NMERI 97/29/33010

IDENTIFICATION AND PROOF TESTING OF NEW TOTAL FLOODING AGENTS: TOXICITY AND GLOBAL ENVIRONMENTAL ASSESSMENT

Robert E. Tapscott, Everett W. Heinonen, and J. Douglas Mather

Center for Global Environmental Technologies
NEW MEXICO ENGINEERING RESEARCH INSTITUTE
The University of New Mexico
901 University Boulevard SE
Albuquerque, New Mexico 87106-4339

Interim Report, February 1997 - August 1997

February 1998

Sponsored by:

The Department of Defense
Strategic Environmental Research and Development Program

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
27 Feb 1998

3. REPORT TYPE AND DATES COVERED
Interim Report, 3 Feb 97 - 31 Aug 97

4. TITLE AND SUBTITLE
Identification and Proof Testing of New Total Flooding Agents: Toxicity and Global Environmental Assessment

5. FUNDING NUMBERS
C MDA972-97-M-0011

6. AUTHOR(S)
Robert E. Tapscott, Everett W. Heinonen, and J. Douglas Mather

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
New Mexico Engineering Research Institute
The University of New Mexico
Albuquerque, New Mexico 87106-4339

8. PERFORMING ORGANIZATION REPORT NUMBER
NMERI 97/29/33010

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
The Department Of Defense
Strategic Environmental Research and Development Program

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11 SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Under the Montreal Protocol, an international treaty, the production of the fire and explosion protection agent Halon 1301 (bromotrifluoromethane, BFC-13B1, $CBrF_3$) was phased out in the United States at the end of 1993. No environmentally acceptable halon substitute that is equivalent to the existing halons in toxicity, effectiveness, and dimensionality has been identified. The objective of the overall effort is to reassess the higher volatility chemicals in the families of phosphorus compounds (with particular attention paid to phosphorus nitrides), silicon compounds (in particular, silanes and siloxanes), fluorinated amines and ethers, and other nonhalocarbons that might be appropriate for Halon 1301 replacement applications. The toxicities, atmospheric lifetimes, ozone depletion potentials (ODP), and global warming potentials (GWP) have been assessed for compounds in these families, and the results are presented in this report. Compound procurement, combustion suppression, and laboratory studies are the subject of another report.

14. SUBJECT TERMS
ozone depletion potential; ODP; global warming potential; GWP; toxicity; amines; phosphorus nitrides; silanes; siloxanes; ethers; fire extinguishment

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unclassified

NSN 7540-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18

PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico, for the Department of Defense, Strategic Environmental Research and Development Program (SERDP), under Contract MDA972-97-M-0011, NMERI Number 8-33010.

The Start Date was 3 February 1997, and the End Date is 2 February 1998. The Technical Program Manager is Dr. Richard G. Gann, National Institute of Standards and Technology; the Contracting Officer's Technical Representative (COTR) is Dr. Andrzej W. Miziolek, Army Research Laboratory, and the NMERI Principal Investigator is Dr. Robert E. Tapscott.

NMERI 97/29/33010

SUMMARY

A. TASK OBJECTIVES

The objective of the overall effort is to assess the higher volatility chemicals in the families of phosphorus compounds (with particular attention paid to phosphorus nitrides), silicon compounds (in particular, silanes and siloxanes), fluorinated amines and ethers, and other nonhalocarbons that might be appropriate for Halon 1301 replacement applications. The present report on work performed from February 1997 through August 1997 covers the overall assessment of toxicological and environmental characteristics. Compound procurement, combustion suppression, and laboratory studies are the subject of another report.

B. GENERAL METHODOLOGY

This project involves four tasks.

1. The toxicities, Ozone Depletion Potentials (ODP), and Global Warming Potentials (GWP) of phosphorus nitrides, silanes, siloxanes, fluorinated amines and ethers, and other nonhalocarbons that might be appropriate for Halon 1301 applications will be reviewed and/or estimated. Estimation techniques will include Quantitative Structure Activity Relationships for toxicity; estimated or known hydroxyl free radical rate constants with globally averaged atmospheric hydroxyl radical concentrations for lifetimes; estimation methods for conversion of lifetimes to ODP and GWP based on data fitting to known values; and estimation of physical removal and photolytic removal based on chemical and physical properties.

2. Specific compounds will be selected for study based on the information obtained in Task 1. Compounds not readily available will be synthesized. To the extent practical, sufficient quantities of synthesized compounds to permit other researchers to examine the materials will be prepared.

3. Cup-burner flame extinguishment evaluations will be performed using the New Mexico Engineering Research Institute (NMERI) Standard Cup Burner. Some determinations may also be performed using the International Standards Organization (ISO) cup burner. As

resources allow, sufficient quantities of the chemicals tested under this program will be provided to other laboratories for testing using opposed-flame burners or similar apparatuses.

4. The information obtained in the above tasks will be assessed to develop a list of optimal candidate Halon 1301 replacement agents. The criteria for this list will be based primarily on (1) predicted toxicity, (2) synthesis and manufacturability, (3) ODP and GWP, and (4) fire suppression and inertion effectiveness.

This report covers only the first task.

C. TECHNICAL RESULTS

A large amount of global environmental data, that has, as far as is known, been compiled elsewhere was obtained. In particular, considerable information is available on ethers related to compounds of interest to fire extinguishment. Little environmental data were, however, available for relevant compounds in the other families examined.

Although the toxicity data are available for phosphorus compounds, most of the information is on compounds of little interest as fire extinguishants or as parent compounds for fire extinguishants.

A general procedure for environmental screening of compounds was developed.

D. IMPORTANT FINDINGS AND CONCLUSIONS

It is highly unlikely that phosphorus compounds will create any global environmental problems. Atmospheric lifetimes are expected to be sufficiently short that global warming and ozone depletion (even with bromine substitution) would be negligible.

The large variability in toxicity of phosphorus compounds and the possibility of cholinesterase inhibition causes toxicity concerns with these compounds. It appears that toxicity tends to decrease as the oxidation state of the phosphorus decreases (i.e., phosphines are generally the most toxic and phosphates are the least toxic). Phosphonitriles appear to have relatively low toxicities, but mutagenicity may be of concern. Compounds with P-halogen bonds are probably unacceptable as halon substitutes.

Silicon compounds are expected to have few, if any, global atmospheric impacts. This may be the case even when bromine is present. There is, however, a real need for studies of the photochemistry of bromine-containing silicon compounds.

Little toxicity data are available on silicon compounds of interest as halon substitutes. On the other hand, many silicon compounds, particularly esters and siloxanes, are expected to have low toxicity. As in the case of phosphorus, compounds containing Si-halogen bonds are probably unacceptable as halon substitutes.

Totally fluorinated amines could cause atmospheric lifetime and global warming problems. On the other hand, amines with partial fluorination are likely to have relatively short atmospheric lifetimes. It is difficult, however, to determine whether the lifetime would be sufficiently short to allow bromine substitution.

Simple alkyl-substituted amines range from nontoxic in the case of totally fluorinated compounds to highly toxic for nonfluorinated materials. A major question is how the toxicity varies with partial fluorine substitution.

The ether linkage enhances reactivity toward hydroxyl free radicals and, therefore, leads to lower atmospheric lifetimes. On the other hand, this is somewhat offset by fluorine substitution. It is possible that bromine substitution would be allowable; however, ethers are not as easily removed from the atmosphere as are amines, for example, and bromine substitution may lead to unacceptable ozone depletion potentials.

The toxicity of ethers is relatively low compared to other materials evaluated in this report. Furthermore, the ether linkage has a relatively low biological and chemical reactivity.

E. SIGNIFICANT HARDWARE DEVELOPMENTS

No hardware has been developed as part of this project.

F. SPECIAL COMMENTS

There are no special comments for this stage of the project.

