

DESTRUCTION OF CHEMICAL WARFARE AGENT SIMULANTS IN CORONA DISCHARGE

Oleg P. Korobeinichev, Anatoliy A. Chernov

Institute of Chemical Kinetics and Combustion SB RASc, Novosibirsk,
630090, Russia

Lev N. Krasnoperov

New Jersey Institute of Technology, Newark, NJ, 07102, USA

Introduction

The program of destruction and disposal of chemical warfare agents encounters growing public resistance. The main concern is the safety of the destruction/disposal technologies. Public opposition is based on a variety of reasons, among which are concerns about preparedness of workers and surrounding populations to accidental releases of chemical agents, release of unburned agent into the environment under normal operations, release of products of incomplete combustion or neutralization and highly toxic byproducts, and uncertainties on the long-term effects of trace amounts of chemical agents on human populations.

Chemical agent destruction processes such as incineration or neutralization, produce gaseous emissions containing trace amounts of residual agent or non-agent materials. These non-agent materials include the intermediates and byproducts of the process (such as the products of incomplete combustion, PICs, in incineration) and other hazardous substances like dioxins and furans [1]. Both the residual agent and non-agent hazardous substances have the potential of causing chronic health effects and are therefore causes of concern to the public. These concerns, while justified, can delay the implementation of disarmament programs.

By eliminating trace amounts of agent and byproducts in discharges from treatment processes, public concerns can be reduced and the process of destruction of chemical warfare can proceed more rapidly and efficiently. Similar problems exist in storage of aging chemical munitions, where leaking agents are disposed into atmosphere through ventilation. A low capital and operational cost technology capable of deep agent destruction and efficient operation at low agent concentration is therefore highly desirable as a technology which is "polishing", complementary to the baseline technologies of incineration and neutralization.

Recently, corona discharge emerged as a promising technology for treatment of low concentration stack emissions. Initial research on the decontamination of organophosphorus compounds was performed in the mid-80s [2-5]. During the last years significant progress was achieved in understanding of corona discharge plasma in application for conversion of volatile organic compounds (VOCs) and oxides of nitrogen and sulfur (NO_x and SO_x) [6-10]. However, the research on the kinetics, products and the mechanism of the destruction of actual Chemical Warfare Agents as well as their surrogates is still very limited [2-5].

In [5], the decomposition of dimethyl methyl-phosphonate (DMMP) diluted in helium at atmospheric pressure in alternating current capacitance coupled discharge was studied as a function of flowrate and concentration. Trace oxygen was found to improve the destruction. No quantitative data on the degree of the destruction as well as on the energy requirements were obtained in these works.

In this paper, an experimental study on the destruction of DIMP in dielectric barrier corona discharge was performed. The efficiency of the destruction was determined as a function of the specific discharge energy deposition.

Experimental

A tubular dielectric barrier AC corona discharge reactor coupled to a mass-spectrometer was used to study the efficiency and the kinetics of DIMP destruction in air at concentrations of 150-300 ppm.

The experimental setup is shown in Fig. 1.

The flow reactors used are glass tubes (length 105 cm, ID = 1 cm) with a thin Ni-Cr coaxial wire (0.43 mm in diameter) used as a high-voltage electrode. The second (grounded) electrode is aluminum foil wrapped outside the tube. A corona discharge is excited by application of high AC voltage (up to 20 kV, 50 Hz) to the central wire. This arrangement results in a uniform discharge along the length of the reactor. The discharge power is varied by varying the input voltage of a high voltage transformer over the range 0 - 90 W. The reactant (DIMP) and the products of the destruction are monitored by a molecular beam sampling quadrupole mass spectrometer (MBMS).

