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# Tropodegradable fluorocarbon replacements for ozone-depleting and global-warming chemicals

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## Abstract

Incorporation of certain molecular features into fluorocarbons can decrease the tropospheric lifetime, providing commercially applicable chemicals with low global warming and stratospheric ozone impacts.

*Keywords:* Global warming; Ozone depletion; Atmospheric lifetime; Fluorocarbons

## 1. Introduction

On 16 September 1987 in Montreal, Canada, the Montreal Protocol on Substances that Deplete the Ozone Layer was agreed to by 47 countries, of which 24 immediately signed. The Protocol, which establishes controls on the production and consumption of ozone depleting materials, went into force on 1 January 1989, and has now been ratified by more than 150 nations. The initial Protocol covered only chlorofluorocarbons (CFCs) and halons, but has since been extended to include other halocarbons, including hydrochlorofluorocarbons (HCFCs) and hydrobromofluorocarbons (HBFCs).

More recent was the adoption on 11 December 1997 of the Kyoto Protocol to the United Nations Framework Convention on Climate Change. When this regulation enters into force, two of the families of chemicals proposed for replacement of halocarbons restricted under the Montreal Protocol — hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) — will also be regulated due to atmospheric lifetime and global warming concerns.

As a result of these international environmental regulations, many of the fluorocarbon chemicals of greatest industrial importance are or will be subject to restriction [1]. One approach that addresses restrictions under both the Montreal and Kyoto Protocols is the development of fluorine-containing chemicals with extremely short atmospheric lifetimes (tropodegradable fluorocarbons). We apply the term "tropodegradable" to compounds with an atmospheric lifetime on the order of hours to a few weeks, lifetimes that we have targeted in hopes of avoiding future problems due to increasingly stringent environmental regulations. Tropodegradable fluorocarbons simultaneously address three environmental concerns — ozone depletion, global warming, and atmospheric lifetime. We recognize, of course, that shortened lifetimes may increase terrestrial environmental problems of local atmospheric pollution. Some tropodegradable fluorocarbons have promise as replacements for ozone-depleting and global-warming fluorocarbons in such applications as fire protection, cleaning, refrigeration, and foam blowing.

## 2. Tropospheric removal processes

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. We have not considered removal by thermal processes since highly reactive species subject to such processes are unlikely to have toxicological and stability characteristics making them suitable for most commercial applications. Some chemicals can also react with such atmospheric species as oxygen atoms in the $^3P$ and $^1D$ electronic states, $NO_x$, nitric acid, and peroxy species. Such reactions are relatively minor tropospheric degradation processes for most chemicals of commercial interest.

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### 2.1. Hydroxyl reactions

All compounds containing a hydrogen atom can undergo hydrogen atom abstraction reactions with tropospheric hydroxyl free radicals (•OH) (Reaction 1) [2].

$$\mathrm{RH} + {}^{\bullet}\mathrm{OH} \overset{k_{\mathrm{OH}}^{1}}{\rightarrow} {}^{\bullet}\mathrm{R} + \mathrm{H_2O} \qquad \text{(Reaction 1)}$$

CFCs have no hydrogen atoms and undergo little, if any, reaction with $^{\bullet}$OH in the atmosphere and, therefore, have long atmospheric lifetimes and high ozone depletion potentials (ODPs). The HCFCs and HFCs, which are CFC replacements, do undergo hydrogen atom abstraction by tropospheric hydroxyl free radicals, though this is not sufficiently rapid to give the ODPs desired for the HCFCs or the global warming potentials (GWPs) desired for the HFCs since are both regulated or proposed for regulation under the Montreal or Kyoto Protocols.

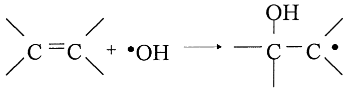
The organic free radical $^{\bullet}$R formed in Reaction 1 rapidly reacts with diatomic oxygen ($O_2$) to form a peroxy radical (ROO$^{\bullet}$), which further reacts to give a series of products. In most cases, these final products are rapidly removed by physical processes so that they do not contribute significantly to ozone depletion or global warming.

