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Thermal destruction of Toxic Compounds

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Highlights
- Kinetic modeling of pyrolysis and combustion of toxic intermediates and pesticides.
- Development of detailed kinetic mechanisms using quantum chemistry.
- Models reproduce well literature experiments.
- Conditions for destruction processes and product emissions in case of fire are investigated.

1. Introduction

The destruction of toxic chemicals, such as obsolete stockpiles or old unexploded ammunitions by thermal treatments requires the development of highly safe processes. Usual techniques implements one of the available processes approved for industrial wastes, such as chemical destruction by hydrolysis or oxidation, incineration, plasma torch, pyrolysis [1,2]. High temperature process development needs the knowledge of the thermal decomposition and combustion kinetics of diverse agents and the distribution of intermediates and final products. These information are also needed in safety models used to model accidental fires. The high-level of toxicity of these compounds induces a high level of complexity for any experiments. As a consequence, there is a lack of knowledge on the behavior of this chemical under high-temperature conditions. A specific attention was paid in this work to chlorinated compounds, such as chloropicrin and phosgene. Chloropicrin (CCl_3NO_2) is a nitroaliphatic compound, which has been widely used as repellent, fumigant, insecticide, nematocide and disinfectant. It is a colorless liquid which volatilizes slowly at room temperature and atmospheric pressure. Its decomposition releases toxic vapors of phosgene, chlorine and nitrogen oxides. Phosgene ($COCl_2$) is an important industrial substance used in organic synthesis as halogenation and acylation reagent for industrial production of insecticides, isocyanates, plastics, dyes, and resins with an estimated production of almost 1 billion pounds per year. Diphosgene ($ClCO-OCCl_3$) can be used as phosgene precursor. In this work, the first detailed chemical kinetic models for these compounds were developed using quantum chemistry methods and validated against experimental data from the literature.

2. Methods

The construction of the detailed kinetic model for the thermal decomposition of chloropicrin, phosgene, and diphosgene followed the methodology previously developed for other toxics, such as mustard gas [3] and HN-3 [4]. The mechanisms were developed in a comprehensive way following radical chain reaction scheme: molecular pericyclic reactions, initiations, propagations, and termination reactions were considered. Unimolecular initiations, chlorine-atom abstractions, decomposition of the radicals, chlorine-nitrogen coupling reactions, as well as some oxidation reactions were taken into account. The kinetic constants were either taken from the literature or obtained from quantum chemistry calculations. In this latter case, the electronic structure of the reactants, products and transition states have been computed at the CBS-QB3 level of theory. In addition, an analysis of vibrational frequencies was systematically performed to confirm the nature of the transition states. Transition state theory allowed to derive rate constants. Thermochemical properties of species were also determined theoretically at the CBS-QB3 level. Eventually, a sub-mechanism was added for the decomposition of nitrogen species [5], and another one dedicated to chlorinated species [6].

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3. Results and discussion

The model was validated against experimental pyrolysis data of the literature [7]. Figure 1 compares simulations to experimental results in the case of chloropicrin pyrolysis in a batch reactor under a pressure of 25 Torr and for a residence time of 10 min. 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 trough the formation of the adduct CCl_3ONO, which can decompose to NO, chlorine atom and phosgene. This latter 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 of chloropicrin due to the absence of hydrogen atoms.
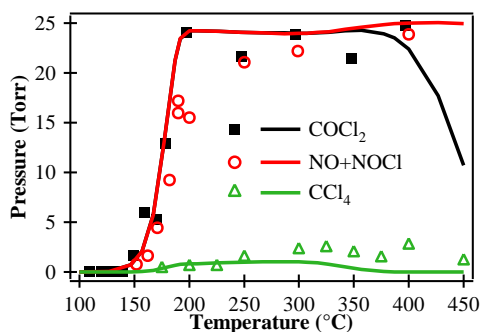

Figure 1. Thermal decomposition of chloropicrin. Initial pressure, 25 Torr; residence time, 10 min. Symbols: experiments [7]; lines: simulation.
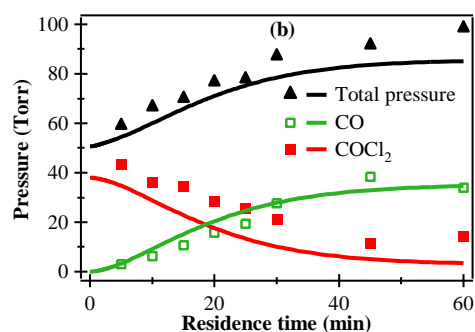

Figure 2. Total pressure and partial pressure of $COCl_2$ and CO with residence time during the thermal decomposition of diphosgene at 500°C. Initial pressure, 25 Torr of diphosgene; symbols: experiments [7] lines: simulations.

Figure 2 displays species profiles in the case of the pyrolysis of diphosgene at 500°C under 25 Torr. It is shown that diphosgene decomposes very fast in these conditions, and that its degradation is ruled mainly by a pericyclic reaction producing two molecules of phosgene, and to a lesser extent, by a roaming radical reaction yielding CO_2 and CCl_4. Phosgene is much more stable than diphosgene under high-temperature conditions and its decomposition starts at higher temperatures. Decomposition products are CO and Cl_2. An equimolar mixture of these latter can be considered as a surrogate of phosgene from the kinetic point of view, but the important endothermic effect of the decomposition reaction can lead to different behaviors, for instance in case of auto-ignition under high pressure and high temperature.

4. Conclusions

This work presents the development and the validation of the first detailed kinetic models of the thermal decomposition and the combustion of chloropicrin, phosgene, and diphosgene, which are common substance in chemical industry. The models allow the prediction of reactivity and product yields in destruction processes or in case of accidental fire. Safer surrogates for field tests are difficult to design due to the specific reactivity of chlorine atoms.

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