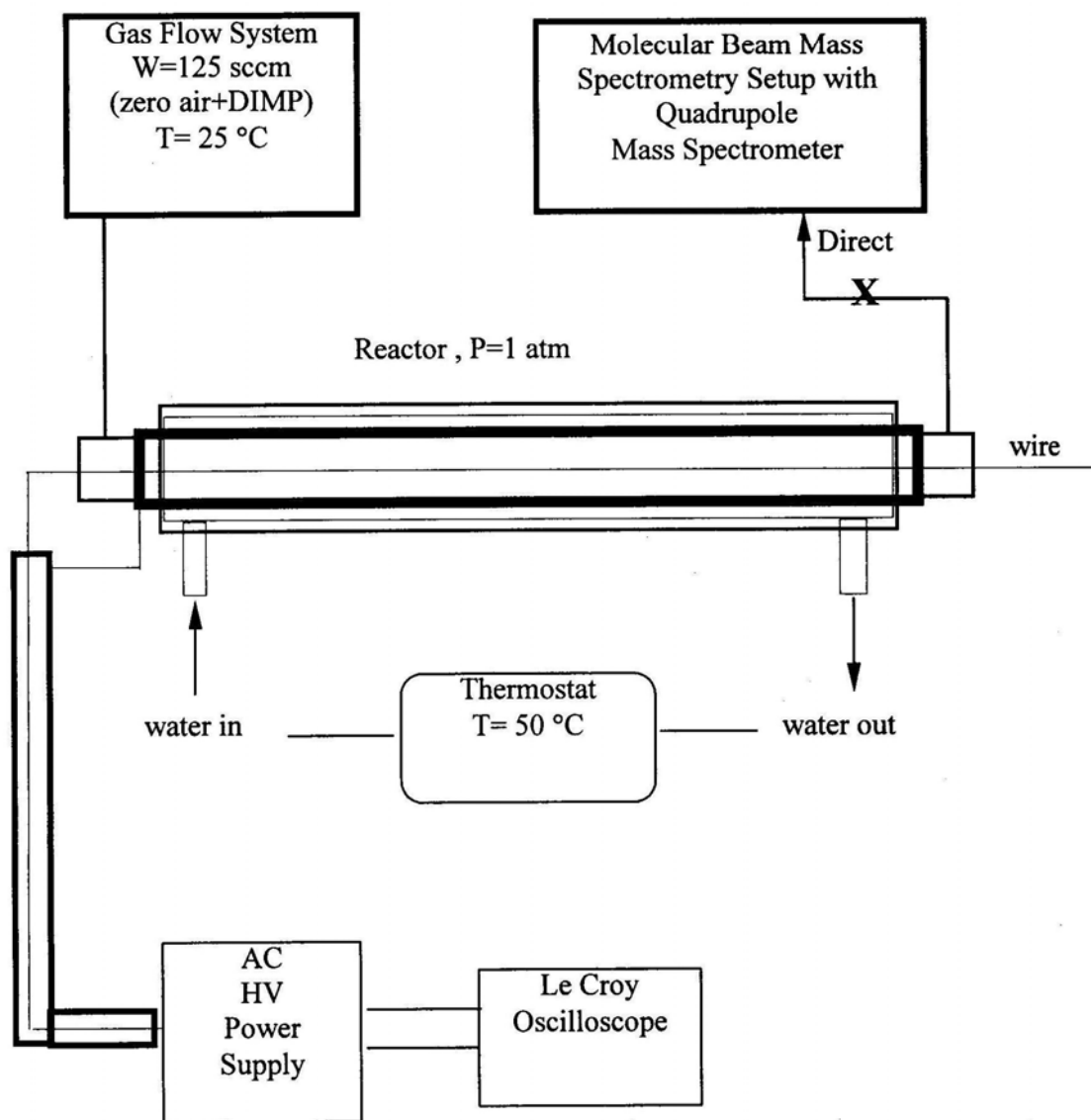


Fig.1 Experimental setup

The efficiency of the destruction was studied as a function of the active power dissipated in the reactor, the contact time, the flow rate and the concentration of organophosphorous compounds.

Active power determinations were based on the current-voltage measurements. The output voltage of high voltage transformer is measured using a two-resistor voltage divider. The discharge current is monitored measuring the voltage across a resistor connected in series with the output grounded wire. Voltage and current oscillograms are recorded using a digital oscilloscope (Le Croy 9310AL), multiplied and averaged to produce the average value of the active power. The parasitic losses in the high-voltage transformer were determined with a disconnected reactor. These losses were subtracted from the active power measured with connected reactor.

Mixtures of diisopropyl methylphosphonate (DIMP) with oxygen were fed into the reactor at pressure 1 atm. DIMP concentration in the mixture was kept low (150-300 ppm). The typical mixture flow rate was 0.6 s (standard cubic centimeters per second). The mixtures were prepared in flow by bubbling oxygen through a thermostated impinger containing DIMP at 25 °C. The reactor temperature was sustained at 75 °C to prevent condensation of DIMP (vapor pressure is 3 Torr at 66 °C). No thermal decomposition of DIMP is anticipated at this temperature. After passing the reactor the mixture is analyzed using molecular beam sampling with a quadrupole filter analyzer.

Results

To determine the extent of the destruction, the mass-spectra peaks of DIMP were recorded with and without the discharge. Neither CO and CO₂ nor other peaks of the main destruction products observed previously when studying DIMP destruction in flames were not found in the current study. Production of ozone is observed.

The extent of the destruction as a function of the discharge power is shown in Fig. 2. The destruction efficiency increases with absorbed power. The destruction follows the first-order kinetics with respect to the discharge power. The absence of the other detected peaks with measurable intensity indicates formation of non-volatile phosphorous containing compounds (such as orthophosphoric acid).