G. IMPLICATIONS FOR FURTHER RESEARCH

A number of areas have been identified in this study for future research. Information is needed on photolysis of bromine-containing silicon compounds and on rate constants for reaction of bromine-containing amines with hydroxyl free radicals. A general study of the variation in toxicity as fluorination increases in trialkylamines is also needed.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

BCC	Business Communications Company
CAS	Chemical Abstracts Service (American Chemical Society)
CFC	chlorofluorocarbon
CGET	Center for Global Environmental Technologies
COTR	Contracting Officer’s Technical Representative
DMMP	dimethyl methylphosphonate
DNA	deoxyribonucleic acid
EPA	U. S. Environmental Protection Agency
GWP	global warming potential
HFA	hydrofluoroamine
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFE	hydrofluoroether
HFPE	hydrofluoropolyether
HOMO	highest occupied molecular orbital
HR	SAX Hazard Rating
NIRI	National Industrial Research Institute
NMERI	New Mexico Engineering Research Institute
ISO	International Standards Organization
ODP	ozone depletion potential
QSAR	Quantitative Structure-Activity Relationship
RTECS	Registry of Toxic Effects of Chemical Substances
TMP	trimethylphosphate
USIC	United States Industry Coalition, Inc.

LIST OF UNITS AND SYMBOLS

cp	centipoise
cm	centimeter
D	molecular diffusivity of a gas in water
g	gram
GWP_{max}	maximum allowable GWP
hr	hour
$h\nu$	photon
K	degree Kelvin
k	reaction rate constant
kg	kilogram
k_{hyd}	rate constant for hydrolysis
k_{other}	second-order rate constant for reaction with species other than O_3 and •OH
k_{OH}	second-order rate constant for reaction with •OH
k_{O3}	second-order rate constant for reaction O_3
k_1	first-order reaction rate constant
k_2	second-order reaction rate constant
kJ	kilojoule
L	liter
LC_{LO}	lowest concentration causing death
LC_{50}	concentration required to cause death in 50 percent of an animal test population
LD_{LO}	lowest dose causing death
LD_{50}	dose required to cause death in 50 percent of an animal test population
m	meter
mg	milligram
mL	milliliter
ODP_{max}	maximum allowable ODP
P_{max}	maximum allowable vapor pressure in screening
P_{vap}	vapor pressure
ppb	parts per billion
ppm	parts per million

LIST OF UNITS AND SYMBOLS (concluded)

s	second
t_{hyd}	atmospheric lifetime due to hydrolysis
t_{max}	maximum allowable tropospheric lifetime
t_{other}	tropospheric lifetime due to reactions other than with tropospheric ozone and •OH
t_{OH}	tropospheric lifetime due to reaction with •OH
t_{O3}	tropospheric lifetime due to reaction with tropospheric ozone
t_{phot}	tropospheric lifetime due to photolysis
t_{phys}	tropospheric lifetime due to physical removal
$t_{1/e}$	e-folding atmospheric lifetime
α	solubility coefficient
β	Henry's law constant in moles/m^3-atm
ΔH_f	enthalpy of formation
ΔH_r	enthalpy of reaction
ΔG_f	free energy of formation
ΔG_t	free energy of reaction
$\sigma_{IR}(\lambda)$	IR absorption cross section as a function of wavelength λ
σ_{mid}	absorption cross section at the tropospheric window midpoint for solar radiation
σ_{max}	maximum allowable value for absorption cross section at window midpoint
μg	microgram
•	denotes odd-electron species or free radical (e.g., •OH and •O)

SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of this effort is to assess the higher volatility chemicals in the families of phosphorus compounds (with particular attention paid to phosphorus nitrides), silicon compounds (in particular, silanes and siloxanes), fluorinated amines and ethers, and other nonhalocarbons that might be appropriate for Halon 1301 replacement applications. Compound procurement, combustion suppression, and laboratory studies are a subject of another report (Reference 1).

B. SCOPE

The overall project consists of four requirements.

1. From literature citations and previously determined principles, assess and/or estimate the toxicity, atmospheric lifetime, Ozone Depletion Potential (ODP), and Global Warming Potential (GWP) of chemicals in the phosphorus nitrides, silanes, siloxanes, fluorinated amines and/or ethers, and other nonhalocarbon families that show potential for replacement for Halon 1301 replacement.

2. Select specific compounds for study. Obtain or synthesize the compounds, and, for those compounds that are not readily available, prepare sufficient quantities to permit other researchers to examine the materials.

3. Perform cup-burner flame extinguishment evaluations of selected compounds. To the extent practical, synthesize (or recommend sources for, in case of compounds commercially available) sufficient quantities of these chemicals to send to other laboratories for testing using opposed-flame burners or similar apparatuses.

4. Using the information obtained in the above tasks, develop a list of optimal candidate Halon 1301 replacement agents based primarily on (1) predicted toxicity, (2) synthesis

and manufacturability, (3) atmospheric lifetime, ODP, and GWP, and (4) fire suppression and inertion effectiveness.

The present report covers only the first task listed.

C. APPROACH

In the first part of this program, the toxicities, ODPs, and GWPs of phosphorus nitrides, silanes, siloxanes, fluorinated amines and ethers, and other nonhalocarbons that might be appropriate for Halon 1301 applications have been reviewed and estimated. Sources of toxicity and safety data include Sax and Lewis (Reference 2) and the Registry of Toxic Effects of Chemical Substances (RTECS) (Reference 3).

SECTION II

GLOBAL ENVIRONMENTAL CHARACTERISTICS

Global environmental impacts of greatest concern here are atmospheric—stratospheric ozone depletion and climate change (in particular, global warming). To a large extent, global atmospheric environmental concerns are closely related to the atmospheric lifetime, which is determined by tropospheric removal processes. Reference 4 gives an overview of global environmental problems and presents a detailed discussion of ODP, GWP, the various tropospheric removal mechanisms, and approximation methods. A brief summary with significant new material and expansions is presented here.

1. ODP and GWP

The ability of a chemical to effect stratospheric ozone depletion is measured by its ODP; the impact of a chemical on global warming is determined by its GWP. The ODP and GWP give, respectively, the ozone depletion and global warming due to release of a unit mass of material relative to that produced by a reference chemical. The reference chemical for ODP is usually the chlorofluorocarbon (CFC) CFC-11 (trichlorofluoromethane, CCl_3F), and the reference chemical for GWP is usually carbon dioxide (CO_2), though CFC-11 is sometimes used for GWP also. Both ODP and GWP are calculated from appropriate rate constant data using multidimensional atmospheric models. GWP values depend on the time period (the "time horizon," typically, 100 or 500 years) used in the calculation, and the time horizon used should be noted when reporting GWPs.

2. Stratospheric Ozone Depletion

A method for estimating ODPs for non-bromine-containing one- and two-carbon halocarbons has been proposed (Reference 5). The method relates the ODP to two factors, one a reactivity factor related to the number of chlorine atoms in the molecule and the other a survival factor giving the fraction of molecules reaching the stratosphere (and, therefore, related to the atmospheric lifetime). The proposed relationship is shown in Equation 1, where n is the number of chlorine atoms, t is the atmospheric lifetime, and c_1, c_2, and c_3 are parameters to be fit. Here, n^{c_2} is the reactivity factor, $e^{-(c_3/t)}$ is the survival factor, and c_1 is a normalizing constant. This equation gives values that are relatively close to the rigorously calculated ODPs used in fitting the parameters. Since the values for the rigorously calculated ODPs and atmospheric lifetimes used in the parameter fitting have changed since the equation was originally proposed, the reported parameters will not be given in the present report.

$$\mathrm{ODP} = c_1 n^{c_2} e^{-(c_3/t)} \qquad [1]$$

In its present form, Equation 1 is not applicable to bromine-containing compounds. It has, however, been reported that the ODPs for bromine-containing compounds can be estimated from Equation 2 (Reference 6). Here, P is the photolysis factor, which is set equal to 1.0 if there are no special structural features that make the molecule subject to tropospheric photolysis. Otherwise, P = 0.180 for a bromine geminal to a chlorine (e.g., Br-C-Cl), P = 0.015 for geminal bromine atoms (Br-C-Br), or 0.370 for vicinal bromine atoms (Br-C-C-Br). A is the normalizing constant (0.446), B is 0.740, C is 32.000, and D is 1.120. The hydrogen factor E is 1.000 if there are no hydrogen atoms; otherwise it is 0.0625. #C, #Br, and #Cl are the numbers of carbon, bromine, and chlorine atoms, respectively.

$$\mathrm{ODP} = AEP[(\#\mathrm{Cl})^{B} + C(\#\mathrm{Br})]D^{(\#\mathrm{C}-1)} \qquad [2]$$

Use of Equation 2 gives, at best, rough approximations, even if the equation is restricted to simple saturated halocarbons (Table 1). The trends, however, are preserved. It may be that a better fit of parameters could be obtained with a larger set of more recent data as a basis.

