

NON-THERMAL PLASMA PROCESSING AND CHEMICAL CONVERSION OF HALONS: REACTOR CONSIDERATIONS AND PRELIMINARY RESULTS

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ABSTRACT

There are a growing number of indicators that the stockpiles of Halons 1301 and 1211 will eventually need to be eliminated as a precaution against any possible future release of these chemicals, which would result in a further threat to the stratospheric ozone layer. The current halon aggregate stockpile is on the order of millions of pounds of relatively chemically pure compounds. A small number of technologies already exist to destroy halons, and halon destruction has commenced in Australia. The authors' approach is aimed at exploring chemical conversion, rather than destruction, technology. This paper describes the approach of using non-thermal plasma (NTP)-based technology for chemical conversion. NTPs offer a unique variety of chemical reactivity in decomposition and final product formation since the halons can be treated in the presence of a number of different carrier gases such as N₂, Ar, H₂, and air. Furthermore, advanced NTP hybrid reactors can also introduce reactive radical species into the gas flow, which could result in the formation of desirable final products of high purity. This paper presents a discussion of NTP approaches as well as results of some preliminary experiments.

INTRODUCTION

The ultimate fate of halons now largely held in halon reserves is uncertain. The recent Cairo meeting of the Parties to the Montreal Protocol produced some of the strongest language yet with regards to their eventual fate with a call for "effective recovery, storage, management, and destruction of halons." The possibility, therefore, exists that at some future date halon use will be forbidden by international agreement and then the remaining halon stockpile will in effect become hazardous waste, which will need to be eliminated. Presently, millions of pounds of halons are stored throughout the DoD. At some point the issue will arise of how best to deal with the elimination of such a large amount of material.

One of the obvious choices will be whether to destroy this stockpile or to convert these relatively pure chemicals into other useful and nonozone-depleting chemicals. In fact, technologies currently exist that can and are being used to deal with halons and other ozone-depleting substances (ODS). For example, Australia is using a thermal plasma arc technology to destroy halons. This technique has some major deficiencies including the generation of environmentally unacceptable byproducts as well as being fairly energy inefficient. In Japan they have developed an inductively coupled, radio frequency plasma reactor in a pilot-scale plant where Halon 1301 (in combination with steam) produces acid gases that are subsequently reacted with calcium hydroxide to form calcium halides [1]. Still other approaches include the use of UV photodissociation to destroy CFCs and halons [2] as well as thermal and catalytic hydrodehalogenation as a means of converting halons to reusable products [3].

Our research team is exploring the use of non-thermal plasmas (NTP) as a means of disposing of the halon stockpiles. The last decade has seen great progress in the development of NTP reactor technology where now such NTP reactors are used in commercial air cleaners and purifiers. The authors' approach is to explore the use of NTPs not only as a means of high efficiency chemical destruction of halons, but also as a means of converting halons with high energy efficiency into commercially viable chemicals. Specifically, the chemical conversion of dilute halon gas streams in argon in a dielectric barrier (silent discharge) reactor configuration using GC/MS for the analysis of plasma reactor exhaust gases is being studied. This paper presents an overview of the NTP technology, a discussion of kinetic considerations, and some preliminary experimental results.

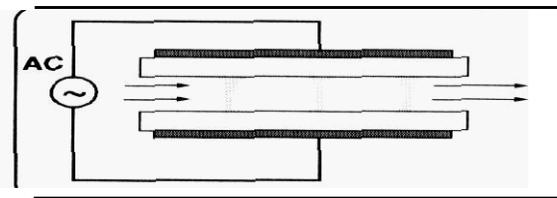
BACKGROUND ON NON-THERMAL PLASMAS

Figure 1 illustrates NTP reactors for gas-phase pollutant processing [4-11]. In an electrical discharge, a high voltage is applied across electrodes in the gas or along a surface adjacent to the gas. An electron-beam reactor requires an electron accelerator to produce the energetic electron beam ($\sim 100 \text{ keV} - 1 \text{ MeV}$) that is injected into the process gas. The energetic plasma electrons are responsible for pollutant decomposition, either through direct electron collisions or indirectly through the creation of free radicals that attack the pollutants.