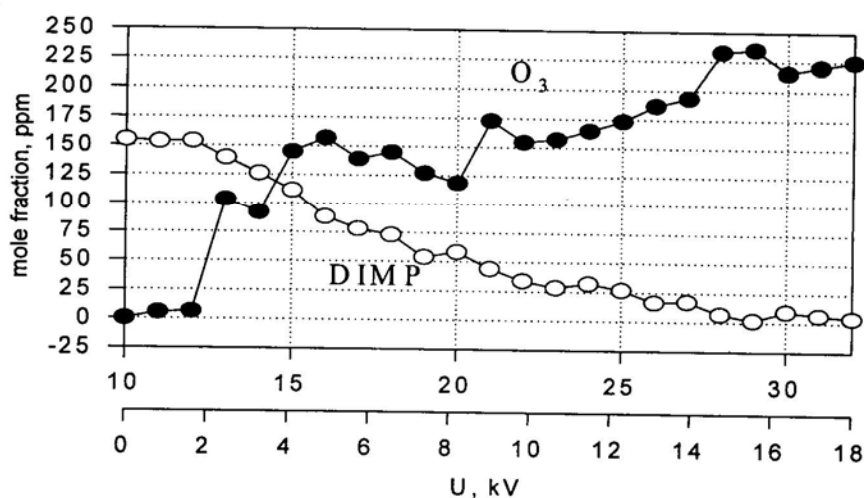


Fig.2 Profile DIMP and O₃ of the discharge voltage

The degree of DIMP destruction observed is ca. 98% at the power dissipated in the discharge of 5-7 W and the flow rate of 0.6 sccs. This destruction efficiency correlates well with those established for a number of Volatile Organic Compounds and Nitrogen Oxides in the previous studies [10]. This indicates an universal mechanism of the destruction in corona discharge. This important result allows to expect similar energy consumption for the destruction of real CW agents. Also, it implies an (expected) increase of the destruction efficiency with the decrease of CW agent concentration, as was observed for hydrocarbons and nitrogen oxides.

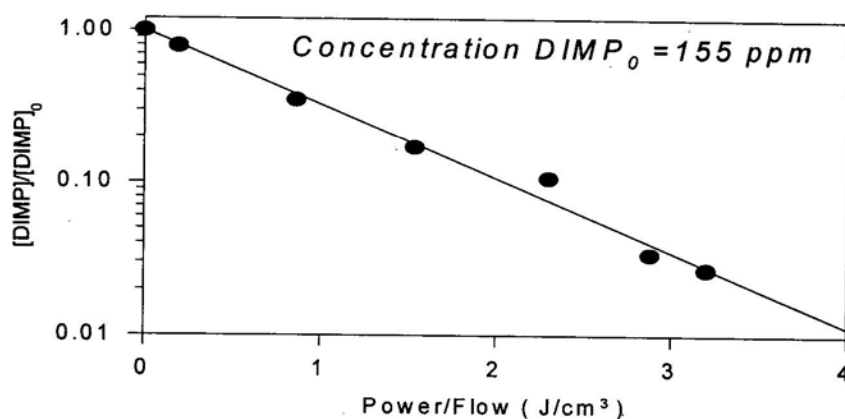


Fig. 3 DIMP destruction at the power dissipated

Acknowledgement

This work was supported by the US Army Research Office (Grant N DAAG55-97-1-0407) and by NATO (Linkage Grant DISRM.LG 961353).

References

1. "Recommendations for the Disposal of Chemical Agents and Munitions" Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Board on Army science and Technology, Commission on Engineering and Technical Systems, National Research Council. National Academy Press, Washington, D.C. 1994
2. E.J.Clothiaux, J.A.Koropchak, R.R.Moore. "Decomposition of an Organophosphorus Material in Silent Electrical Discharge" Plasma Chem. Plasma Process. 1984, V.4, N 1, p.15-20.
3. M.E.Fraser. "Simulant Decomposition Products and Mechanisms". CRDC Joint Service Technical Symposium on Plasma Air Purification Technology, CRDC,1984.
4. M.E.Fraser, D.A.Fee, R.S.Sheinson Plasma Chem. Plasma Process.1985, V.5, p.163.
5. M.E.Fraser, H.J.Eaton, R.S.Sheinson, "Initial Decomposition Mechanisms and Products of Dimethyl Methylphosphonate in an Alternating Current Discharge", Environ. Sci. Technol. 1985, 19, 946 - 949.
6. B.M. Penetrante and S.E Schultheis, editors. "Non-Thermal Plasma Techniques for Pollution Control." Springer-Verlag, NATO ASI Series, Vol. G34, Parts A & B (1993).
7. D. Evans, L.A. Rosocha, G.K. Anderson, J.J. Coogan, and M.J. Kushner. "Plasma Remediation of Trichloroethylene in Silent Discharge Plasmas." J. Appl. Phys. Vol 74, p. 5378 (1993).
8. C.M. Nunez, G.H. Ramsey, W.H. Ponder, J. Abbott, L.E. Hamel and P.H. Kariher. "Corona Destruction: an Innovative Control Technology for VOCs and Air Toxics". Air & Waste, Vol. 43, p. 242 (1993).
9. L.N. Krasnoperov, L.G. Krishtopa, J.W. Bozzelli. "Study of Volatile Organic Compound Destruction by a Dielectric Barrier Corona Discharge" International Symposium on Environmental Technologies: Plasma Systems. Atlanta, Georgia, October 8-11, 1995. Proceedings, V.2, 583-595.
10. L.N. Krasnoperov, L.G. Krishtopa. "Kinetic Study of NOx and VOCs Destruction by Dielectric Barrier Corona Discharge" The Second International Symposium on Environmental Application of Advanced Oxidation Technologies, San Francisco, Feb. 28-March 2, 1996, Abstracts, p. 91.