Tropodegradable Bromocarbons as Halon Replacements

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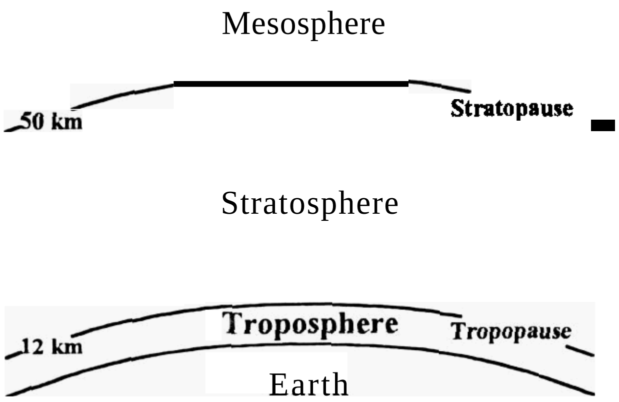
OVERVIEW

Despite the large ozone impact by bromine entering the stratosphere, stratospheric ozone depletion by bromocarbons can be made negligibly small by ensuring a sufficiently short tropospheric lifetime. With this in mind, we have been developing "tropodegradable" bromocarbons, compounds with lifetimes of hours to weeks, as potential halon replacements [1, 2]. Tropodegradable materials address three environmental problems simultaneously — ozone depletion, global warming, and atmospheric lifetime. In a continuing program, analysis of tropospheric sinks and modeling of physical and toxicological properties and fire suppression assessment have allowed us to target specific bromocarbons.

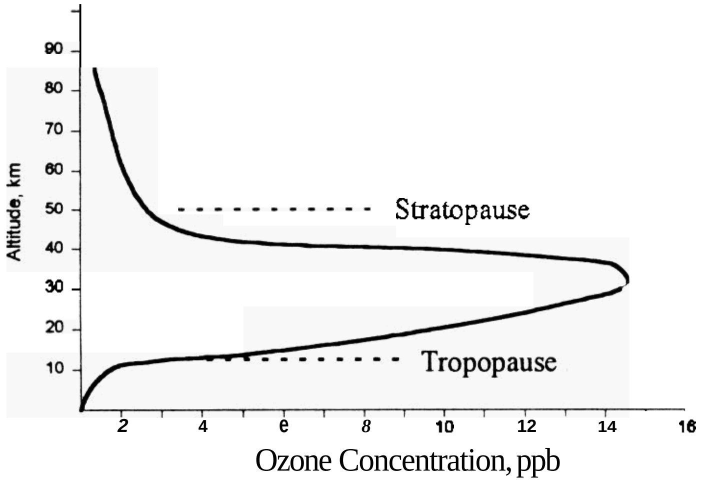
GLOBAL ENVIRONMENTAL PROBLEMS

Atmospheric Regions

Based on the locations of the atmospheric temperature changes, the earth's atmosphere can be divided into regions. The most important of these for the topics of interest here are the troposphere, the region nearest the earth's surface, and the stratosphere, the region containing most of the earth's protective ozone layer.



Ozone Depletion



The Ozone Depletion Potential (ODP) is a measure of the ability of a chemical to destroy stratospheric ozone. ODPs are the calculated ozone depletions per unit mass of material released relative to a standard, normally CFC-11 (CCl_3F). **A** chemical causing twice as much ozone depletion as CFC-11 would be assigned an ODP of **2.** ODPs are calculated; they cannot be measured. It is well established that bromine is much more damaging to ozone than is chlorine on a per atom basis. Exactly how much more, however, is not precisely known and lends some uncertainty to the ODPs of bromocarbons. Although ODPs **vary** somewhat depending on the calculation method, relative values for compounds containing the same ozone-depleting element are believed to be relatively reliable. Thus, ODPs of bromocarbons can be reliably compared with each other though not necessarily with ODPs of non-brominated compounds.

Atmospheric Lifetime

The atmospheric lifetime is a measure of how long a chemical remains in the atmosphere after release. Atmospheric lifetimes are generally modeled as “e-folding’’ lifetimes. The concentration decays exponentially following the equation $C_t = C_0e^{-t/L}$, where C_0 is the initial concentration, C_t is the concentration at any time t, and L is the atmospheric lifetime. After one lifetime, the gas concentration drops to 1/e (approximately 0.369) of its initial value. Note that according to this equation, the concentration never reaches zero, although it can approach zero very closely. For example, after **5** lifetimes, the concentration drops to 0.0067 of its initial value

Atmospheric lifetimes of halogenated organic chemicals can range from less than a day to thousands of years. ***As*** atmospheric lifetime decreases, the contribution to global warming generally decreases. Moreover, for those chemicals that can deplete stratospheric ozone (chemicals containing bromine and chlorine), a shorter atmospheric lifetime usually indicates a lower ODP. Finally, long atmospheric lifetimes are of concern even in the absence of global warming and ozone depletion effects since there is worry of unknown environmental impacts.