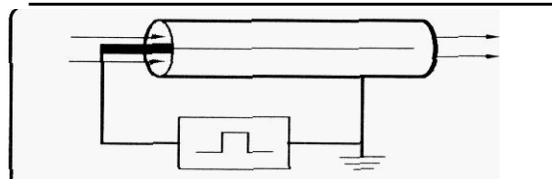
All three electric-discharge reactors—silent discharge (dielectric barrier), pulsed corona, and electrified packed bed—create transient electric-discharge streamers in the gas. The streamer is the source of energetic electrons and other active species. A relatively high voltage (determined by the reactor geometry, gas composition, and gas pressure) is required to cause electrical breakdown in the gas. The necessary voltage is supplied by a drive circuit connected to the reactor. In corona, a non-homogeneous electric field is used to stabilize the discharge and prevent thermal arc formation. Silent discharges use charge buildup on a capacitive barrier to achieve a similar end result. An electrified packed bed is closely related to a barrier discharge.

A related discharge reactor uses streamers across a dielectric surface. Streamers can be thought of as cylindrical current filaments with typical radius $\approx 100 \mu\text{m}$. They are transient discharges (e.g., lasting only a few nanoseconds for oxygen or air), fed by ionization and detachment and then arrested when the electric field is reduced to the point where electron attachment becomes dominant.

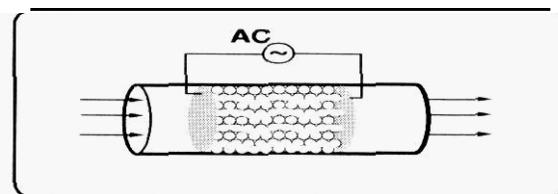
For streamers in pure oxygen and air, the average electron energy and electron density are $T_e \approx 3-5 \text{ eV}$, $[e] \approx 10^{14}/\text{cm}^3$, while a typical breakdown reduced electric field strength in the gas is $E/N \sim 100 - 200 \text{ Td}$. Multiple streamers typically give accumulated plasma energy loadings of 10s-1000s J/liter atm. In an electron-beam reactor, the source of electrons (cathode) can be separate from the accelerating-field section (as in thermionic-cathode and plasma-cathode devices) or integrated with the accelerating-field section (as in a field-emission-cathode electron gun). Electron-beam reactors must use a foil or window to separate the vacuum section of the accelerator from the process gas. The electron beam penetrates the foil, depositing energy in the process gas by collisions and molecular excitation processes coupled to the creation of a large-volume non-thermal plasma. For typical electron-beam reactors, the mean electron energies can be much larger than those for discharge reactors (e.g., $\approx 10 \text{ eV}$ for electron-beam, as compared to \sim few eV for discharges). Similar energy loadings can usually be obtained in both types of reactors.



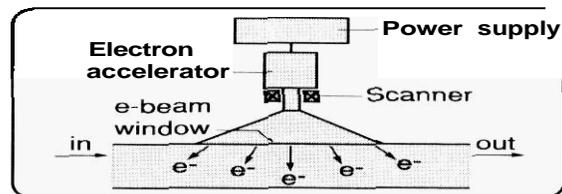
**Silent discharge
(dielectric-barrier discharge)**



Pulsed or DC corona



**Electrified
packed bed**



Electron beam

Figure I. Commonly employed NTP reactors.

