Destruction and Reuse of Halons

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ABSTRACT

International agreements and national regulations have been signed to restrict the production of chemicals, i.e. halons, CFC's, and other bromine and chlorine containing compounds, that can cause further damage to the stratospheric ozone. Although the regulations have been passed, the halons are still mainly stored in tanks of fire-protection equipment and partially in the "banking" system. Until now, no technologically promising processes in which halons are decomposed or disposed have been developed. Thus, it is urgent to find a practical process of converting waste halons to safe species. We intend to employ selective dissociation of halons to convert them to useful materials. The process relies on the absorption properties of halons in the first absorption band, i.e., the UV region of the electromagnetic spectrum, or in the IR region. The cleavage of the C-Br bond can be promoted by one photon dissociation with a pulsed ArF excimer laser or by multiphoton dissociation with a CO_2 laser resulting in halocarbon and Br radicals (mediating species). These radicals can be reacted between themselves and with different additives (H_2, CH4 and I_2) and induce radical reactions which lead to neutralization of the products. The dissociation of halon 1301 (CF_3Br) results in specific dissociation products such as C_2F_6 and Br_2. Photodecomposition of CF_3Br and its reaction with additives seems to be a promising new method for destruction of brominated hydrocarbons and their conversion to desirable products, where one of the products (obtained with I_2 as an additive) the fluoroiodocarbon (CF_3I) is considered as an "ideal halon replacement". The photodecomposition together with the reaction with additives may serve as the basis for development of a system that will decompose and neutralize effectively halons.

Introduction

Brominated halocarbons (halons), along with chlorofluorocarbons (CFCs), are a part of a family of chemicals that have been implicated in depleting the Earth's protective stratospheric ozone. The halon compounds are clean, effective, as well as non-conducting fire suppression agents, characteristics which have led to their widespread use in fire-extinguishing systems, especially in means of transportation (ships, airplanes) and military services. The CFCs were developed in the 1930s as safer alternatives to toxic and/or flamable refrigirants in use at that time, primarily sulphur dioxide and ammonia. Since then and until the last years their use was expanded and they were widely used in industry and in daily life as insulating foams, solvents, in air conditioning and refrigiration systems and as propellants for aerosol products. These compounds are extremely chemically stable in the Earth's troposphere and are transported to the stratosphere where they release chlorine and bromine atoms. In 1974, Stolarski and Cicerone [1] proposed a catalytic ozone destruction cycle for chlorine. Independently, Molina and Rowland [2] proposed the ozone destruction cycle, which includes the Cl-ClO chain, and recognized CFC compounds as a potentially significant source of stratospheric chlorine. The average Cl atom removes about 10^5 ozone molecules before final termination by rainout of HCl [3]. By replaceing the Cl atoms with Br atoms (resulting from decomposition of halons) we get the same destruction cycle for ozone and on an atom-for-atom basis in the stratosphere, bromine is 30 - 120 times more effective at destroying ozone than is chlorine. Thus, even though emissions of man-made halons are much smaller than those of the chlorine source gases, the potential effects of bromine are more significant.

The intense concern regarding the destniction of ozone in Earth's atmosphere stems from its ability to shield us from the Sun's harmful ultraviolet (UV) radiation. The much more abudant oxygen (O_2) also blocks UV light; but only ozone strongly absorbs in the region of the spectrum called UV-B, i.e., wavelengths between 280 and 320 nm that can damage DNA in living systems. Ozone is produced continually in the upper stratosphere where solar UV radiation dissociates molecular oxygen to form atomic oxygen and is destroyed when it absorbs UV light that otherwise would reach Earth's surface. As pointed above, ozone is continually being destroyed through reactions with Cl and Br radicals that are carried into the stratosphere by CFC's and halons.