Global Warming

The Global Warming Potential (GW) is the calculated change in warming resulting from the emission of a unit mass of a chemical relative to that of a reference. In the past, CFC-11 was often used as the reference; carbon dioxide is now typically used. The GW depends on three variables: (1) the integrated infrared (IR) radiation absorption spectrum band strength, **(2)** the location of the IR bands, and **(3)** the atmospheric lifetime of the chemical emitted. The GW can vary significantly depending on the time period used for the comparison of the global warming of the chemical relative to that of the reference. The time period used to calculate the GWP is termed the "time horizon," and is primarily a policy decision. Time horizons of 100 and 500 years are often used in calculated GWP values; however, other time horizons may be more appropriate. **GWPs** with longer time periods are believed to be more inaccurate that those with shorter periods.

TROPODEGRADABILITY

We use the term "tropodegradable" for any compound with an atmospheric lifetime on the order of hours to weeks. Tropodegradable bromocarbons not only have extremely short tropospheric lifetimes, they have very low Ozone Depletion Potentials (ODPs) and Global Warming Potentials **(GWPs).** Note that we do exclude hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as tropodegradable compounds since the tropospheric removal processes for these compounds are comparatively inefficient and give atmospheric lifetimes that are longer than hours to weeks by at least an order of magnitude.

Trouosuheric Removal Mechanisms

Four primary processes exist for removal of organic molecules from the troposphere—(1) reaction with atmospheric hydroxyl free radicals, (2) photolysis, **(3)** physical removal, and **(4)** reaction with tropospheric ozone. Thermal and other processes may also remove highly reactive chemicals; however, sufficiently reactive chemicals are unlikely to be practical for most applications. Compounds can also be degraded by reaction with oxygen atoms in the ^{3}**P** and ^{1}D electronic states, NO„ nitric acid, and peroxy species. Analysis indicates that such reactions are unimportant tropospheric removal processes for the types of chemicals of interest here.

Reaction with Hvdroxvl Free Radicals

For the compounds of interest here, the hydroxyl free radicals can abstract a hydrogen atom and/or add to an unsaturated molecule to yield products (Reaction 1). The effectiveness of hydroxyl radical reactions in removing compounds from the atmosphere depends on the reaction rate constant (k_{OH}) and the atmospheric concentration of hydroxyl free radicals (•OH) [3]. The rate constant k_{OH} gives the time rate of change of the concentration of a compound C in the atmosphere due to reaction with •OH only (Equation **2)** and can be written as the sum of the rate constants for hydrogen atoms abstraction (k^1_{OH}) and for hydroxyl addition to an unsaturated compound (k^2_{OH}). The atmospheric half-life of a chemical for which the sole removal mechanism is reaction with hydroxyl free radicals is given by Equation **3.** Here, the hydroxyl radical concentration is taken to be constant. Equation **3** can be rewritten to yield the atmospheric lifetime (i.e., the e-folding lifetime) to give Equation 4. One can use Equation 4 to estimate lifetimes by assuming pseudo first-order behavior and using the globally averaged hydroxyl free radical concentration of **9.7 x** 10^5 molecules/cm^3 [4].

$$C + \bullet OH \xrightarrow{k_{OH}} \text{products} \qquad (1)$$

$$\frac{d[C]}{dt} = -k_{OH}[C][\bullet OH] \qquad [2]$$

$$t_{1/2} = \frac{\ln 2}{k_{OH}[\bullet OH]} \qquad (3)$$

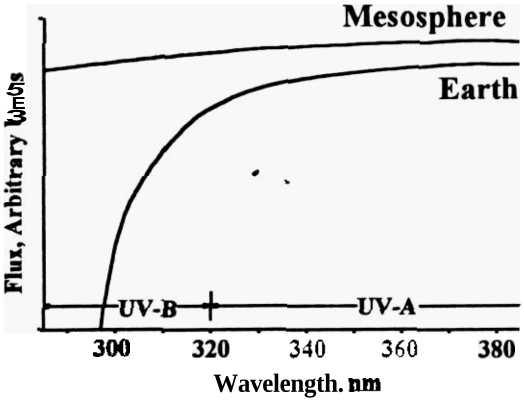
$$t_{1/e} = \frac{1}{k_{OH}[\bullet OH]} \qquad (4)$$