For most saturated haloalkanes, Reaction 1 is too inefficient to give tropodegradable compounds as defined here (compounds with atmospheric lifetimes on the order of days or weeks). This can be seen in the atmospheric lifetimes of 0.4–19.5 years for common HCFCs and from 1.5–250 years for common HFCs [3]. Hydrogen atom abstraction by atmospheric hydroxyl free radicals is the primary tropospheric removal process for both HCFCs and HFCs.

Note, however, that Reaction 1 is more rapid for many compounds other than the normal haloalkanes. The activation energy for hydrogen atom abstraction decreases and the reaction rate with hydroxyl free radicals increases (as expected) with decreasing dissociation energy of the C–H bond [4,5]. For example, for a wide range of compounds, replacement of either a fluorine atom or a hydrogen atom by an oxygen atom alpha to a CH group decreases the bond dissociation energy and increases the reaction rate (decreasing the atmospheric lifetime). Thus, aldehydes, (RC(O)H) react sufficiently rapidly (Reaction 2) that they have atmospheric lifetimes on the order of days [6,7]. A similar phenomenon is seen for alcohols. Beta substitution generally has a much lower substituent effect on bond dissociation energies [8].

$$\mathrm{RC(O)H} + {}^{\bullet}\mathrm{OH} \quad \rightarrow {}^{\bullet}\mathrm{CR(O)} + \mathrm{H_2O} \qquad \text{(Reaction 2)}$$

$^{\bullet}$OH free radicals can also add to unsaturated organics — alkenes, alkynes, and aromatics — effecting a highly effective removal process. For alkenes, the hydroxyl radical adds to give a highly energetic product radical (Reaction 3). If it does not lose another group, the energetic product can then either revert back to reactants, or it can be stabilized by collision with another molecule, which can carry off the excess energy.



(Reaction 3)

The rate equation (Eq. (1)) for reaction of •OH with atmospheric contaminants (Reaction 4), where $k_{\mathrm{OH}}$ is the sum of the rate constants for hydrogen atom abstraction $\left(k_{\mathrm{OH}}^{1}\right)$ and for hydroxyl addition $\left(k_{\mathrm{OH}}^{2}\right)$, is pseudo first-order if the atmospheric hydroxyl free radical concentration can be averaged. This allows derivation of Eq. (2) to estimate the $e$-folding atmospheric lifetime of a chemical (the time required to reach $1/e$ of its initial concentration) for which $^{\bullet}$OH provides the sole removal mechanism [9]. The globally averaged tropospheric hydroxyl free radical concentration has been reported as $9.7 \times 10^5$ molecules/cm$^3$ [10].

$$\mathrm{C} + {}^{\bullet}\mathrm{OH} \overset{k_{\mathrm{OH}}}{\rightarrow} \text{products} \qquad \text{(Reaction 4)}$$

$$\frac{\mathrm{d[C]}}{\mathrm{d}t} = -k_{\mathrm{OH}}[\mathrm{C}][{}^{\bullet}\mathrm{OH}], \tag{1}$$

$$t_{1/e} = \frac{1}{k_{\mathrm{OH}}[{}^{\bullet}\mathrm{OH}]}. \tag{2}$$

### 2.2. Photolysis

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 nm), many molecules do not encounter electromagnetic radiation of a sufficiently short wavelength for absorption until they reach the stratosphere. For example, the CFCs 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 to 700 nm [11]. The photodissociation rate constant $k_{\mathrm{photo}}$ is a function of the absorption cross section as a function of the wavelength $\lambda$, $\sigma(\lambda)$; the solar intensity as a function of $\lambda$, $I(\lambda)$; and the photodissociation quantum yield, $\varphi(\lambda)$ (Eq. (3)). The atmospheric lifetime for photodissociation only is then given by Eq. (4).

$$k_{\mathrm{photo}} = \int_{290\,\mathrm{nm}}^{700\,\mathrm{nm}} \sigma(\lambda) I(\lambda) \varphi(\lambda) \mathrm{d}\lambda, \tag{3}$$

$$t_{1/e} = 1/k_{\mathrm{photo}}. \tag{4}$$

In general, halocarbons require one of the groups carbonyl, nitrosyl, bromine, or iodine or conjugated multiple bonds for significant photodissociation in the troposphere (i.e., absorption for $\lambda = 299$–$700$ nm).