Also, the CFCs and halons possess strong absorption bands in the thermal infrared, which make them extremely effective greenhouse gases [4]. On a molecule-per-molecule basis the CFCs are at least 10,000 times more effective than carbon dioxide. Hence, although the increases in concentration may be modest compared with the large increases in carbon dioxide, it has been predicted [5] that they would cause around 50 % more warming than carbon dioxide alone. For example, CFC's were estimated to have contributed approximately **20 %** to total greenhouse forcing over the period 1950 - 1985 (compared with **22 %** due to methane, **6 %** due to nitrous oxide and 52 % due to carbon dioxide) [4].

Therefore, international regulations 16-81 were signed to restrict the production of chemicals that can cause further damage to the stratospheric ozone and to intense efforts to develop acceptable substitutes. The existing controls on CFC's and carbon tetrachloride have been further tightened, with a 75 % cut from 1986 production levels by January 1994 to complete phaseout by January 1996. For halons it has been decided that they may no longer be produced after January 1, 1994 since there is so much halon already that it will last **well** into the next century if it carefully banked and conserved [9].

As seen from the above description, response to the problem of ozone depletion comes rapidly from governments and industry. International agreements and national regulations have been passed to reduce chlorine and bromine contribution from man made sources, while industry is rapidly developing and implementing alternative compounds and technologies required to continue consumer demands now served by the CFC's and halons. At this point it should be noted that so far no definitive alternatives have been found that come close to matching of halons effectiveness at extinguishing fires, lack of toxicity, and volatility while avoiding their global environmental liabilities of high ozone-depletion (ODP) and global-warming potentials (GWP) [10]. Nevertheless, a new candidate is raising hopes, i.e., the fluoroiodocarbon (CF_3I) since: 1) it is an extremely effective fire suppressant, **2)** iodine helps to reduce its tropospheric lifetime through photolysis, and therefore CF_3I has low global environmental impacts (ODP, GWP and atmospheric lifetime), 3) it is assumed to have low toxicity (still under investigation), and 4) it has low volatility.

It is worth noting that until now, ***no technologically promising process in which halons are decomposed or disposed has been developed.*** **Also,** it has to be taken into account that although the regulations have been passed, the halons are still stored in fire-protection systems and in the "banking" system. Thus, it is very *urgent* to find a practical process of converting waste halons to safe species in order to prevent them from reaching the atmosphere. We intend to explore selective photodecomposition of halon compounds with neutralization of the products to convert them to harmless materials. The photolysis promotes C - Br bond cleavage by pulsed W or IR laser photolysis, which results in halocarbon and Br radicals (mediating species) and induce chain radical reactions. The neutralization will include addition of additives that react with the radicals. This concept will be the basis of an apparatus that can be designed either for portable or fixed location uses, working manually or automatically, in areas where halons are likely to be employed and/or released.

Experiment

The experiments are camed out with an ArF laser operating at **a** wavelength of 193 nm, pulse duration of - 16ns and repetition rate of 7 - 10 Hz that irradiates the halon contained in a reaction cell. The reaction cell is made of brass and equipped with quartz (S1-UVA) windows ***5*** cm diam. and 10 cm length. The cell is connected to **a** pressure gauge **and** to **a** rotary pump that enables control of the halon pressure in the cell. The background pressure in the cell is - 10^{-3} Torr and the overall pressure after the entrance of the halon is in the range 1 - 760 Torr. At the entrance window of the cell the laser enrgy is SO mJ and the beam area is ***2.5*** **x** 1 cm. The CF_3Br (99 %), halon 1301, is used without further purification. The products are analysed, after **a** specified irradiation period, with **a** mass spectrometer (MS) (Balzers, QMG 511) which allows qualitative and quantitative identification of the products. Characteristic mass spectra of CF_3Br and of C_2F_6 (Aldrich,99 %) are monitored and are used for calibration of the products.