ADVANCED PLASMA HYBRID SYSTEMS FOR HALON CONVERSION

As mentioned above, three approaches have been attempted using plasma technologies. One, a thermal plasma method using a dc (method used in Australia) and rf plasma [1] torches. Two, a non-thermal plasma method using pulsed corona discharge [12]. Three, an indirect plasma method using a plasma UV lamp [2]. All three methods have already demonstrated high destruction efficiency in bench-scale and pilot-scale tests. However, the energy efficiency of the above three approaches is not high, since pulsed corona power supplies, rf plasma torch and power supply, plasma UV source efficiency are all relatively low (<60-70%). Swan and Flowers [2] proposed to apply absorbent-UV hybrid system and Ciang and Yamamoto [13] used non-thermal plasma-absorbent hybrid system to overcome this problem. Swan and Flowers proposed that the absorbent would accumulate the low concentration ODS in the first stage and discharge it for UV treat-

ment for decomposition in second stage when ODS density becomes higher and where more energy efficient UV decomposition can be accomplished. Chang and Yamamoto treated ODS by a highly energy efficient non-thermal plasma in the first stage and unwanted gas discharge by-products were treated in second stage by adsorbents.

For the fully developed non-thermal plasma-adsorbent/catalyst hybrid system, which would be used for halon treatment in this proposed approach, the energy efficient non-thermal plasma in combination with secondary adsorbents are expected to decompose halons to simple intermediate molecules. These would be further chemically converted to usable products with tandem operation of a non-thermal plasma-adsorbent hybrid system [14]. In addition to these hybrid approaches, there is the possibility of directly injecting reactive species (such as NH_2 radicals from NH_3) using a process known as a corona radical shower (CRS).

EXPERIMENTAL

The experimental apparatus consists of a plasma reactor system, gas handling manifold, plasma diagnostics, and a GC/MS for exhaust gas analysis. The gas handling manifold is composed of mass flow controllers, a bubbler for addition of humidity to the process stream (not used in this study), and a mixing chamber. Gas mixtures are assumed to be fully homogenized before entering the plasma reactor cell. In these preliminary experiments, two gas mixtures were treated in the reactor. The first was 2.5 vol.% CF_3Br in argon and the second was 2.5 vol.% CF_3Br and 1.25 vol.% air in argon. The air was high purity (Zero Gas) as supplied by Matheson Gas Products.

The plasma reactor system, a silent discharge plasma reactor (Model SDPR-1), was manufactured for this laboratory by High Mesa Technologies /Coyote Aerospace of Los Alamos, NM. A simplified schematic of the system is shown in Figure 2. The system consists of a power supply and tuning circuit, cell electrical diagnostics, and the reaction cell. Electrical diagnostics are monitored on an XY oscilloscope and allow the calculation of the plasma power. In addition to the electrical diagnostics, the cell pressure, harrier temperature. gas inlet temperature, and gas outlet temperatures are monitored. Active cooling of the reaction cell is handled by two small fans, dependent on the gas mixture that determines the breakdown amplitude of the plasma. For all experiments, the plasma was run at a power of 110 W.

The reactor cell used in this study is a silent discharge plasma generated by a dielectric-ballasted, electric discharge. The reactor cell consists of two Pyrex-like glass plates, which serve as the dielectric barriers and are separated by 3 mm and confine the gas flow. On the outside of the plates has been deposited a nickel grid that serves as the electrode. A non-thermal, silent discharge plasma, consisting of many self-terminating micro-discharges, is generated in the gap between the two dielectric plates when high voltage AC power is applied to the electrodes at breakdown amplitude. The AC power is supplied by a sinusoidal power supply whose frequency has been preset to the system design of 4.0 kHz. This is coupled through a proprietary impedance-matched circuit to a high voltage step-up transformer, which drives the reactor cell.