3. Atmospheric Lifetime

To a great extent, ODPs and GWPs are determined by tropospheric lifetimes. Regardless of the chemical, the ODP and GWP will be negligible given a sufficiently short tropospheric lifetime. Thus, tropospheric removal is one area of primary concern when evaluating global environmental impacts. Tropospheric removal reactions are either bimolecular or unimolecular. Bimolecular reactions involve reaction with atmospheric species such as hydroxyl free radicals (•OH), tropospheric ozone (O_3), oxygen atoms (•O in ^3P, ^1D electronic states), etc. Formally unimolecular reactions include photolysis, thermal dissociation, and

TABLE 1. ESTIMATED AND REPORTED ODPs FOR SELECTED HALOCARBONS.

Compound	Formula	Calculated ODP (relative to CFC-11)	Reported ODP (relative to CFC-11)	Reference
Halon 1301	$CBrF_3$	14.3	12	7
Halon 1211	$CBrClF_2$	2.6	5.1	7
Halon 2402	$CBrF_2CBrF_2$	17.4	6.6	a
HBFC-22B1	$CHBrF_2$	0.89	0.74	8
HBC-30B2	CH_2Br_2	0.03	0.17	9
HBC-40B1	CH_3Br	0.89	0.64	7
HCFC-123	$CHCl_2CF_3$	0.050	0.014	7

[a] Connell, P. S., and Wuebbles, D. J., "Ozone Depletion Potential, Halons, and Halon Alternatives," NMERI Halon Alternatives Program Review, Albuquerque, NM, 23-24 Jan 1991.

heterogeneous absorption (aqueous or particulate aerosols). The rate of disappearance of a species C due to a bimolecular reaction with an atmospheric species A can be expressed as shown in Equation 3,* where [C] and [A] are the concentrations of species C and A, and k_2 is a second-order reaction rate constant. Similarly, the rate of removal through unimolecular reactions is expressed by a first-order differential equation with the first-order reaction rate constant k_1 as shown in Equation 4. Typical units for k_2 and k_1 are, respectively, cm^3/molecule-s and $seconds^{-1}$ with concentrations in molecules/cm^3. The rate constants k_1 and k_2 are constant only under a given set of conditions. For example, for photolysis, k_1 depends on the radiation flux and wavelength; for reaction with atmospheric particulate, k_1 depends on the concentration (and composition and other characteristics) of particulate.

$$\frac{d[C]}{dt} = -k_2[C][A] \qquad [3]$$

$$\frac{d[C]}{dt} = -k_1[C] \qquad [4]$$

Careful consideration shows that all reactions can actually be considered "bimolecular" in form since the concentration of particulate, for example, is incorporated into k_1

for particulate removal, and the “concentration” (actually, the flux) of photons is incorporated into k_1 for photolysis. Even thermal decomposition involves collisions with other molecules to transfer kinetic energy to the species undergoing decomposition (which is the reason that the term “formally unimolecular” is used above).

The concentration of a species undergoing reaction, as shown in Equation 3 or Equation 4, decays exponentially as given by Equation 5. Here $[C]_o$ is the initial concentration, $[C]_t$ is the concentration at any time t, and $t_{1/e}$ is the “e-folding” atmospheric lifetime, i.e., the time required for the concentration of an atmospheric species to decay to 1/e (approximately 0.369) of its initial value. The e-folding lifetime is related to the reaction rate constant by or depending on whether the reaction is bimolecular (Equation 6) or unimolecular (Equation 7).

$$[C]_t = [C]_o e^{t/t_{1/e}} \qquad [5]$$

$$t_{1/e} = 1/k_2[A] \qquad [6]$$

$$t_{1/e} = 1/k_1 \qquad [7]$$

Using Equation 6, one can estimate the atmospheric lifetime due to various removal processes by using globally averaged values for concentrations of reactant species. In this report, a globally averaged tropospheric hydroxyl free radical concentration of 9.7×10^5 molecules/cm^3 (Reference 10) and a globally averaged tropospheric ozone concentration of 5.0×10^{11} molecules/cm^3 (Reference 11) are used for such estimations. In the global averaging approximation, one should use reaction rate constants for a mean tropospheric temperature. A temperature of 277 K has been recommended (Reference 12); however, values around 298 K, which are more prevalent, are often used and are generally used in this report.

In the global average approximation, atmospheric lifetime is directly proportional to the second-order rate constant (k_{OH}) for reaction with •OH, when this is the primary tropospheric removal process. Thus, an alternative way to estimate the atmospheric lifetime for a compound B removed only by reaction with •OH is to use Equation 8 to relate the lifetime of B ($t^{B}_{1/e}$) to that ($t^{C}_{1/e}$) of a second compound C (Reference 13). Here, k^{B}_{OH} and k^{C}_{OH} are the

---

*Throughout this report, equation numbers are placed in brackets and reaction numbers are second-order hydroxyl reaction rate constants for the two materials. Methyl chloroform (CH_3CCl_3) is usually the reference compound (C). This method is equivalent to using the globally averaged •OH concentration when this concentration has been determined from measurements of atmospheric removal of methyl chloroform, as in the case of the value used in this report (Reference 10). Note that with the appropriate rate constants, one could use an equation similar to Equation 8 when a removal mechanism other than reaction with a hydroxyl free radical predominates, as long as the removal mechanism for the compound of interest (B) is the same as that for the reference compound (C).

$$t_{1/e}^{B} = t_{1/e}^{C}(k_{OH}^{C} / k_{OH}^{B}) \qquad [8]$$

Attempts to use Quantitative Structure-Activity Relationship (QSAR) to predict k_{OH} values have not been highly successful (Reference 14). A procedure based on the C-H bond energy (and, thus, related to the activation energy for hydrogen atom abstraction by •OH) reported in Reference 5 gives rather disappointing fits to rigorously calculated atmospheric lifetimes, though reparameterization with more recent data may help. Since many of the compounds of interest as halon replacements contain fluorine atoms, there is one trend of interest. Examination of rate constants for a variety of fluorinated compounds indicates that fluorine substitution activates hydrogen atoms on the same carbon atom toward •OH abstraction, but deactivates hydrogen atoms on carbon atoms immediately adjacent. For example, the reaction of •OH with CH_3CH_2F proceeds primarily (85 percent) with the hydrogen atoms on the CH_2F group (Reference 15).

Better results may be available through quantum mechanical calculations. There is strong evidence that k_{OH} values vary linearly with the calculated values for the highest occupied molecular orbital (HOMO) in hydrofluorocarbons (Reference 16).

4. Decision Tree

From the information presented in Reference 4 and in the present report, a decision tree for compound acceptability can be developed. The overall procedure evaluates in turn (1) atmospheric release, (2) hydrolysis, (3) physical removal, (4) photolysis, (5) reaction

---

placed in parentheses.

with hydroxyl free radicals, (6) reaction with tropospheric ozone, (7) other reactions, (8) stratospheric ozone removal, and (9) global warming, allowing decision points at each stage. The overall methodology for the decision tree can be summarized as shown in Figure 1.