Results

The mass spectrum of CF_3Br irradiated by **a** pulsed ArF excimer laser is shown in Fig. 1. It shows the appearance of ions with mass 119 (C_2F_5) which represents the production of C_2F_6, characteristic peaks of the mother compound, i.e. 129, 131, and 148, 150 typical to CF_2Br and CF_3Br, respectively, and **peaks** of the smaller fragments which represent fragmentation of both CF_3Br and C_2F_6. Comparison of the characteristic peaks of CF_3Br in the irradiated sample to those obtained in the mass spectrum of neat CF_3Br shows that their intensity **is** smaller as a result of irradiation. Higher masses such as **260, 258, 210, 208, 200, 198** typical to $C_2F_4Br_2$, CF_2Br_2 and C_2F_5Br, respectively, do not appear in the spectrum. According to this result it is clear that the photodissociation is specific and leads only to the production of C_2F_6.

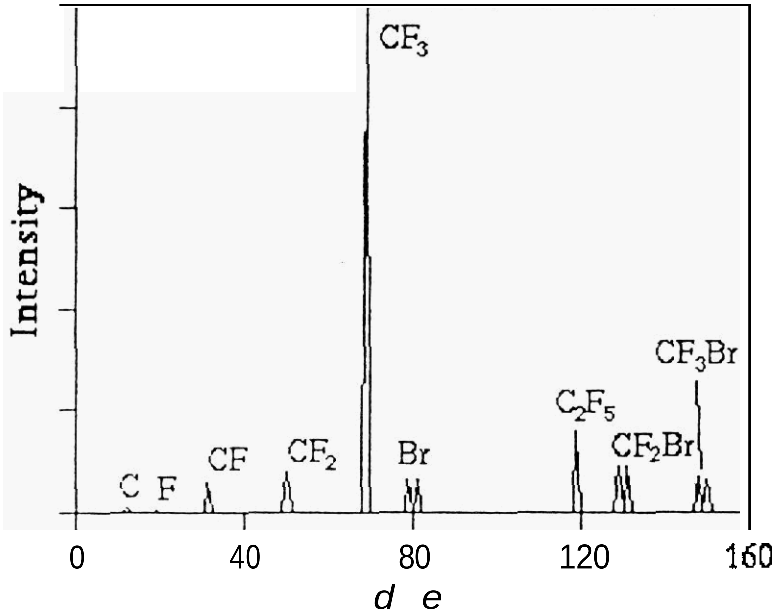

Fig. 1. Mass spectra of 1 Torr of CF_3Br irradiated by an ArF excimer laser (27,000 pulses of 50 mJ at 10 Hz).

Testing the mass spectra observed as a result of different irradiation periods allows us to obtain the relation between the intensity of the C_2F_5 ion (119), that measures the production of the C_2F_6, and the number of excimer pulses. Fig. 2 shows that the intensity of the C_2F_5 ion increases with the number of ArF laser pulses. First it increases linearly, and then moderately up to a plato, where the increase (over 100,000 pulses) of the period of irradiation does not affect the production of C_2F_6 anymore.

Figure **3** shows the results of irrdiation of 1 Torr of CF_3Br. **A** linear dependence is observed for the increase in the intensity of the C_2F_5 ion (119) and for the decrease of the molecular peak of

CF_3Br ion (148, 150) as a function of the number of pulses. Also, the efficiency of the decomposition of the CF_3Br is much higher at the lower pressure than at 60 Torr.