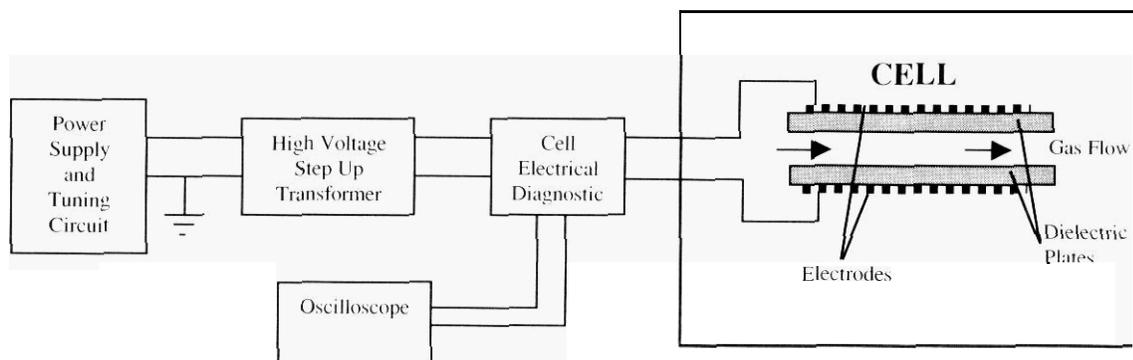


Figure 2. Simplified block diagram of Silent Discharge Plasma Reactor system.

The exhaust gas is sampled either with a gas syringe or a sampling switch to introduce a sample into the GC/MS. A Hewlett-Packard Model 5890/5965A/5970 GC/FTIR/MS with supplied software is used to analyze the gas composition. Analysis of results are performed on an attached personal computer. In these experiments, a 1.0 mL sample was introduced to the inlet port of the GC via a gas sampling syringe. All compounds were ionized at a preset energy. Future experiments include plans to soften the ionization energy to allow exact identification of all stable species by interfacing the SDPR reactor exhaust stream to a triple quadrupole mass spectrometer.

PRELIMINARY EXPERIMENTAL RESULTS

The principal compounds found in the exhaust stream were HF (see explanation below), CF_3 radical (a fragmentation product), and CF_3Br . The CF_3Br is either unreacted, which is unlikely due to the environment through which it passes, or a product of recombination reactions of radicals. Approximately 25% of the CF_3Br introduced passed through the reactor cell unchanged when the gas mix contained just halon and argon. This was reduced to 20% with the addition of air, with a consequent appearance of oxygen containing compounds such as CF_2O . Much of the HF detected is suspected of being generated in the GC/MS system as there is a known and unresolved leak in the vacuum system, which leads to a high water background evident in blank and calibration runs.

The CF_3 radical ion detected in the mass spectrometer has two primary sources, from CF_3Br and from C_2 and higher fluorocarbon compounds. A mass peak attributed to C_2F_6 (mass 138) constituted 0.2% of the total ion current. Other C_2 species present were C_2F_4 , C_2F_5 (likely daughter from $\text{C}_2\text{F}_5\text{H}$), $\text{C}_2\text{F}_5\text{O}$ (likely from $\text{C}_2\text{F}_5\text{OH}$), and $\text{C}_2\text{F}_4\text{Br}$. Hydrogen is present in the form of HCl , which is a known impurity in the CF_3Br , and whatever moisture may be present in the gas handling system. Hydrogen is undetected by the MS system. Efforts were made to dry the system prior to each experiment, but evidence of water's presence was always observed. Upon the addition of air to the gas stream, oxygenated species appeared in the analysis, with the predominant compound being CF_2O . While a trace amount was detected in the samples without air, 2.2% of the exhaust stream of the air containing samples was CF_2O . Summing contributions from daughter ions indicates that the CF_2O was present at a level of almost 4% of the exhaust stream. This may pose a problem as this is an extremely toxic compound.

No C₃ or higher compounds were observed in any of the trials. Examination of gas blanks, sampled exhaust stream with the plasma off, also showed no compounds of C₂ or higher. HF was present in small amounts, but was attributed to the vacuum leak in the MS system. No oxygenated species were present in the blank samples, indicating that these were generated in the plasma environment. Adjusting the plasma conditions and gas composition should allow the tailoring of the exhaust stream composition to enhance the production of a desired compound. This will be easily accomplished as the majority of the halon presently employed in firefighting applications is stored in a relatively pure form, containing only trace impurities (such as 0.25% HCl, as mentioned previously).

