GLOBAL ENVIRONMENTAL CHARACTERISTICS OF SECOND-GENERATION HALON REPLACEMENTS

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INTRODUCTION

The search for halon replacements has not yet resulted in satisfactory chemicals with the same measure of success as has the search for CFC replacements to be used as refrigerants, solvents, and foam blowing agents. The species suggested so far may be acceptable in terms of toxicity and environmental impact, but they are inferior as fire extinguishants. These first-generation agents may be used now, but at the cost of substantial system and equipment modifications. There is incentive therefore to look beyond these agents to second-generation candidates which possess the desired extinguishant capabilities. Several categories of compounds have been suggested (1). In this paper we examine the global environmental characteristics of these possibilities.

The environmental impacts of halons are basically two in kind: a) global warming (a tropospheric problem), and b) ozone depletion (restricted to the stratosphere). Both of these impacts are a consequence of the long atmospheric lifetimes that characterize halons. Before considering factors that limit atmospheric lifetimes of molecules, we very briefly review several relevant features of the atmosphere.

First, the common perception is that the troposphere is a reasonably thick blanket that shrouds the Earth. However, the troposphere is approximately 12 km thick and the diameter of the Earth is close to 13,000 km, a ratio of about 0.001. To adjust to a familiar scale, if Earth were reduced to the size of an apple with a diameter of 3.5 in., the troposphere would be a layer 0.003 in. thick, about the thickness of the skin of the apple. It is in this layer that all our weather exists and in which we conduct our activities.

The stratospheric ozone layer is a band of relatively high ozone concentration lying in the elevation range of 25-50 km. The peak ozone concentrations in this band are typically in the few hundreds of parts per million of atmosphere. Ozone concentrations are often reported in Dobson units, which is the integrated amount of ozone in a column of air beginning at sea level and extending to the top of the stratosphere. The tropical average of ozone concentration is 260 Dobson units, or 260 milliatmosphere centimeters. (A tropical average was chosen for this illustration because it varies little over the course of a year.) This value converts to 2.6 atmosphere millimeters, which may be interpreted as the thickness of the total ozone layer when translated to sea level, 2.6 mm.

Second, molecular oxygen and ozone are the only two constituents of Earth's atmosphere that absorb incident solar radiation at wavelengths longer than 200 nm. Oxygen absorbs strongly at the shorter wavelengths from a threshold at **242** nm. Only ozone absorbs longer wavelengths; its peak absorbance occurs near 260 nm and it drops steadily with increasing wavelength having an appreciable absorbance to about *320* nm *(2).*

Finally, at *260* nm the ozone column over the tropics, *260* Dobson units, has a great enough optical depth that the fraction of solar radiation transmitted is very small, $I/Io \cong 10^{-29}$. On the other hand, the fraction of light transmitted at 300 nm is much larger, I/Io 50.01; furthermore, a reduction of 10% in the total ozone column increases the fraction of *300* nm transmitted light by 65%. The significance of the *300* nm wavelength is that the energy content here is 95 kcal mol^{-1} of photons and the energy of a C-C bond in a typical organic molecule is -95 kcal mol^{-1}.

An inescapable conclusion is that the existence of large organic molecules at Earth's surface depends upon the presence of stratospheric ozone near current concentrations. Evidence is now incontrovertible that the halon fire extinguishants are an important vehicle for introducing atomic bromine catalysts for ozone decomposition into the stratosphere *(3).* **A** major reason that this can be is the long atmospheric lifetime of halons. We assert however that there is no necessary relationship between fire extinguishing ability and long atmospheric lifetime. The challenge therefore for identification of second-generation halon replacements is to find species that a) are good fire extinguishants and b) have short atmospheric lifetimes.

LIFETIME-LIMITING PROCESSES

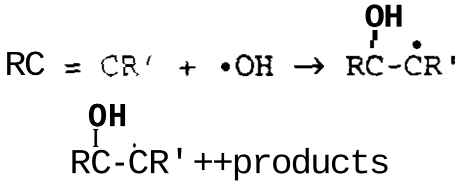
The primary lifetime-limiting processes for species in the troposphere are reaction with hydroxyl radical (OH), photolysis, and rain-out.

Although hydroxyl radical concentrations are extremely low, 10^5-10^6 radical cm^{-3}, they are highly reactive, typically reacting by abstraction of a hydrogen atom:

$$RH + {}^{*}\mathbf{OH} \rightarrow R\bullet + H_2O$$

$$R\bullet \text{ ++products}$$

or by addition to double bonds in unsaturated molecules:



$$RC = CR' + \bullet OH \rightarrow \overset{OH}{\overset{|}{RC}}-\dot{C}R'$$

$$\overset{OH}{\overset{|}{RC}}-\dot{C}R' \text{ ++products}$$

The reaction products are often soluble enough in water to be subsequently removed from the atmosphere by rain-out.