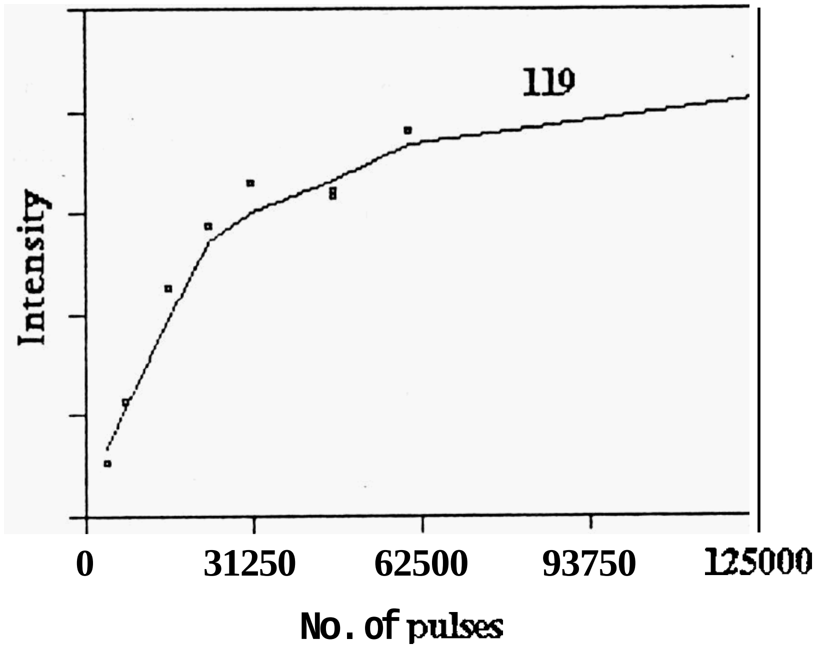

Fig. 2. Intensity of C_2F_5 ions (m/e = 119) as a function of the number of pulses of ArF laser. The pressure of the irradiated CF_3Br sample is 60 Torr.

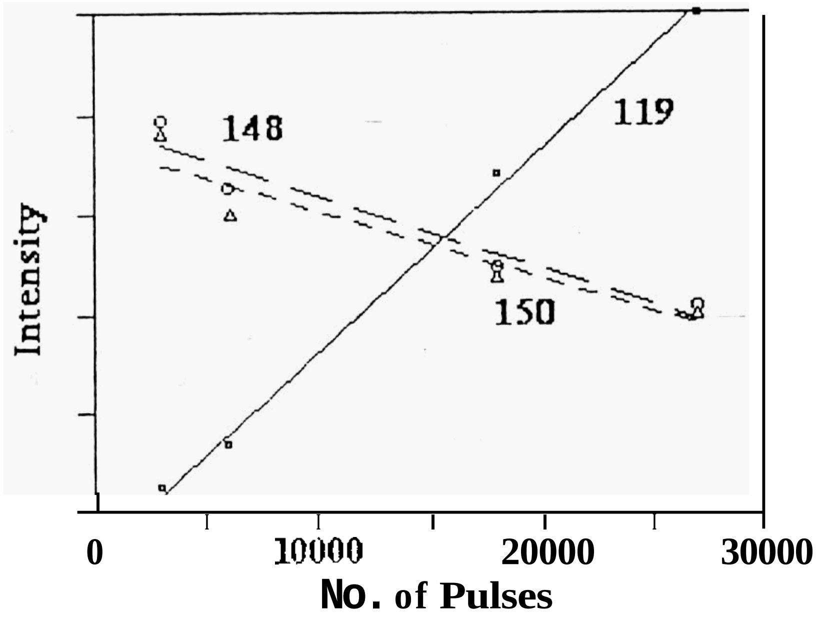

Fig. 3. The intensity of the C_2F_5 (m/e = 119) and CF_3Br (m/e = 148, 150) ions as a function of the number of pulses of ArF laser. The pressure of the irradiated sample of CF_3Br is 1 Torr.

Confirmation of the last result is observed in Fig. **4.** that represents the influence of the pressure of the CF_3Br sample on the production of the C_2F_6. The experiments are camed out at different pressures between 1 - 60 Torr, with the laser energy kept constant on 50 mJ and an irradiation period of 10 minutes (6,000 pulses.) **As** can be **seen,** the intensity of the C_2F_5 ions increases as the pressure of the CF_3Br decreases. Therefore, it is clear that under our conditions it **is** essential to work at low pressure of CF_3Br in order to convert it efficiently to C_2F_6.

