temperature conditions, phosgene reacts by Cl-atom abstractions by NO and Cl in both conditions, but the

role of NO decreases slightly in air compared to pyrolysis. In presence of O₂, the NO₂/NO ratio is indeed strongly modified by the oxidation of NO to NO₂. Reaction pathways of ClNO are affected: reaction with Cl-atoms remains the main consumption channel, but reaction with NO₂ accounts for 18% of ClNO consumption in air, but is almost negligible in pyrolysis.

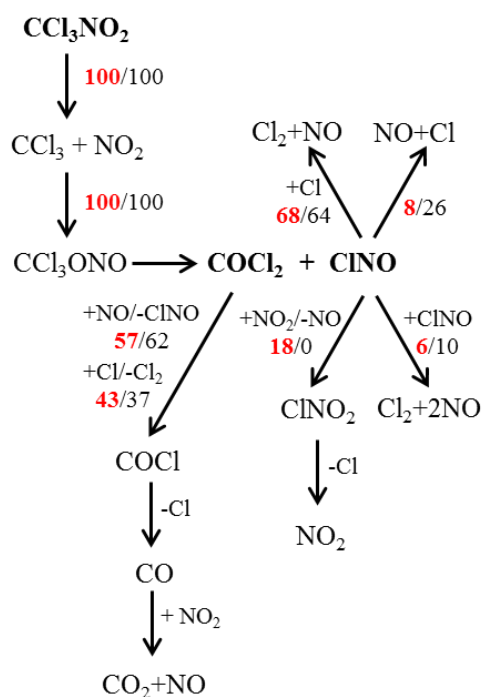


Figure 8. Flux analysis for the reaction of 5% of chloropicrin in nitrogen and in air at 1000K in a PSR (P=1atm, $\tau=1s$). Red bold numbers are flow rate (%) in combustion, black number in pyrolysis.

Conclusions

The first detailed kinetic model of the thermal decomposition and the combustion of chloropicrin has been developed and validated. The mechanism is composed of sub-mechanisms from the literature describing the reactions of the nitrogen containing and chlorinated species. The comprehensive mechanism for the decomposition of chloropicrin includes unimolecular reactions, Cl-atom abstractions, decomposition of the radicals formed, chlorine-nitrogen coupling reactions, as well as some oxidation reactions not included in the

sub-mechanism of chlorinated and nitrogenous species. The kinetic constants were either taken from the literature or theoretically computed using the CBS-QB3 level of theory or evaluated by analogy with reactions included in the mechanism of the chlorinated species. Simulations are in good agreement with experimental results from the literature obtained in pyrolysis in an isothermal closed reactor. Chloropicrin decomposes easily at low temperature to reach a complete decomposition in few minutes in a vessel at temperatures as low as 200°C. Its main products are phosgene, which is much more stable and reacts only at a higher temperature, above 370°C, and nitrosyl chloride, which decomposes to NO, Cl₂ and Cl atoms. Simulations predict that chloropicrin reacts identically in pyrolysis and combustion, because of the absence of H-atom and of little interaction of oxygen with decomposition intermediates. The effect of O₂ is mainly a change in the NO₂/NO ratio, which changes slightly reactions routes of phosgene and ClNO, but does not significantly change the overall kinetics.

Supplemental material

The detailed chemical kinetic model is available as supplemental material.