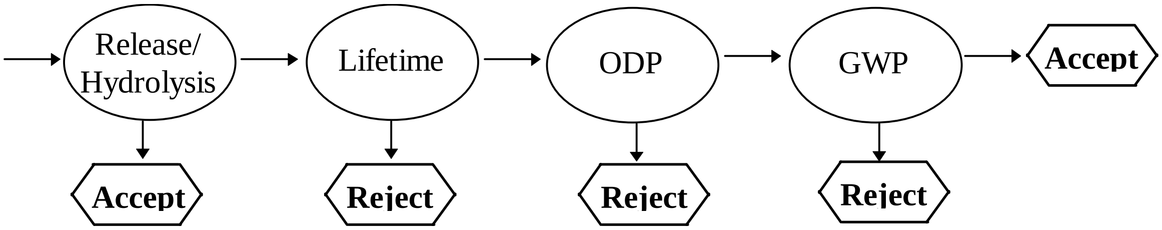


Figure 1. Abbreviated Decision Tree.

A more detailed decision tree is shown in Figure 2. Here, t_{max} is the maximum allowable atmospheric lifetime and t_{hyd}, t_{phys}, t_{phot}, t_{OH}, and t_{O3} are the tropospheric lifetimes due to hydrolysis, physical removal, photolysis, reaction with •OH, and reaction with tropospheric ozone. The maximum allowable atmospheric lifetime and other criteria, which may change as the regulatory environment changes, must be established. The first step is to determine whether the vapor pressure (P_{vap}) is sufficient (less than some maximum allowable value P_{max}) to permit release. Hydrolysis is then accessed from k_{hyd}, the hydrolysis rate constant. Lifetimes for various physical removal processes can be estimated—for rainout using α, the solubility coefficient (Reference 17); for aerosol scavenging using P_{vap}, the vapor pressure (at 298 K) (Reference 17); and for absorption (solution) into oceans using β, the (ocean) water solubility of a gas in moles/m^3-atm (essentially, a Henry’s law constant), and D, the molecular diffusivity of a gas inwater in m^2/year. One can estimate the possibility for photolysis from σ_{mid}, the absorption cross section at the tropospheric window midpoint for solar radiation, and σ_{max}, the maximum allowable value for this cross section. One must collect chemical information on the material of interest to determine whether reaction with •OH, O_3, or other species is possible. If reactions are possible, the lifetimes (t_{OH}, t_{O3}, t_{other}) due to such reactions can be estimated from kinetic rate constants (k_{OH}, k_{O3}, k_{other}) using a global averaging approximation. The final step, if needed, is to estimate the ODP and GWP (from $\sigma_{IR}(\lambda)$, the IR absorption cross section as a function of wavelength λ) and compare the numbers obtained with ODP_{max}, and GWP_{max}, the maximum allowable values for these variables. Estimation methods are available for ODP and GWP (above and Reference 4).

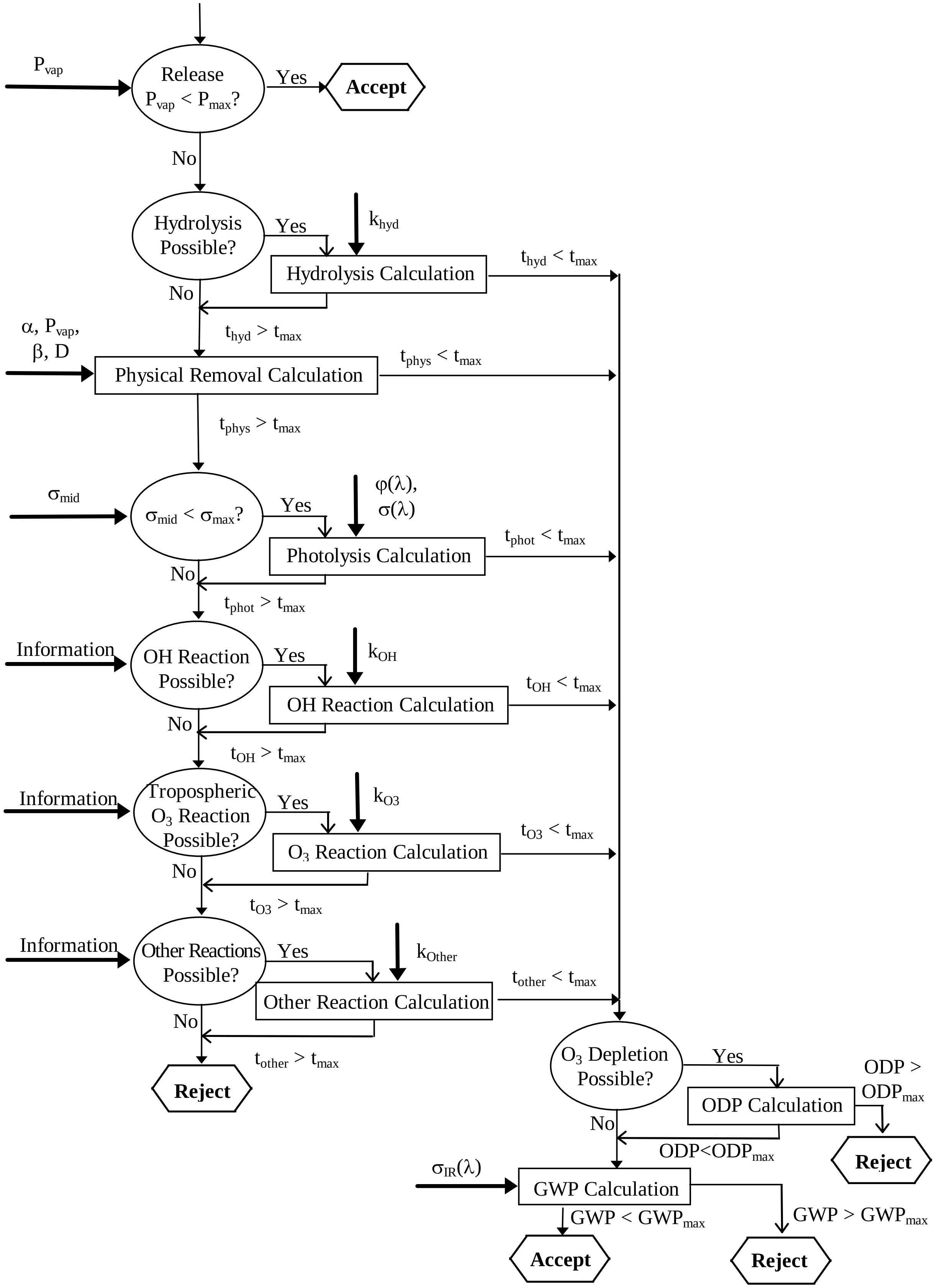


Figure 2. Decision Tree for Global Environmental Impact Screening.

SECTION III
PHOSPHORUS COMPOUNDS

A detailed overview of phosphorus chemistry, particularly as it relates to compounds that might be useful in fire extinguishment, is presented in Reference 18 and is not repeated here except as noted. The conclusions are developed both from material presented here and from data presented in Reference 18.

A. ATMOSPHERIC LIFETIME, ODP, AND GWP

Atmospheric reactions due to the presence of phosphorus have not been studied. It is expected, of course, that organic substituents will generally undergo the same type of reactions found in the absence of phosphorus though modifications in actual rate constants are likely.