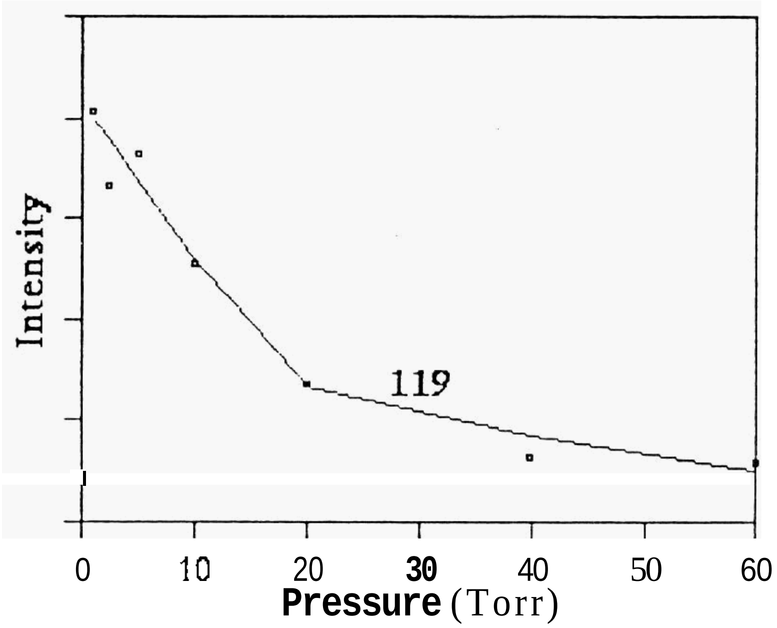

Fig. **4.** The intensity of tlie C_2F_5 ions (m/e = 119) as a function of the pressure of CF_3Br, irradiated by 6000 pulses of 50 mJ of the ArF laser.

Calibration curves showing the intensities of the C_2F_5 ions as **a** function of the composition of **a** mixture containing CF_3Br and C_2F_6 are prepared to quantify the formation of C_2F_6 as **a** result of the irradiation of CF_3Br. Comparison of the intensity of the C_2F_5 ion resulting from the irradiation of 1 Torr of CF_3Br during one hour (36,000 pulses) to that obtained from the calibration curves reveals that **43.0** % of C_2F_6 are produced, while for **a** pressure of 10 Torr the yield of C_2F_6 decreases to 27.4 %. For a pressure of 1 Torr and an irradiation period of half an hour (18,000 pulses) the yield of C_2F_6 is 27.5 %.

Discussion

The photolysis process relies on the absorption properties of the halons in the first absorption band, i.e., the UV region of the elecromagnetic spectrum. The absorption cross section of CF_3Br [11] at 193 nm (1 x 10^{-19} cm^2) is almost at its maximum value, and enables an efficient absorption and photolysis. The excitation of the CF_3Br to the continuous region of the absorption spectrum, leads to rupture of the C-Br bond with near unit quantum yield [12], according to reaction (1):

CF_3Br → CF3 + Rr. **AH** = 69.4 kcal/mole (1)

There are two additional low energy pathways for primary photodissociation:

CF_3Br → CF_2 + BrF, AH = **97.6** kcal/mole (2)
CF_3Br - CF_2Br + F . **AH** - 120 kcal/mole (3)

From the above enthalpies of reactions, the rupture of the C - F and C - Cl bonds (in the relevant compounds) becomes increasingly more important at shorter wavelengths and requires higher photon energies. Relying on these data, **an** ArF laser operating at 193 nm is chosen for one photon dissociation (OPD) since we are interested in an efficient process and in well defined products which can be achieved by photolysis of the molecule in the first absorption band. The halocarbon and halogen radicals produced by the photolysis react between themselves and therefore may lead to the production of C_2F_6 ***(5)*** and may also recombine to form CF_3Br.