Photolysis

Photolysis requires absorption of electromagnetic radiation with resulting molecular decomposition. The photodecomposition reactions have the form shown in Reaction **5**, where the products are fragments of the original reactant molecule. Planck's constant (h) multiplied by the frequency of the electromagnetic radiation (v) gives the energy of a single photon of radiation with that frequency, and "hv" is often used as a symbol for a photon in a chemical equation. **As** the frequency of the electromagnetic radiation increases and the wavelength (λ) decreases, the energy per photon increases. Thus, shorter wavelength electromagnetic radiation, such as ultraviolet (UV), **is** usually more effective in effecting photodegradation than is longer wavelength radiation, such as visible and infrared (IR). Photolysis of a molecule depends on two parameters, the absorption cross section (σ)(which determines how much of the available light is absorbed) and the quantum yield (φ) (the fraction of the absorbed photons that affects photolysis). If every photon absorbed produces a reaction, $\varphi = 1$.

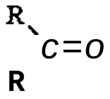
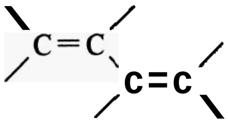
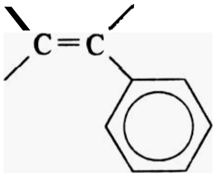
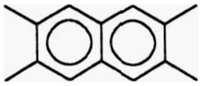
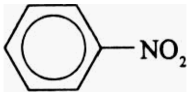
$$\text{Reactant} + hv \rightarrow \text{Products} \qquad (5)$$

Most organic compounds exhibit decreasing absorption cross sections as the radiation wavelength increases (at least for the ultraviolet and visible spectral regions). Since much of the lower wavelength, higher energy solar radiation is removed by stratospheric ozone before sunlight reaches the troposphere (particularly UV-B radiation, with wavelengths between 180 and 320 nanometers, many molecules do not encounter electromagnetic radiation of a sufficiently short wavelength for absorption until they reach the stratosphere. For example, the CFCs (chlorofluorocarbons) absorb little if any solar radiation required for photolytic decomposition as they pass through the troposphere. On the other hand, in the stratosphere, where short wavelength UV radiation is intense, the CFCs photodecompose to release chlorine.



Photodissociation in the troposphere requires that a compound absorb radiation in the wavelength range from **299** nm to **700** nm. The photodissociation rate constant k_{photo} is determined by Equation 6, where $\sigma(\lambda)$ is the absorption cross section as a function of the wavelength λ, $I(\lambda)$ is the solar intensity as a function of λ, and $\varphi(\lambda)$ is the photodissociation quantum yield. Thus, a chemical compound has two characteristics that determine the importance of photolysis: (1) the absorption cross section (how well it absorbs electromagnetic radiation encountered in the troposphere) and **(2)** the quantum yield. Both of these are **a** function of the electromagnetic radiation wavelength. The atmospheric lifetime for photodissociation only is then given by Equation 7.

$$k_{photo} = \int_{290\text{nm}}^{700\text{nm}} \sigma(\lambda)I(\lambda)\varphi(\lambda)d\lambda \tag{6}$$

		
		-Br or -I

require carbonyls, groups containing conjugated double bonds, bromine, or iodine to be present for there to be significant absorption and photodissociation in the troposphere (i.e., absorption for a = 299 nm to 700 nm). only fluorinated alkenes with tropospheric ozone is uncertain. For a globally averaged tropospheric ozone concentration of $[O_3] = 5.0 \times 10^{11}$ molecules/cm^3 and with a maximum rate constant of 2×10^{-16} cm^3/molecule-s [5], one can calculate a first-order reaction rate constant of $k_1 = (k_{O3})[O_3] = 1 \times 10^{-4}$. The determination of this rate constant allows a calculation for the atmospheric lifetime of $t_{1/e} = 1/k_1 = 10^4$ seconds or less than one day. Thus, removal by tropospheric ozone could be significant for alkenes.

Trouosuheric Removal

A rate constant can be assigned to each of these processes—k_{OH} for reaction with hydroxyl free radicals, $k_{physical}$ for physical removal, k_{photo} for photolysis, and k_{O3} for reaction with tropospheric ozone. The rate constants vary with the chemical being removed from the troposphere and the atmospheric location of the chemical (which determines the hydroxyl free radical concentration, temperature, and solar flux). **As** an approximation, one can use, for all but k_{photo}, globally averaged rate constants. ***An*** overall pseudo first-order* rate constant k_1 can be written, where $k_1 = k_{OH}[\bullet OH] + k_{physical} + k_{photo} + k_{O3}[O_3]$, $[.OH]$ is a globally averaged tropospheric hydroxyl free radical concentration, and $[O_3]$ is the globally averaged tropospheric ozone concentration. The rate constant allows calculation of the time rate of change of the atmospheric concentration of a compound C as shown in Equation 8. The atmospheric lifetime $(t_{1/e})$ is then given by $t_{1/e} = 1/k_1$.