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References

- (1) Jackson, K. E. Chloropicrin. *Chem. Rev.* **1934**, *14*, 251–286.
- (2) Raman, P. Chloropicrin. In *Encyclopedia of Toxicology (Third edition)*; Elsevier: Oxford, 2014; pp 903–906.
- (3) Pesonen, M.; Häkkinen, M.; Rilla, K.; Juvonen, R.; Kuitunen, T.; Pasanen, M.; Vähäkangas, K. Chloropicrin-Induced Toxic Responses in Human Lung Epithelial Cells. *Toxicol. Lett.* **2014**, *226*, 236–244.
- (4) Gupta, R. C. *Handbook of Toxicology of Chemical Warfare Agents*; Academic Press, 2015.
- (5) Triky-Dotan, S.; Westerdahl, B.; Martin, F. N.; Subbarao, K.; Koike, S. T.; Ajwa, H. A. Fumigant Dosages below Maximum Label Rate Control Some Soilborne Pathogens. *Calif. Agric.* **2016**, *70*, 130–136.
- (6) Bunnett, J. F.; Mikolajczyk, M. *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and Mustard Munitions*; Springer Science & Business Media, 2013; Vol. 19.
- (7) Gardner, J. A.; Fox, F. W. CVIII.—Chloropicrin. Part I. *J. Chem. Soc. Trans.* **1919**, *115*, 1188–1194.
- (8) Radulescu, D.; Zamfirecu, G. Sur La Décomposition Thermique de La Chloropicrine. *Bull Soc Chem Rom.* **1935**, *17*, 87–92.
- (9) Steacie, E. W. R.; Smith, W. M. The Unimolecular Decomposition of Gaseous Chloropicrin. *J. Chem. Phys.* **1938**, *6*, 145–149.
- (10) Dubikhin, V. V.; Nazin, G. M.; Manelis, G. B. Thermal Decomposition of Chloropicrin. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1971**, *20*, 1245–1246.
- (11) Battin-Leclerc, F.; Baronnet, F.; Paternotte, G.; Leclerc, J. P.; Gourhan, R. Thermal Decomposition of Chloropicrin, Diphosgene and Phosgene between 100 and 530°C. *J. Anal. Appl. Pyrolysis* **2000**, *53*, 95–105.
- (12) Ashmore, P. G.; Norrish, R. G. W. A Study of Sensitized Explosions. VIII. Experimental Work on the Hydrogen-Oxygen Reaction Sensitized by Chloropicrin. *Proc. R. Soc. Lond. Ser. Math. Phys. Sci.* **1950**, *203*, 454–471.
- (13) Ashmore, P. G.; Norrish, R. G. W. A Study of Sensitized Explosions. X. The Kinetics of Decomposition of Chloropicrin and of the Hydrogen-Oxygen and Hydrogen-Chlorine Reactions Sensitized by Chloropicrin. *Proc. R. Soc. Lond. Ser. Math. Phys. Sci.* **1950**, *204*, 34–50.
- (14) Sirjean, B.; Lizardo-Huerta, J.-C.; Verdier, L.; Fournet, R.; Glaude, P.-A. Kinetic Modeling of the Thermal Destruction of Mustard Gas. *Proc. Combust. Inst.* **2017**, *36*, 499–506.
- (15) Lizardo-Huerta, J.-C.; Sirjean, B.; Verdier, L.; Fournet, R.; Glaude, P.-A. Kinetic Modeling of the Thermal Destruction of Nitrogen Mustard Gas. *J. Phys. Chem. A* **2017**, *121*, 3254–3262.
- (16) Lizardo-Huerta, J.-C.; Sirjean, B.; Verdier, L.; Fournet, R.; Glaude, P.-A. Thermal Decomposition of Phosgene and Diphosgene. *J. Phys. Chem. A* **2018**, *122*, 249–257.
- (17) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A Complete Basis Set Model Chemistry. VI. Use of Density Functional Geometries and Frequencies. *J. Chem. Phys.* **1999**, *110*, 2822–2827.
- (18) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A Complete Basis Set Model Chemistry. VII. Use of the Minimum Population Localization Method. *J. Chem. Phys.* **2000**, *112*, 6532–6542.
- (19) Malick, D. K.; Petersson, G. A.; Jr, J. A. M. Transition States for Chemical Reactions I. Geometry and Classical Barrier Height. *J. Chem. Phys.* **1998**, *108*, 5704–5713.