Many molecules undergo light-induced decomposition, photolysis, following absorption of ultraviolet radiation.

$$RX + h\upsilon \rightarrow RX \rightarrow R\bullet + X\bullet$$

$R\bullet$ -+-+products

Effective tropospheric photolysis requires dissociative absorption of W B light. This is a relatively unusual property for molecules.

Rain-out removal from the atmosphere requires appreciable water solubility *of* the species. This is an efficient process for inorganic (ionic) halides such as $NaCl$, HCl, $CaCl_2$, etc., but a low efficiency process for organic halides like halons, CFCs, etc. In the case of organic halides, removal is a multi-step process for which any step may be rate determining. The steps include transport to droplet surfaces, mass accommodation at the surface, saturation of the surface layer, and diffusion into the droplet **or** chemical reactions at the surface or within the droplet.

Lifetime-limiting processes of secondary importance are adsorption on particulates, hydrolysis, or reactions with other atmospheric species than $\bullet OH$.

There are several absorption mechanisms that may be important. These include sticky collisions with aerosol surfaces, physical absorption on cloud condensation nuclei, and adsorption on soils (which may be followed by microbiological degradation).

Many classes of organic compounds are subject to acid-catalyzed reactions with water (hydrolysis). For example, ethers may be hydrolyzed as follows:

$$R\text{-}O\text{-}R' + H20 \xrightarrow{H^+} ROH + R'OH$$

Commonly, the products are more water-soluble than are the reactants.

A few additional radicals occur in the atmosphere that may play a role in pollutant decomposition. There are low concentrations of $O(^1D)$ in the lower stratosphere which reacts as

$$RH + O(^1D) \rightarrow R\bullet + \bullet OH$$

or

$$R'Cl + O(^1D) \rightarrow R'\bullet + ClO\bullet$$

In the troposphere low concentrations are found of O_3 (7×10^{11} molecules cm^{-3}), NO (2.5×10^8 molecules cm^{-3}), NO_2 (2.5×10^8 molecules cm^{-3}), and H02 (10^9 molecules cm^{-3}). Generally, none of these is involved in the primary reaction step with halons.

CANDIDATE **FAMILIES**

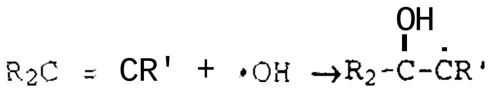
The question now becomes what families **of** chemicals are there that may be expected to have atmospheric lifetimes restricted by one or more of these mechanisms? We suggest three:

bromofluoroalkenes, fluoroiodocarbons, and polar-substituent bromocarbons.

The molecule $BrHC = CFCF_3$ is an example of a bromofluoroalkene Because this molecule has a hydrogen atom, it is reasonable to expect the primary degradation step to be tropospheric hydrogen abstraction by $\cdot OH$

$$RH + \cdot OH \rightarrow R\cdot + H20$$

or addition of $\cdot OH$ to the double bond



$$R_2C = CR' + \cdot OH \rightarrow R_2\text{-}\overset{OH}{C}\text{-}\dot{C}R'$$