### 2.3. Physical removal processes

Physical removal processes include (1) rainout (absorption by water droplets), (2) aerosol scavenging, and (3) solution into oceans [11]. The science of physical removal lags far behind that of the other tropospheric removal processes, and much is qualitative.

#### 2.3.1. Rainout

Rainout is a highly effective tropospheric removal mechanism for polar compounds such as hydrogen halides. For highly hydrophilic compounds such as nitric acid, the global time constant for rainout is about 7 days [12]. As the polarity of a compound decreases, physical removal by water absorption becomes less and less effective.

Eq. (5) has been proposed to estimate the atmospheric lifetime for rainout [13]. Here, $\alpha$ is the solubility coefficient defined by Eq. (6). The saturation vapor density is the density of vapor in equilibrium with liquid at a particular temperature (which can be taken as 298 K). Rainout could be significant for highly water soluble compounds (large values of $\alpha$) such as alcohols, amines, and carbonyl compounds (esters, carboxylic acids, aldehydes, ketones); however, substitution with fluorine will greatly decrease the solubility and, consequently, the rainout. For the relatively nonpolar CFCs, HCFCs, HFCs, and PFCs of commercial interest, the water solubility is sufficiently low and the vapor pressure sufficiently high that tropospheric rainout is negligible. For example, HCFCs (probably the most polar of these materials) have Henry's law constants around 100 L atm/mol [14] corresponding to values of around $10^{-3}$ for $\alpha$ and $t_{1/e}$ values of $10^6$ years.

$$t_{1/e} \approx \frac{8000}{\alpha}\,\text{years}, \tag{5}$$

$$\alpha = \frac{\text{solubility (g/L)}}{\text{saturation vapor density (g/L)}}. \tag{6}$$

#### 2.3.2. Aerosol scavenging

Aerosol scavenging involves adsorption of a chemical onto solid particulates. Eq. (7) has been advanced to predict the atmospheric lifetime due to aerosol scavenging [13]. Here, $P_{\text{vap}}$ is the vapor pressure of a compound in torr at 298 K. For adequate tropodegradability of the compounds of interest in this project, the atmospheric lifetime should be less than one month ($2.625 \times 10^6$ s). Solving for the $P_{\text{vap}}$ required to achieve this, one obtains $P_{\text{vap}} = 1.625 \times 10^{-7}$ torr. This vapor pressure is far too low for any halocarbon sufficiently volatile to be considered for use in most CFC and halon applications.

$$t_{1/e} = 10^6(10^7 P_{\text{vap}} + 1)\ \text{seconds}. \tag{7}$$

#### 2.3.3. Solution into oceans

The lower limit for the tropospheric lifetime due to absorption (solution) into oceans can be estimated by Eq. (8) [15]. Here $\beta$ is the (ocean) water solubility of a gas in moles/m$^3$ atm (essentially, a Henry's law constant), $D$ the molecular diffusivity of a gas in water in m$^2$/year [16], and $z$ the film thickness in the classical stagnant film model for gas exchange. The film thickness is approximately $30 \times 10^{-6}$ m, and an upper limit on diffusivity at 298 K (giving a lower limit on the lifetime) is approximately $6 \times 10^{-5}$ cm$^2$/s ($1.9 \times 10^{-1}$ m$^2$/year) [15]. This gives an upper limit on $D/z$ of $6 \times 10^3$ m/year and a lifetime with a lower bound given by Eq. (9). This is a lower bound to the atmospheric lifetime, which is not only because a particularly large value was placed on $D/z$, but also because of release from the ocean back into the atmosphere, a process not taken into account in this approximation. To obtain a lifetime of less than one month by this process, one needs compounds with a water solubility greater than 60 moles/m$^3$ atm. This is a rather large solubility. For example, the solubility of carbon dioxide, a highly water soluble gas, is only about 40 moles/m$^3$ atm [15]. There is a possibility that ocean solubility could play some role in removal of carbonyl compounds and alcohols, but the contribution is likely to be small.

$$t_{1/e} = \frac{3 \times 10^5}{\beta D/z}, \tag{8}$$

$$t_{1/e} \geq \frac{50}{\beta}\ \text{years}. \tag{9}$$

### 2.4. Reaction with tropospheric ozone

The only chemicals exhibiting rapid reaction with tropospheric ozone are the alkenes. The mechanisms of these reactions are not well understood, and the potential for reaction of highly 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 $2 \times 10^{-16}$ cm$^3$/molecule s [11], one can calculate a first-order reaction rate constant of $k_1 = (k_{O_3})[O_3] = 1 \times 10^{-4}$. The determination of this rate constant allows a calculation for the atmospheric lifetime of $t_{1/e} = 1/k_1 = 10^4$ s or less than one day. Thus, removal by tropospheric ozone could be significant for alkenes.