1. Stratospheric Ozone Depletion

The effect of phosphorus on stratospheric ozone has not been reported. A general cycle that may enable ozone depletion by phosphorus is shown in Reactions 1 and 2. Note, however, that the large stability and expected reluctance to add additional oxygen atoms make $\bullet PO_3$ and higher oxides unlikely candidates for direct participation in ozone depletion. $\bullet NO_3$ is known to photolyze sufficiently rapidly that at least some possible reactions are believed to be insignificant in atmospheric chemistry (Reference 19), and the higher oxides of phosphorus are likely to photolyze even more rapidly.

$$\bullet PO_x + O_3 \rightarrow \bullet PO_{x+1} + O_2 \quad (1)$$

$$\bullet PO_{x+1} + \bullet O \rightarrow PO_x + O_2 \quad (2)$$

Nitrogen oxides are believed to deplete stratospheric ozone by the reactions shown in Reactions 3 through 5 (Reference 20). Here and elsewhere in this report, enthalpies of reaction (ΔH_r) and free energies of reaction (ΔG_r) are calculated from standard enthalpies of formation (ΔH_f) and standard free energies of formation (ΔG_f) at 298.15 K taken from Reference 21 unless otherwise indicated. By analogy, one might propose Reactions 6 and 7 for ozone depletion by phosphorus. Reaction 6 is highly exothermic and has been proposed as the cause for the chemiluminescence observed for the reaction of ozone with phosphine (Reference 22). Here, however, the relatively large O-PO bond dissociation enthalpy (calculated as 540 kcal/mol from the standard enthalpies) compared to the O-NO bond dissociation energy (306 kJ/mole) makes the second reaction in the cycle (Reaction 7) unfavorable at 298.15 K. The higher stability of phosphorus dioxide can be seen from the total enthalpy of 1129 kJ/mole for dissociation of PO_2 into its constituent atoms compared with the calculated value of 938 kJ/mole for NO_2.

$\bullet NO + O_3 \rightarrow \bullet NO_2 + O_2$, ΔH_r = -200 kJ/mole, ΔG_r = -199 kJ/mole (3)
$\bullet NO_2 + \bullet O \rightarrow \bullet NO + O_2$, ΔH_r = -192 kJ/mole, ΔG_r = -196 kJ/mole (4)
Net: $\bullet O + O_3 \rightarrow 2O_2$, ΔH_r = -392 kJ/mole, ΔG_r = -395 kJ/mole (5)

$\bullet PO + O_3 \rightarrow \bullet PO_2 + O_2$, ΔH_r = -435 kJ/mole, ΔG_r = -433 kJ/mole (6)
$\bullet PO_2 + \bullet O \rightarrow \bullet PO + O_2$, ΔH_r = 42 kJ/mole, ΔG_r = 38 kJ/mole (7)

An alternative mechanism is described in Reactions 8 and 9, where, the second reaction is again distinctly unfavorable. This cycle is similar to the chlorine ozone depletion cycle in Reactions 10 and 11. Here, again, the large phosphorus-oxygen bond strength is an obstacle. The bond strength in diatomic PO is 599.1 kJ/mole compared with 269 kJ/mole for •ClO (Reference 23).

$\bullet P + O_3 \rightarrow \bullet PO + O_2$, ΔH_r = -483 kJ/mole, ΔG_r = -490 kJ/mole (8)
$\bullet PO + \bullet O \rightarrow \bullet P + O_2$, ΔH_r = 91 kJ/mole, ΔG_r = 95 kJ/mole (9)

$\bullet Cl + O_3 \rightarrow \bullet ClO + O_2$, ΔH_r = -163 kJ/mole, ΔG_r = -171 kJ/mole (10)
$\bullet ClO + \bullet O \rightarrow \bullet Cl + O_2$, ΔH_r = -229 kJ/mole, ΔG_r = -224 kJ/mole (11)

A number of other reactions are possible. Bromine and chlorine jointly provide a highly effective mechanism for stratospheric ozone depletion through a cycle of Reactions 5 and 12 through 14 (Reference 24). Here, ΔH_f and ΔG_f for •BrO are taken from Reference 23. A similar cycle can be proposed for phosphorus by coupling Reactions 8, 12, and 15. The free energy change for Reaction 15, however, is very large, positive, and, therefore, unfavorable.

$\bullet Br + O_3 \rightarrow \bullet BrO + O_2$, ΔH_r = -129 kJ/mole, ΔG_r = -137 kJ/mole (12)

$\bullet ClO + \bullet BrO \rightarrow \bullet Cl + \bullet Br + O_2$, ΔH_r = 6 kJ/mole, ΔG_r = -18 kJ/mole (13)

Net: $2O_3 \rightarrow 3O_2$, ΔH_r = -285 kJ/mole, ΔG_r = -326 kJ/mole (14)

$\bullet PO + \bullet BrO \rightarrow \bullet P + \bullet Br + O_2$, ΔH_r = 326 kJ/mole, ΔG_r = 301 kJ/mole (15)

The analysis presented above provides a strong indication that any ozone depletion must involve reaction of O_3 with •PO (e.g., Reactions 6 and 7). The phosphorus-oxygen bond in this diatomic molecule is too strong to allow formation of significant concentrations of atomic phosphorus. As noted above, however, the second reaction in the cycle (Reaction 7) is unfavorable at 298.15 K. The minimum stratospheric temperature (at the tropopause) varies from approximately 193 K to 223 K depending on the latitude, and the maximum stratospheric temperature (at the mesopause) is approximately 285 K depending on the season and latitude (Reference 25). Data from the JANAF tables (Reference 21) indicate that the reaction becomes even less favorable (ΔH_r and ΔG_r both become more positive) as the temperature decreases from 298.15 K. A major question is how fast •PO is removed by reaction with O_3 (Reaction 6) before it reacts with O_2 (the reverse of Reaction 7). Ozone concentrations vary widely in the stratosphere; however, we can take the concentration of ozone in the stratosphere to be approximately 10^{10} to 10^{11} molecules/cm^3 (Reference 26) compared to a maximum of around 10^9 molecules/cm^3 for •O(^{3}P) (Reference 27).* Thus, the mixing ratio (the ratio to air) for •O(^{3}P) is calculated as approximately 1 ppm in the stratosphere. This implies that Reaction 7 would lie far to the left and that the concentration of •PO would be small.

Missing, of course, from this analysis is an assessment of kinetics for Reactions 6 and 7. Also missing is any discussion of other reactions of •PO and •PO_2, both of which are highly polar and are likely to be absorbed onto ice crystals. Despite the shortcomings of this analysis, it is obvious that stratospheric ozone depletion by phosphorus-containing compounds is very unlikely.

---

*The concentration of oxygen atoms in other than the ^{3}P ground state would be even smaller.

2. Reactions with Tropospheric •OH

Relatively little data are available on atmospheric lifetimes for phosphorus compounds. Atkinson has reported the rate constants for several phosphorus compounds (Reference 15), and these are shown in Table 2 along with atmospheric lifetimes estimated from the globally averaged tropospheric •OH concentration. Very limited data indicate that the presence of a phosphorus atom increases •OH reactivity. Thus, for example, methane (CH_4) has a rate constant of 0.0836×10^{-12} cm^3/molecule-s at 298 K (Reference 15), a value considerably smaller than that found for phosphine (PH_3), even though methane has one more reactive site (i.e., one more hydrogen atom). The activation energy for hydrogen atom abstraction decreases (as expected) with decreasing dissociation energy of the M-H bond (References 28 and 29), and this undoubtedly explains the higher rate constant for PH_3 (bond strengths: H-PH_2, 351.0 kJ/mol; C-CH_3, 438.9 kJ/mol) (Reference 23). It is difficult to compare compounds with and without phosphorus and containing hydrogen bonded only to carbon, since there are no isostructural

TABLE 2. RATE CONSTANTS •OH REACTIONS WITH PHOSPHORUS COMPOUNDS.