KINETIC CONSIDERATIONS

Introduction

The destruction of CF₃Br and CF₂ClBr in NTPs is best treated as a two-step process. In the first, CF₃Br and CF₂ClBr are transformed by chemical attack or by electron collisions. In the second, the products of the initial reactions react with each other or are further oxidized or reduced by the ambient gas. In this section, the likely reactions that may occur for Halon 1301 and Halon 1211 in the presence of different carrier gases will be considered. The discussion will focus primarily on neutral reactions while ionic species as well as reactions arising from electron interaction with the halons will not be considered.

Initiating Reactions

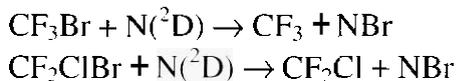
Initiation is a consequence of electron impact processes. The products are ions, excited atomic or molecular states of the carrier gases, or dissociation products of the halons. The subsequent chemistry requires a knowledge of the cross sections of these processes as a function of energy. Following the initiation processes, the halon destruction process is probably dominated by chemical processes as is thought to be the case for the destruction of trichloroethylene in atmospheric pressure barrier discharges [15]. The action of the electrons is to make reactive species from the carrier gas which then act on the halons, which assumes that the halons are minor constituents of the gas flowing through the discharge. Electron-halon interactions would be important for halon rich gas streams.

Reactive Neutral Species Arising from Electron Interaction with the Carrier Gases

First, consider the purely chemical processes that might be of importance. Start with a list of all possible neutral reactive species likely to be produced in the discharge. In the case of pure argon, the active species will be the metastable excited Ar(³P_{2,0}), with excitation energies of 11.55 and 11.72 eV. The rate constants for many reactions have been measured by Setser and co-workers [16], who, in general, found rate constants close to the collision rate. There are good data on product yields from Golde's group [17-19]. The latter concluded that the major channel in the reactions of Ar(³P_{2,0}) with the chlorofluoromethanes was molecular dissociation (they did not study any bromine-containing molecules).

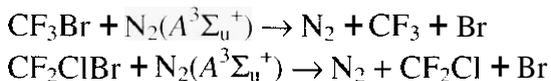
In the case of nitrogen, the ground state of atomic nitrogen, N(⁴S) is unreactive, but there are two excited atomic states, N(²D) and N(²P) that could be reactive, although no data have been reported for reactions with bromine-containing species [20]. The only data of any relevance are for the reactions of N(²D). In the case of CF₄, the rate constant is $k \leq 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$,

probably all due to physical quenching. For CF_3H , $k=1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The latter may be an insertion reaction leading to products $\text{CF}_3 + \text{NH}$. The comparable reactions of CF_3Br and CF_2ClBr with $\text{N}(^2\text{D})$ could thus be:



Although there are no real thermochemical data for these reactions, we can estimate from the comparable reaction $\text{CF}_3\text{Cl} + \text{N}(^2\text{D}) \rightarrow \text{CF}_3 + \text{NCl}$ that they are exothermic. $\text{N}(^2\text{P})$ is in general less reactive than $\text{N}(^2\text{D})$, but there are no data of any kind to use as a basis for guessing.

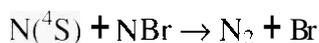
There is also a whole manifold of excited molecular states. Of greatest interest, because of its metastability, is $\text{N}_2(\text{A}^3\Sigma_u^+)$. There is a large body of rate data available for reactions of this species with carbon-containing molecules, unfortunately none of which contains bromine [20]. The reaction with CF_3Cl is relatively slow, $k=6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$ for $\text{N}_2(\text{A}^3\Sigma_u^+, v=0)$, but is enhanced going to higher vibrational levels. In the case of reaction with CF_3I , a much greater rate constant is found, i.e., $k=2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, and the mechanism is probably decomposition to $\text{CF}_3 + \text{I}$. There is thus a real chance that CF_3Br and CF_2ClBr may be decomposed at a finite rate by reaction with $\text{N}_2(\text{A}^3\Sigma_u^+)$.