$2Br \rightarrow Br_2$, (4)
$2CF_3 \rightarrow C_2F_6$. (5)

Our results indicate that both processes take place and the efficiency of conversion of CF_3Br to C_2F_6 is much higher at low pressures where the recombination reaction is less important. This is in line with the reaction rate constants (k) available from Wurzberg *et al.* [13] since k for the recombination of CF_3 and Br to give the mother compound is ***6.2*** x 10^{-11} cm3 molec^{-1} s^{-1}, while that for the dimerization of the CF_3 radicals is 0.9 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}. These rate constants show that the recombination reaction is much more efficient than the dimerization and therefore it is impossible to get, under our conditions, only the C_2F_6 as a product.

It is worth noting that in multiphoton dissociation (MPD) of CF_3Br by a pulsed CO_2 laser [13] operating at 9.6 µm the major pathway for primary dissociation is process (1), but in addition to the C_2F_6 product, products like CF_2Br_2, C_2F_5Br and $C_2F_4Br_2$ are observed in the mass spectra of the irradiated sample. These products may be formed via recombination of radicals like CF_3, Br, CF_2, and F where the last two are a result of secondary photodissociation.

As shown above, OPD and MPD provide simple methods for selective production of high concentrations of free radicals in the gaseous phase. Therefore, reaction of these radicals with properly chosen additives (H_2, CH_4 and I_2) may *leal* to the production of desirable products and to disposal of the halons. The concept of selective dissociation of halocarbons and their neutralization by additives can be the basis of an apparatus that will be designed either for portable or fixed location uses in areas where halons are likely to be employed and/or released, and is represented in detail in Ref. [14].

As mentioned in the introduction there is an increasing interest in CF_3I as an effective alternative of halon, and therefore conversion of halon to CF_3I is a most worthwhile process. In this case the photodissociation of CF_3Br has to be carried out in the presence of I_2. Iodine crystals have to be placed in *a* side arm of the reaction cell and have to be heated in order to obtain high enough pressure of I_2. The photodissociation of CF_3Br in the presence of I_2 involves cleavage of the C-Br bond (1) and subsequent formation of a CF_3I molecule according to reaction (6):

$$CF_3 + I_2 \rightarrow CF_3I + I, \qquad (6)$$

with a rate constant of 2.4 x 10^{-13} cm^3 $molec^{-1}s^{-1}$. Again, relying on the rate constants it is seen that the recombination reaction of CF_3 + Br is more efficient than reaction (6). However, by choosing the correct pressure of I_2 it is possible to obtain practically only CF_3I as a product.

Using 193 nm irradiation, photodissociation of I_2 to iodine radicals **is** expected **as well**, since the absorption cross section of I_2 is quite high $\sim 5 \times 10^{-18}$ cm^2/molec. This **may** lead to the reaction

$$CF_3 + I \rightarrow CF_3I \ , \qquad (7)$$

with **a** rate constant of 2.1×10^{-11} cm^3 molec^{-1}s^{-1}. Since this rate constant is **only** three times lower than that of the recombination it is obvious that reaction **(7)** may enhance the conversion of CF_3Br to CF_3I.

In fact Letockhov and coworkers [15] already used the **MPD** method to synthesize CF_3I. They have shown that the yield of dissociation of CF_3Br depends **on** the pressure of I_2 ($p(I_2)$). At $p(I_2) < 3$ Torr. partial recombination of the radicals took place and this resulted in reformation of the CF_3Br and **also** C_2F_6. At $p(I_2) > 6$ Torr the photodissociated CF_3Br molecules were almost completely converted to CF_3I, while at $p(I_2) > 20$ Torr only partial conversion of CF_3Br to CF_3I has been observed. The partial conversion at the higher pressure was attributed to vibrational deactivation of the molecules (excited in the **MPD**) as a result of collisions with I_2 [15].

Conclusions

Selective photodissociation of CF_3Br in the presence of additives seems to be a promising method for destruction of halons and conversion to desirable products, in particular CF_3I. The suggested method may he considered **as** the basis of a system that will effectively convert halon to CF_3I and will allow destruction of the halons present in the banking and in the fire-protection systems. This concept may he applied to other halons and **CFC's** as well.

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