Compound	k_2 at 297 K, cm^3/molecule-s	Estimated tropospheric lifetime, days
PH_3	$13 \pm 3 \times 10^{-12}$	0.9
$(CH_3O)_3PO$	$7.37 \pm 0.74 \times 10^{-12}$	1.6
$(C_2H_5O)_3PO$	$55.3 \pm 3.5 \times 10^{-12}$	0.2
$(CH_3O)_2P(O)SCH_3$	$9.29 \pm 0.68 \times 10^{-12}$	1.3
$(CH_3S)_2P(O)OCH_3$	$9.59 \pm 0.75 \times 10^{-12}$	1.2
$(CH_3O)_3PS$	$69.7 \pm 3.9 \times 10^{-12}$	0.2
$(CH_3O)_2P(S)SCH_3$	$56.0 \pm 1.8 \times 10^{-12}$	0.2
$(CH_3O)_2P(O)N(CH_3)_2$	$31.9 \pm 2.4 \times 10^{-12}$	0.4
$(CH_3O)_2P(S)N(CH_3)_2$	$46.8 \pm 1.4 \times 10\text{-}^{12}$	0.3
$(CH_3O)_2P(S)NHCH_3$	$233 \pm 15 \times 10^{-12}$	0.05
$(CH_3O)_2P(S)NH_2$	$244 \pm 9 \times 10^{-12}$	0.05
$(CH_3O)_2P(S)Cl$	$59.0 \pm 3.8 \times 10^{-12}$	0.2

compounds. The rate constant of 3.92 x 10^{-12} cm^3/molecule-s at 298 K for 2,2-dimethoxypropane ($C(CH_3)_2(OCH_3)_2$) is smaller than that of trimethyl phosphate ($(CH_3O)_3PO$), which has three fewer hydrogen atoms. The rate constant of 11.7 x 10^{-12} cm^3/molecule-s at 298 K for 2,2-diethoxypropane ($C(CH_3)_2(OC_2H_5)_2$) is smaller than that of triethyl phosphate ($(C_2H_5O)_3PO$), which has nearly the same number of hydrogen atoms (Reference 15). Since the predominant mechanism for reaction with the compounds in Table 2 appears to be hydrogen atom abstraction (Reference 15), it may be that a decreased bond strength accounts for the possibly higher reactivity for phosphorus-containing compounds; however, bond strength data to confirm this are lacking.

3. Reactions with Tropospheric O_3

Phosphorus compounds studied to date are quite unreactive toward ozone. An upper limit of 6 x 10^{-20} cm^3/molecule-s has been determined for reaction of trimethyl phosphate ($(CH_3O)P{=}O$) with ozone at 296 K (Reference 30). Using a globally averaged tropospheric ozone concentration, one estimates from this value a minimum lifetime of 386 days for reaction of trimethyl phosphate with tropospheric ozone. Atkinson (Reference 31) has reported rate constants with upper limits on the order of 10^{-19} at 296 K to 298 K for gas-phase reactions of O_3 with phosphorus-containing compounds, giving estimated minimum lifetimes of around 200 days. In none of these cases was a reaction observed.

4. Other Tropospheric Removal Mechanisms

It is likely that many phosphorus compounds are sufficiently polar that rainout is an important tropospheric removal mechanism. Atmospheric hydrolysis is possible for phosphonitriles containing direct P-halogen bonds even when the halogen is fluorine, and this is likely to be an effective tropospheric removal mechanism for such compounds. Photolysis is more important for compounds containing phosphorus than for corresponding carbon compounds; however, insufficient data are available to determine whether photolysis provides effective atmospheric removal.

5. Lifetimes and GWPs

No rigorous calculations of atmospheric lifetimes or GWPs of phosphorus-containing compounds have been reported. A 3-day lifetime has been estimated for trimethyl phosphate based on the rate constant for reaction with •OH (Reference 30). This value differs slightly from that given in Table 2 due to the use of a slightly different globally averaged •OH.

6. Conclusions

Phosphorus compounds are unlikely sources of stratospheric ozone depletion due to the presence of phosphorus only. When hydrogen atoms are present, limited data indicate effective removal by tropospheric •OH and short atmospheric lifetimes. Insufficient data are available to judge tropospheric removal and atmospheric lifetimes for phosphorus compounds containing no hydrogen; however, it is likely that rainout and/or hydrolysis will give short atmospheric lifetimes. In summary, there is no evidence to suggest that phosphorus compounds will have unacceptable global atmospheric environmental properties (e.g., unacceptable ODP, GWP, or lifetime).

B. TOXICITY

A review of the toxicity of phosphorus compounds is provided in Reference 18. Except where noted, the present report includes only toxicity data obtained since Volume III (Reference 18) was prepared. One concern is that a number of phosphorus compounds (particularly phosphite esters) are cholinesterase inhibitors.

1. Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene toxicity

An acute oral toxicity assessment utilizing male and female Fischer 344 rats and genotoxicity testing utilizing the Ames assay has been performed on hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene ($P_3N_3(OCH_2CF_3)_6$) (Reference 32). No deaths or signs of toxic stress were observed in any of the rats orally dosed at the limit test value of 5 grams of $P_3N_3(OCH_2CF_3)_6$ per kilogram body weight. Body weights of the male rats during the subsequent 14-day observation period appeared unaffected by treatment. In the Ames assay, $P_3N_3(OCH_2CF_3)_6$ produced no mutagenicity (base-pair substitution or frameshift mutation) in the bacterial (Salmonella) system. In summary, $P_3N_3(OCH_2CF_3)_6$ produced no toxicity via the oral route of administration and was determined not to be genotoxic.

2. Phosphonitrilic Chloride Compounds (Chlorophosphazene)

In 1979, Ethyl Corporation submitted to the U. S. Environmental Protection Agency (EPA) *in vitro* and *in vivo* studies on two similar phosphonitrilic chloride compounds, each with the same CAS (Chemical Abstracts Service) No. (25034-79-1):

- A refined $(PNCl_2)_n$ composed of 87.7 percent $(PNCl_2)_3$ and 12.5 percent $(PNCl_2)_4$, identified as compound code 3899-A
- A crude product, consisting of 69.0 percent $(PNCl_2)_3$, 12.8 percent $(PNCl_2)_4$, 5.1 percent $(PNCl_2)_5$, and 1.8 percent $(PNCl_2)_6$ (total of 88.7 percent), identified as compound code 3899-B.

Sixteen reports, each covering a separate toxicological test for each compound, were submitted as follows:

a. *In vitro* mammalian cell transformation assay (Reference 33 for refined compound and Reference 34 for crude compound).

b. *In vitro* mammalian cell transformation assay in the presence of exogenous metabolic activation assay (Reference 35 for refined compound and Reference 36 for crude compound).

c. *In vivo* mammalian cell point mutation assay (Reference 37 for refined compound and Reference 38 for crude compound).

d. *In vitro* mammalian cell point mutation assay in the presence of exogeneous metabolic activation assay (Reference 39 for refined compound and Reference 40 for crude compound).

e. *In vivo* cytogenetic assay in rodents for mutagenicity (Reference 41 for refined compound and Reference 42 for crude compound).

f. *Salmonella*/Microsomal assay for bacterial mutagenicity assay (Reference 43 for refined compound and Reference 44 for crude compound).

g. Differential inhibition of repair deficient and repair competent strains of *Escherichia Coli*: DNA (deoxyribonucleic acid) repair assay (Reference 45 for refined compound and Reference 46 for crude compound).

h. Dominant lethal assay in rodents for mutagenicity assay (Reference 47 for refined compound and Reference 48 for crude compound).

Table 3 paraphrases the results of the eight toxicity tests for each compound. Due to the limited solubility of the test compounds in vehicles compatible with mammalian cell culture systems, it was difficult to establish the exact concentration of that chemical in solution for the *in vitro* tests, a problem noted in the reports cited.

The fact that a positive effect was obtained in a number of *in vitro* tests indicates that the material may be a potential mutagen. Thus, this class of materials may be mutagenic. Note that compound 3899-B (the crude compound) generally appeared more toxic, especially in the following tests: *in vitro* mammalian cell transformation assay (both with and without exogenous metabolic activation); *in vitro* cytogenetic assay in rodents for mutagenicity; *Salmonella*/ Microsomal assay for bacterial mutagenicity; and the differential inhibition of repair deficient and repair competent strains of *Escherichia Coli* (*E coli*): DNA repair assay. This indicates that impurities and other chemicals may increase toxicity to an unacceptable level even if the pure compounds are not unacceptably toxic.