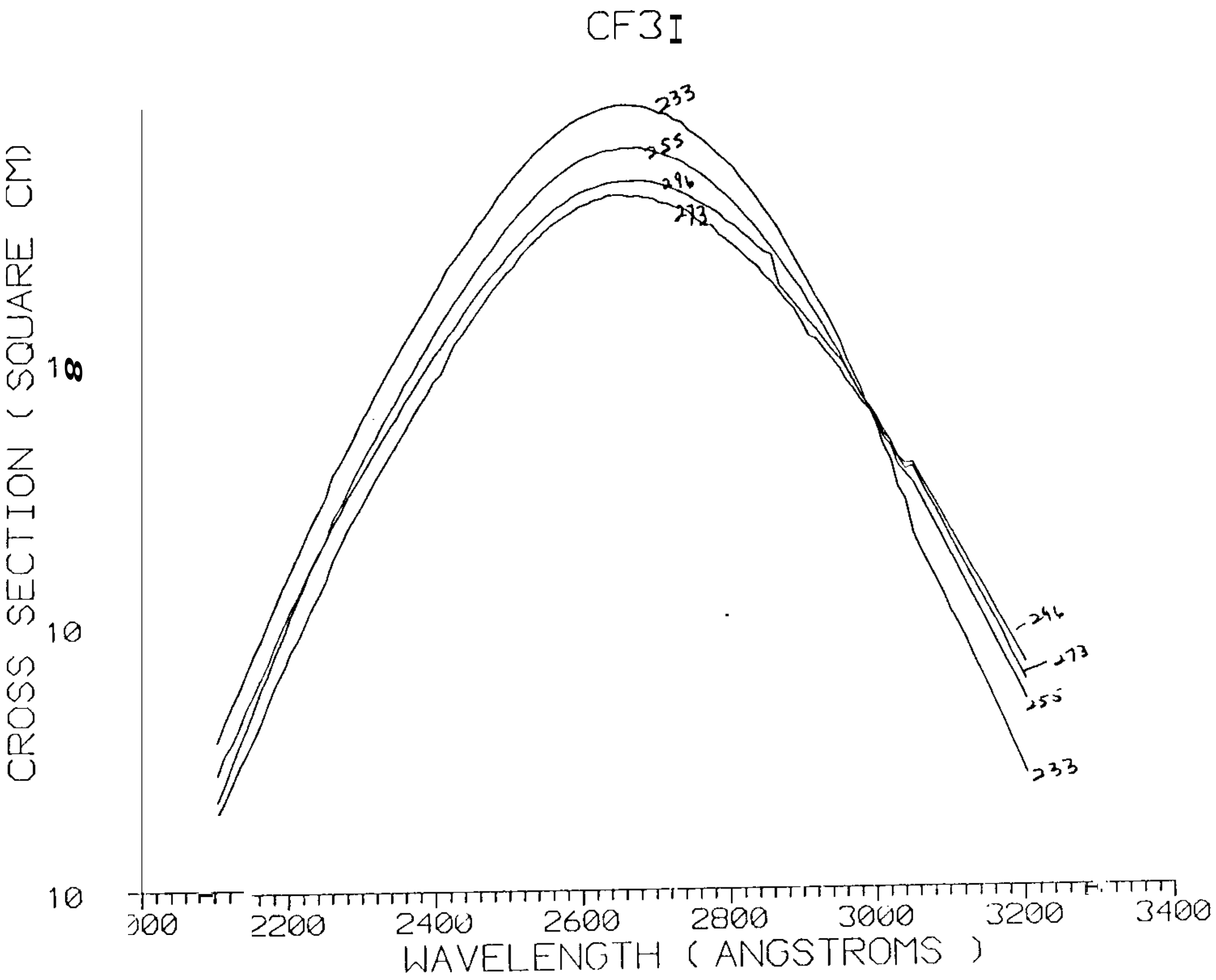
At the same time this species contains a bromine atom which appears to play an important role in fire extinguishment, perhaps by catalyzing hydrogen atom recombination (4). Furthermore, it is likely that molecules of this type will be subject to decomposition by one or more of the secondary degradation mechanisms. Specifically, the polarity may be high enough to make water solubility, and hence rain-out, a practical tropospheric removal pathway. The UV absorption may be shifted to long enough wavelengths so UVB radiation is absorbed, but uncertainties remain as to the probability of photolytic decomposition at these wavelengths (280-320 nm). Compounds such as shown may react readily with other trace radicals found in the troposphere.

Fluoroiodocarbons, e. *g.* CF_3I, contain a weakly bound halogen, iodine in this case, that can be thermally released to quench flames and at the same time have **W** absorption maxima shifted to longer wavelengths. Figure 1 shows the temperature dependence of the **W** absorption cross section for CF_3I. The maximum occurs near 260 nm and is still appreciable to 320 nm. The unstructured curve indicates photolysis, $CF_3I + h\nu \rightarrow CF3 + I$, occurs with a high quantum efficiency over the entire absorption band. Therefore, photolysis in the troposphere will be the primary degradation mechanism. Secondary removal mechanisms include reactions with OH throughout the troposphere and reactions with $O(^1D)$ in the lower stratosphere. A number of compounds are known in this class which cover a range of physical properties from gases to liquids at room temperature.

Polar-substituent bromocarbons refers to a group of substituted ethers, of which $CF_2H\text{-}OCF_2Br$ is an example. A number of the perfluorinated ethers exhibit good fire extinguishing properties and others have physiological applications, such as anesthetics. Upon modification as in the example, the polarity and reactivity may be adequate to make the primary tropospheric degradation mechanisms be rain-out or reaction with hydroxyl, $\cdot OH$. Another conceivable mechanism is acid catalyzed hydrolysis, possibly in or on sulfate aerosol surfaces:

$$ROR' + H20 \xrightarrow{H^+} ROH + R'OH$$

FIGURE 1: ABSORPTION CROSS SECTIONS FOR



CONCLUSION

The object of a search for second-generation halon requirements is to identify species that are good extinguishants while possessing the property of short tropospheric lifetimes. The primary lifetime-limiting mechanisms are reaction with ·OH, W photolysis, and rain-out. Three families of candidates suggested for further consideration and evaluation are bromofluoroalkenes, fluoroiodocarbons, and polar-substituent bromocarbons.

It is recommended that a systematic screening and evaluation program be initiated for these candidate families which in the first phase would include a) determination of W absorption cross sections and photodissociation efficiencies; b) kinetics of reactions with ·OH, $O(^1D)$, HO_2, H_2O...; c) determination of water solubility, Henry's law constants, and mass accommodation coefficients for aerosols.

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