## 3. Atmospheric lifetimes and tropodegradable compounds

For each process considered, a rate constant can be determined or estimated — $k_{\text{OH}}$ for reaction with hydroxyl

Table 1
Tropodegradable compounds

| Primary removal mechanism | Families |
|---|---|
| Hydroxyl reaction | Alkenes, aromatics, amines and ethers, particularly with hydrogen atoms on carbon atoms alpha to nitrogen or oxygen |
| Photolysis | Esters, carboxylic acids, ketones, aldehydes |
| Physical removal | Ketones, alcohols, some esters |
| Tropospheric ozone reaction | Alkenes |

Table 2
Toxicological results

| Formula | Number of rat deaths |
|---|---|
| $CH_2{=}CBrCF_3$ | 0 |
| $CHBr{=}CHCF_3$ | 0 |
| $CH_2{=}CHCBrF_2$ | 7 |
| $CH_2{=}CHCF_2CBrF_2$ | 0 |
| $CH_2{=}CBrCF_2CF_3$ | 0 |
| $CH_2{=}CBr(OCF_3)CFCF_3$ | 10 |
| $CH_2{=}CBrCF_2CF_2CF_3$ | 1 |
| $CH_2{=}CBrCFC(CF_3)_2$ | 10 |

free radicals, $k_{\text{physical}}$ for physical removal, $k_{\text{photo}}$ for photolysis, and $k_{O_3}$ 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 $k_{\text{photo}}$, globally averaged rate constants. An overall pseudo first-order rate constant $k_1 = k_{\text{OH}}[^{\bullet}\text{OH}] + k_{\text{physical}} + k_{\text{photo}} + k_{O_3}[O_3]$. Here, $[^{\bullet}\text{OH}]$ is a globally averaged tropospheric hydroxyl free radical concentration ($9.7 \times 10^5$ molecules/cm$^3$), and $[O_3]$ is the globally averaged tropospheric ozone concentration ($5.0 \times 10^{11}$ molecules/cm$^3$). The rate constant allows calculation of the time rate of change of the atmospheric concentration of a compound C as shown in the following equation. The atmospheric lifetime ($t_{1/e}$) is then given by $t_{1/e} = 1/k_1$.

$$\frac{\text{d}[\text{C}]}{\text{d}t} = -k_1[\text{C}].$$

We have calculated or approximated rate constants for the various removal processes. These analyses identify the families shown in Table 1 as the most promising tropodegradable materials. Of particular interest is that the location of the hydrogen atom in fluoroalkyl amines and fluoroalkyl ethers is very important in determining the atmospheric lifetime. Thus, hydrogen atoms attached to carbon atoms adjacent to oxygen in ethers or adjacent to nitrogen in amines appear to be particularly susceptible to abstraction by hydroxyl free radicals.

We are now investigating the use of these materials as replacements for ozone-depleting and global-warming fluorocarbons in a number of applications including fire protection, cleaning, refrigeration, and foam blowing. One major problem is that introduction of the required functional groups often decreases volatility. Thus, many of these materials are more applicable to applications such as solvents and fire protection, where higher boiling points may be acceptable. Nevertheless, a significant number of compounds have volatilities sufficient to be considered in applications such as refrigeration.

Of particular interest are the fluorine-containing alkenes, which have exceedingly short atmospheric lifetimes. We have been investigating the use of bromofluoroalkenes, both as replacements for halons, and as additives to reduce flammabilities of normally flammable solvents, foam blowing agents, and refrigerants. Little toxicity data are available for such compounds; however, we have carried out inhalation limit tests on eight bromofluoroalkenes, exposing groups of 10 rats to concentrations of 5% by volume for 30 min. The results are shown in Table 2. Even at this extremely high concentration, half of the compounds tested showed no lethality.

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