3. Other Phosphorus Compounds

In a study of a number of phosphorus compounds, no toxic signs were observed following fifteen 6-hour exposures of two male and two female rats to 200 ppm tributyl phosphite, $P(OC_4H_9)_3$ (Reference 49). The blood, urine, and organs (upon autopsy) were normal. The same study showed that tris(hydroxymethyl)propane bicyclic phosphite (I) has an unexpectedly high toxicity and is stated to be “one of the most toxic compounds handled in this laboratory.” All rats died following a 1-hour exposure to 10 ppm. The marked action on the central nervous system is probably due to its sufficient stability to penetrate cell membranes as a non-ionized molecule, possibly with subsequent hydrolysis. Note, however, that its hydrolysis product, dihydroxybutylphosphonic acid, has a low oral and parental toxicity.

TABLE 3. RESULTS OF TOXICITY STUDIES FOR CHLOROPHOSPHAZENES.

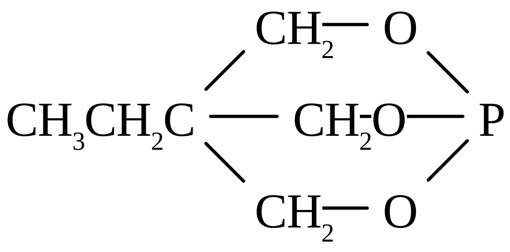
3899-A	3899-B
In Vitro Mammalian Cell Transformation Assay	
a. Although the cytotoxicity tests were not reproducible in showing the toxic effects of the test compound with target cells, a dose response effect was observed in each of the cytotoxicity studies. b. The test compound was incapable of inducing morphological transformants (Type III foci) in the BALB/3T3 clone A31 cell system.	a. The cytotoxicity studies demonstrated a dose response effect. b. The test chemical was demonstrated to be positive in producing a Type III foci at 60 µg/mL concentration. Relative to solvent (acetone), the number of morphologically transformed (Type III) foci present at this concentration was statistically significant (P<0.05).
In vitro Mammalian Cell Transformation Assay in the Presence of Exogenous Metabolic Activation	
a. Cytotoxic effects of the test agent appeared to increase in the presence of an exogeneous source of metabolizing activity (S-9). b. The test chemical was effective in inducing morphological transformation (Type III foci) at the 30 µg/mL concentration. Relative to the negative control, the number of morphologically transformants per number of cells at risk at the 30 µg/mL concentration was not statistically significant (P>0.05).	a. Cytotoxic effects of the test agent appeared to increase in the presence of an exogeneous source of metabolizing activity (S-9). b. The test chemical was effective in inducing morphological transformation (Type III foci) in the BALB/3T3 Clone A31 cell system at all concentrations employed.
In Vitro Mammalian Cell Point Mutation Assay	
a. Although the cytotoxicity tests were not reproducible in showing the toxic effects of the test compound with target cells, a dose response effect was observed in each of the cytotoxicity studies. b. The test compound was incapable of inducing oubain-resistant colonies at all of the doses tested.	a. The cytotoxicity tests demonstrated a dose response effect. b. The test chemical was incapable of inducing oubain-resistant colonies at all concentrations.

TABLE 3. RESULTS OF TOXICITY STUDIES FOR CHLOROPHOSPHAZENES (continued).

3899-A	3899-B
In Vitro Mammalian Cell Point Mutation Assay in the Presence of Exogeneous Metabolic Activation	
a. Cytotoxic effects of the test agent appeared to increase in the presence of an exogenous source of metabolizing activity (S-9). b. The test chemical was ineffective in inducing ouabain-resistant colonies in the BALB/3T3 Clone A31 cell system at all concentrations employed.	a. The cytotoxic effects of the test agent appeared to increase in the presence of an exogenous source of metabolizing activity (S-9). b. The test chemical was ineffective in inducing ouabain-resistant colonies at all concentrations employed.
In Vitro Cytogenetic Assay in Rodents for Mutagenicity	
The test compound exhibited little or no clastogenic activity. No dose response was observed. Under the conditions of this test, the data suggest that the test compound exhibits little or no mutagenic activity.	The test compound exhibited moderate clastogenic activity. A dose response was observed. Under the conditions of this test, the data suggest that the compound exhibits mutagenic activity.
Salmonella/Microsomal Assay for Bacterial Mutagenicity	
a. The test agent did not induce a significant increase in the number of point mutations in *Salmonella* typhimurium strains in the absence of activating system for strains TA1535, TA1537, TA1358, TA100, and TA98. b. It did not induce a significant increase in the number of point mutations with the addition of an exogenous source of liver enzymes for metabolic activation in strains of TA1535, TA1537, TA1358, TA100, and TA98.	a. The test agent did not induce a significant increase in the number of point mutations in *Salmonella* typhimurium strains in the absence of activating system for strains TA1535, TA1537, TA100, and TA98. b. It did induce a significant increase in the number of point mutations in the absence of the activating system for strain TA1538. c. It did not induce a significant increase in the number of point mutations with the addition of an exogenous source of liver enzymes for metabolic activation in strains of TA1535, TA1537, TA1358, TA100, and TA98.

TABLE 3. RESULTS OF TOXICITY STUDIES FOR CHLOROPHOSPHAZENES (CONCLUDED).

3899-A	3899-B
Differential Inhibition of Repair Deficient and Repair Competent Strains of *Escherichia Coli* (*E. coli*): DNA Repair	
The test chemical did not produce a statistically significant difference in its ability to produce cell death between repair deficient (polA$^-$) and repair competent (polA$^+$) strains in *E. coli*.	The test chemical did produce a statistically significant difference at 2 µl per plate in its ability to produce cell death between repair deficient (polA$^-$) and repair competent (polA$^+$) strains in *E. coli*.
Dominant Lethal Assay in Rodents for Mutagenicity	
The tests compound appeared to exhibit minimal activity in total implantations, number of live implantations per pregnant female, and pre-implantation losses. No statistically significant dose response was observed. The data suggest that the compound exhibits little or no mutagenic activity in the dominant lethal test.	The tests compound appeared to exhibit minimal activity in total implantations, number of live implantations per pregnant female, and pre-implantation losses. No statistically significant dose response was observed. The data suggest that the compound exhibits little or no mutagenic activity in the dominant lethal test.



I

Table 4 contains information on toxicity and safety of some phosphorus-containing compounds related to compounds of interest here (Reference 18). Furthermore, the table has been updated with the addition of compounds having mouse and rat inhalation (inh) data from Reference 2 and the RTECS numbers where available.

4. Conclusions

A large amount of toxicity data is available for phosphorus compounds. In part this is because a number of phosphorus compounds (particularly phosphite esters) are cholinesterase inhibitors. The toxicity of phosphorus compounds is highly variable. As noted, many phosphorus compounds are cholinesterase inhibitors and, in some cases, highly toxic. Thus, toxicity must be given careful consideration. There is limited information indicating that toxicity may increase from phosphates to phosphites to phosphines. Phosphonitriles appear to have relatively low toxicities, but some show indications of mutagenicity. The presence of P-halogen bonds can cause severe irritation and lung damage owing to hydrolysis with formation of phosphorus-containing and hydrohalic acids. For this reason, compounds containing direct bonds to phosphorus are poor candidates as halon substitutes.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS.