For oxygen, the ground state of atomic oxygen, $\text{O}(^3\text{P})$, is unreactive at ambient temperatures. The first excited state, $\text{O}(^1\text{D})$, is in part quenched to $\text{O}(^3\text{P})$, and in part reacts, possibly by insertion, to yield products. In the case of CF_2Cl_2 , ClO has been identified as a major product [21]. One might then expect BrO to be a product for the halon reactions. Excited molecular states of oxygen such as $\text{O}_2(^1\Delta_g)$ are probably unreactive. OH might also be considered since it will be present in air streams or most laboratory systems. It also is unreactive. Thus, argon, nitrogen, and oxygen could provide reactive species to effect the destruction of the halons. Table 1 lists the possible initiating reactions for different carrier gases.

Secondary Reactions

Depending on the nature of the carrier gas and the initiating reactions, the chemistry following the initial events will consist of reactions of primary species with each other or, in the presence of air, oxidation and possibly reduction. In argon, one expects dimerization and disproportionation of radicals to yield a series of haloalkanes or haloalkenes and the halogens Cl_2 , Br_2 , and ClBr . In addition to these radical reactions, one expects to see products of $\text{N}(^4\text{S})$ reactions arising from reactions such as:

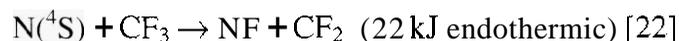


Reactions with the CF_x radicals may be endothermic, although the thermochemical database is uncertain.

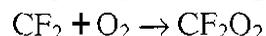
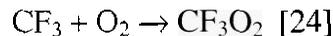
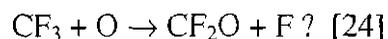
TABLE 1. POTENTIAL CHEMICAL INITIATING REACTIONS FOR NON-THERMAL PLASMA PROCESSING OF CF₃BR AND CF₂CLBR IN ARGON, NITROGEN AND AIR.

Reactive Species	CF ₃ Br Products/Rate Constant	Source	CF ₂ ClBr Products/Rate Constant	Source
Ar(³ P)	CF ₃ + Br k=3e-10	16-19	CF ₂ Cl, CF ₂ Br CF ₂ , Cl, Br k≅4e-10?	16-19
N(⁴ S)	Unreactive	26	Unreactive	26
N(² D)	CF ₃ + NBr ?	20	CF ₂ Cl + NBr ?	20
N ₂ (A ³ Σ _u ⁺)	CF ₃ + Br k≅1e-11?	20	CF ₂ Cl + Br k≅1e-11?	20
O(³ P)	Unreactive	26	Unreactive	26
O(¹ D)	BrO + CF ₃ ? k=4e-11	21	BrO/ClO + CF ₂ Cl/CF ₂ Br ? k=1e-10	21
O ₂ (¹ Δ _g)	Unreactive		Unreactive	
HO	Unreactive	26	Unreactive	26

The rate constant had been reported to be fast:



In air, in addition, oxidation reactions will be important:



Undesirable Products and Their Amelioration

The products of any imaginable sequence of reactions may include bad actors such as ClO₂, F₂CO, Cl₂CO, etc. Some can be removed by scrubbing, others may require interdiction. The species might be removed by adding hydrogen, converting the halogens to the acids and scrubbing. Others might be removed by passing the effluent through a heated zone with added methane or other gas.

SUMMARY

NTPs offer the possibility of not only destroying the halon stockpiles with high energy efficiency, but also of producing desired commercially viable chemicals. This paper described our initial efforts in this field. The experimental results so far are too preliminary to indicate how

successful the NTP approach could be for practical processing of halon stockpiles. Further experimental and kinetic modeling work are needed to demonstrate the viability of this approach. Nevertheless, current NTP technology is very mature and offers a surprising number of options for parent compound destruction and/or chemical conversion.

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