- (20) Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.; et al. Gaussian 09, Revision B.01. 2009.
- (21) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Jr, J. A. M.; Frisch, M. J. Calibration and Comparison of the Gaussian-2, Complete Basis Set, and Density Functional Methods for Computational Thermochemistry. *J. Chem. Phys.* **1998**, *109*, 10570–10579.
- (22) Cox, J. D.; Wagman, D. .; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.
- (23) Johnson III, R. D. NIST Computational Chemistry Comparison and Benchmark Database NIST Standard Reference Database Number 101, Release 16a <http://cccbdb.nist.gov/> (accessed Mar 13, 2015).
- (24) Khalifa, A.; Ferrari, M.; Fournet, R.; Sirjean, B.; Verdier, L.; Glaude, P. A. Quantum Chemical Study of the Thermochemical Properties of Organophosphorous Compounds. *J. Phys. Chem. A* **2015**, *119*, 10527–10539.
- (25) Lizardo-Huerta, J.-C.; Sirjean, B.; Bounaceur, R.; Fournet, R. Intramolecular Effects on the Kinetics of Unimolecular Reactions of β -HORO \cdot and HOQ \cdot OOH Radicals. *Phys. Chem. Chem. Phys.* **2016**, *18*, 12231–12251.
- (26) Vansteenkiste, P.; Neck, D. V.; Speybroeck, V. V.; Waroquier, M. An Extended Hindered-Rotor Model with Incorporation of Coriolis and Vibrational-Rotational Coupling for Calculating Partition Functions and Derived Quantities. *J. Chem. Phys.* **2006**, *124*, 044314.
- (27) Konnov, A. A.; Barnes, F. J.; Bromly, J. H.; Zhu, J. N.; Zhang, D. The Pseudo-Catalytic Promotion of Nitric Oxide Oxidation by Ethane at Low Temperatures. *Combust. Flame* **2005**, *141*, 191–199.
- (28) Leylegian, J. C.; Zhu, D. L.; Law, C. K.; Wang, H. Experiments and Numerical Simulation on the Laminar Flame Speeds of Dichloromethane and Trichloromethane. *Combust. Flame* **1998**, *114*, 285–293.
- (29) Pelucchi, M.; Frassoldati, A.; Faravelli, T.; Ruscic, B.; Glarborg, P. High-Temperature Chemistry of HCl and Cl₂. *Combust. Flame* **2015**, *162*, 2693–2704.
- (30) Drakon, A.; Eremin, A. Promotion of Methane Ignition by the Fire Suppressants CCl₄ and CF₃H. *Combust. Flame* **2015**, *162*, 2746–2747.
- (31) Buda, F.; Bounaceur, R.; Warth, V.; Glaude, P. A.; Fournet, R.; Battin-Leclerc, F. Progress toward a Unified Detailed Kinetic Model for the Autoignition of Alkanes from C₄ to C₁₀ between 600 and 1200 K. *Combust. Flame* **2005**, *142*, 170–186.
- (32) Kumaran, S. S.; Su, M.-C.; Lim, K. P.; Michael, J. V.; Wagner, A. F.; Harding, L. B.; Dixon, D. A. Ab Initio Calculations and Three Different Applications of Unimolecular Rate Theory for the Dissociations of CCl₄, CFCl₃, CF₂Cl₂, and CF₃Cl. *J. Phys. Chem.* **1996**, *100*, 7541–7549.
- (33) Zhu, R. S.; Lin, M. C. CH₃NO₂ Decomposition/Isomerization Mechanism and Product Branching Ratios: An Ab Initio Chemical Kinetic Study. *Chem. Phys. Lett.* **2009**, *478*, 11–16.
- (34) Zhang, J.-X.; Li, Z.-S.; Liu, J.-Y.; Sun, C.-C. Theoretical Mechanistic Study on the Radical-Molecule Reaction of CHCl₂/CCl₃ with NO₂. *J. Comput. Chem.* **2006**, *27*, 661–671.
- (35) Liu, K.; Xiang, T.; Wu, W.; Zhao, S.; Su, H. Reaction Mechanisms of C₂Cl₃ + NO₂ via Nitro and Nitrite Adducts. *J. Phys. Chem. A* **2008**, *112*, 10807–10815.
- (36) Fernández-Ramos, A.; Martínez-Núñez, E.; Ríos, M. A.; Rodríguez-Otero, J.; Vázquez, S. A.; Estévez, C. M. Direct Dynamics Study of the Dissociation and Elimination Channels in the Thermal Decomposition of Methyl Nitrite. *J. Am. Chem. Soc.* **1998**, *120*, 7594–7601.

- (37) Brudnik, K.; Twarda, M.; Sarzyński, D.; Jodkowski, J. T. Theoretical Study of the Kinetics of Chlorine Atom Abstraction from Chloromethanes by Atomic Chlorine. *J. Mol. Model.* **2013**, *19*, 4181–4193.
- (38) Zhu, R. S.; Lin, M. C. Ab Initio Studies of ClO_x Reactions: Prediction of the Rate Constants of ClO+NO for the Forward and Reverse Processes. *ChemPhysChem* **2004**, *5*, 1864–1870.
- (39) Zhu, R. S.; Lin, M. C. Ab Initio Studies of ClO_x Reactions: Prediction of the Rate Constants of ClO+NO₂ for the Forward and Reverse Processes. *ChemPhysChem* **2005**, *6*, 1514–1521.
- (40) Manion, J. A.; Huie, R. E.; Levin, R. D.; Burgess Jr, D. R.; Orkin, V. L.; Tsang, W.; McGivern, W. S.; Hudgens, J. W.; Knyazev, V. D.; Atkinson, D. B.; et al. NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.12, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320.
- (41) Kee, R. J.; Rupley, F. M.; Miller, J. A. *CHEMKIN II. A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*; Sandia Laboratories Report, SAND 89-8009B, 1993.