$$\frac{d[C]}{dt} = -k_1[C] \tag{8}$$

CHEMICAL FEATURES LEADING TO LOW TROPOSPHERIC LIFETIMES

Calculations indicate that abstraction of hydrogen atoms from simple haloalkanes will not provide the short lifetimes targeted for tropodegradable halocarbons. There is evidence, however, that hydrogens on carbon atoms adjacent to nitrogen and oxygen have enhanced hydroxyl reaction rate constants. Thus, when coupled with photolytic degradation due to the presence of bromine, this effect could provide short lifetimes for hydrobromoamines and hydrobromoethers containing hydrogen atoms on alpha carbons. Calculations and some data indicate that unsaturated halocarbons such as arenes and alkenes will have atmospheric lifetimes on the order of days due to hydroxyl addition.

Most organic compounds exhibit decreasing absorption cross sections as the radiation wavelength increases (at least for the ultraviolet and visible spectral regions). Since much of the lower wavelength, higher energy solar radiation is removed by stratospheric ozone before sunlight reaches the troposphere (particularly W - B radiation, with wavelengths between 180 and **320** nanometers), many molecules do not encounter electromagnetic radiation of a sufficiently short wavelength for absorption until they reach the stratosphere. In general, halocarbons require one

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'Pseudo first-order behavior assumes that the concentration of the hydroxyl free radical or tropospheric ozone remains constant and can be "averaged" into the second-order rate constants to give a pseudo first-order rate constant (k_1).

of the groups shown here to be present for there to be significant absorption and photodissociation in the troposphere (i.e., absorption for $\lambda = 299$ to 700 nm).

Rainout could be significant for highly water-soluble compounds such as alcohols, amines, and carbonyl compounds (esters, carboxylic acids, aldehydes, ketones); however, substitution with fluorine greatly decreases the solubility and, consequently, the rainout. Reaction with tropospheric ozone is likely to provide an exceedingly effective tropospheric sink for alkenes giving atmospheric lifetimes on the order of days or less.

Primary Removal Mechanism	Families
hydroxyl reaction	alkenes, aromatics, amines and ethers with hydrogen atoms on alpha carbons
photolysis	esters, carboxylic acids, ketones, aldehydes
physical removal	ketones, alcohols, some esters
tropospheric ozone reaction	alkenes

TROPODEGRADABLE BROMOCARBONS

We have been examining bromocarbons containing appropriate functional groups for the molecular design of tropodegradable bromocarbons. Use of ODP prediction algorithms indicate that these compounds have ODPs of 0.02 or lower (often considerably lower). For unsaturated compounds, we have calculated estimated lifetimes of a few days.

Connection of appropriate functional groups to a group containing bromine, allows the molecular design of tropodegradable bromocarbons. Most of the materials are highly fluorinated (to decrease flammability and hepatotoxicity), but in many cases are not completely fluorinated. Use of ODP prediction algorithms indicate that these compounds have ODPs of 0.02 or lower (often considerably lower. The use of Quantitative Structure Activity Relationships (QSARs) and related techniques have allowed the prediction of toxicological characteristics for many compounds, though this process is still under way and the QSAR methodologies are being refined. Models also allow the prediction of unknown physical properties, and models still under construction allow prediction of azeotropic compositions for blends.

Testing shows that a number of alkenes, aromatics, and alcohols have excellent flame suppression capabilities (vapor-phase extinguishment concentrations of around 3 to 4 percent), though alcohols are the poorest of this group. Of particular interest (and concern) is that the flame extinguishment abilities of unsaturated compounds vary widely, and, so far, we have been unable to make reliable predictions. Some compounds are highly efficient while others are actually flammable. For example, chloropentafluorobenzene (C_6F_5Cl) is a flame extinguishant whereas the bromo- and fluoro derivatives (C_6F_5Br and C_6F_6) are flammable. Unsaturated materials are, of course, ideal for incorporation into certain polymeric systems and, even though they may lose their unsaturation when incorporated, should pose no atmospheric environmental threat in the matrix.

Use of these procedures and prediction platforms have allowed identification of highly promising replacements for halons used in fire and explosion protection. We have developed methods for estimating (with a high degree of accuracy) the fire extinguishing effectiveness of halocarbons for some scenarios, and have made use of this technology to prioritize compounds for our current testing program. Models for effectiveness in other applications are being developed.

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