Compound	Formula	CAS No.	Observations[a]
bis(trifluoromethyl)-chlorophosphine	$PCl(CF_3)_2$	650-52-2	[BLO280] Ignites spontaneously in air. HR = 3.
dibutylphosphate	$O=P(OH)(OC_4H_9)_2$	107-66-4	{RTECS HS630000} [DEG600] LD_{50} (rat, oral) = 3200 mg/kg. Moderately toxic by ingestion. HR = 2.
dibutylphosphonate	$O=PH(OC_4H_9)_2$	1809-19-4	{RTECS HS6475000} [DEG800] LD_{50} (rat, oral) = 3200 mg/kg, LD_{50} (rabbit, skin) = 1990 mg/kg. Moderately toxic by ingestion, skin contact. Severe eye irritant. HR = 2.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. “HR” denotes the SAX Hazard Rating.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
diethylphosphonate	$O{=}PH(OC_2H_5)_2$	762-04-5	{RTECS TG7875000} [DJW400] LD_{50} (rat, oral) = 3900 mg/kg, LD_{50} (rabbit, skin) = 2165 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.
diisopropyl methylphosphonate	$O{=}P(CH_3)$-$[OCH(CH_3)_2]_2$	1445-75-6	{RTECS SZ9090000} [DNQ875] LD_{50} (rat, oral) = 826 mg/kg, LD_{50} (mouse, oral) = 1041 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.
diisopropylphosphonate	$O{=}PH[OCH(CH_3)_2]_2$	1809-20-7	{RTECS SZ7660000} [DNQ600] LD_{50} (rat, oral) = 3100 mg/kg, LD_{50} (rabbit, skin) = 5700 mg/kg. Moderately toxic by ingestion. Mildly toxic by skin contact. HR = 2.
dimethyl(1,2-dibromo-2,2-dichloroethyl) phosphate	$O{=}P(OCH_3)_2$-$(OCHBrCBrCl_2)$	300-76-5	{RTECS TB9540000} [DRJ600] LD_{50} (rat, inh) = 7700 μg/kg, LD_{50} (mouse, inh) = 156 mg/kg, LD_{50} (rat, oral) = 250 mg/kg, LD_{50} (rabbit, skin) = 1100 mg/kg. Poison by ingestion, inhalation. Moderately toxic by skin contact. Skin irritant. Insecticide of the cholinesterase inhibitor type. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. “HR” denotes the SAX Hazard Rating.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
dimethyl(2,2-dichloroethenyl)-phosphate	$O{=}P(OCH_3)_2$-$(CH{=}Cl_2)$	62-73-7	{RTECS TC0350000} [DRK200] LC_{50} (rat, inh, 4 hr) = 15 mg/m^3, LC_{50} (mouse, inh, 4 hr) = 13 mg/kg, LD_{50} (rat, oral) = 25 mg/kg, LD_{50} (rabbit, skin) = 107 mg/kg. Poison by ingestion, inhalation, skin contact, intraperitoneal, intravenous, subcutaneous. Experimental teratogen, suspected carcinogen Cholinesterase inhibitor. HR = 3.
dimethylphosphonate	$O{=}PH(OCH_3)_2$	868-85-9	{RTECS SZ7710000} [DSG600] LD_{50} (rat, oral) = 3050 mg/kg, LD_{50} (rabbit, skin) = 2400 mg/kg. Moderately toxic by ingestion, skin contact. Experimental carcinogen. Skin, eye irritant. HR = 3.
hexaethyltetraphosphate	$OP(OC_2H_5)_2$-$[OP(O)(OC_2H_5)]_2$-$OP(O)(OC_2H_5)_2$	757-58-4	{RTECS XF1575000} [HCY000] LD_{50} (rat, oral) = 7 mg/kg, LD_{50} (mouse, oral) = 56 mg/kg, LD_{LO} (rat, skin) = 15 mg/kg. Poison by ingestion, skin contact, intraperitoneal, subcutaneous, intravenous, intramuscular. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. “HR” denotes the SAX Hazard Rating.

[b] The most probable (phosphonate) structure is given for these compounds, which can also be assigned the phosphite structure ($P(OR)_3$). Both forms may exist.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
tris(2-chloroethyl) phosphite	$O{=}P(OCH_2CH_2Cl)_2$-(CH_2CH_2Cl) [b]	140-08-9	{RTECS KK2810000} [PHO000] LD_{50} (rat, oral) = 100 mg/kg, LD_{50} (rabbit, skin) = 810 mg/kg. Poison by ingestion, intraperitoneal. Moderately toxic by skin contact. Severe eye irritant. HR = 3.
tris(2-fluoroethyl) phosphite	$O{=}P(OCH_2CH_2F)_2$-(CH_2CH_2F) [b]	63980-61-0	{RTECS KL1925000} [PHO250] LC_{LO} (rat, inh, 10 min) = 500 mg/m^3, LC_{LO} (mouse, inh, 10 min) = 1000 mg/m^3. Poison by inhalation. HR = 3.
tetraethylpyrophosphate	$P(O)(OC_2H_5)_2$-$OP(O)(OC_2H_5)_2$	107-49-3	{RTECS UX6825000} [TCF250] LD_{50} (rat, oral) = 500 µg/kg, LD_{50} (mouse, oral) = 7 mg/kg, LD_{50} (rat, skin) = 2400 µg/kg. Poison by ingestion, skin contact, intraperitoneal, intramuscular, other. Cholinesterase inhibitor. HR = 3.
triethylphosphate	$O{=}P(OC_2H_5)_3$	78-40-0	{RTECS TC7900000} [TJT750] LD_{LO} (rat, oral) = 1600 mg/kg, LD_{LO} (mouse, oral) = 1600 mg/kg. Moderately toxic by ingestion, intraperitoneal, and intravenous. Reproductive effects. Mutagenic data. Cholinesterase inhibitor. HR = 2.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. “HR” denotes the SAX Hazard Rating.

[b] The most probable (phosphonate) structure is given for these compounds, which can also be assigned the phosphite structure ($P(OR)_3$). Both forms may exist.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
triethylphosphite	$O{=}P(C_2H_5)(OC_2H_5)_2$[b]	122-52-1	{RTECS TH1130000} [TJT800] LD_{50} (rat, oral) = 3200 mg/kg. Moderately toxic by ingestion. Skin, eye irritant. HR = 2.
tris(1-bromo-3-chloroisopropyl)-phosphate	$O{=}P[OCBr(CH_3)(CH_2Cl)]_3$	7328-28-1	{RTECS TC8600000} [TNE500] Mutagenic data. HR = D (insufficient data).
triisooctylphosphite	$O{=}P[(CH_2)_5CH(CH_3)_2][O(CH_2)_5CH(CH_3)_2]_2$[b]	25103-12-3	{RTECS TH1150000} [TKT000] LD_{50} (rat, oral) = 9200 mg/kg, LD_{50} (rabbit, skin) = 3970 mg/kg. Moderately toxic by skin contact. Mildly toxic by ingestion. Skin irritant. HR = 2.
triisopropylphosphite	$O{=}P[CH(CH_3)_2][OCH(CH_3)_2]_2$[b]	116-17-0	{RTECS TH2800000} [TKT500] LD_{50} (rat, oral) = 167 mg/kg. Poison by ingestion. Moderately toxic by intraperitoneal. HR = 3.
trimethylphosphite	$O{=}P(CH_3)(OCH_3)_2$[b]	121-45-9	{RTECS TH1400000} [TMD500] LD_{50} (rat, oral) = 1600 mg/kg, LD_{LO} (rabbit, skin) = 2200 mg/kg. Moderately toxic by ingestion, skin contact. Experimental teratogen. Severe skin, eye irritant. HR = 2.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. “HR” denotes the SAX Hazard Rating.

[b] The most probable (phosphonate) structure is given for these compounds, which can also be assigned the phosphite structure ($P(OR)_3$). Both forms may exist.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
triphenylphosphite	$O{=}P(C_6H_5)(OC_6H_5)_2$[b]	101-02-0	{RTECS TH1575000} [TMU250] LD_{50} (rat, oral) = 1600 mg/kg, LD_{50} (mouse, oral) = 1333 mg/kg. Poison by intraperitoneal, subcutaneous. Moderately toxic by ingestion. Severe skin irritant. HR = 3.
tris(2-bromoethyl) phosphate	$O{=}P(OCH_2CH_2Br)]_3$	27568-90-7	{RTECS TC8480000} [TNE600] LC_{LO} (rat, inh) = 260 mg/m^3. Poison by inhalation. Mutagenic data. HR = 3.
tributylphosphine oxide	$O{=}P(C_4H_9)_3$	814-29-9	{RTECS SZ1575000} [TNE750] Poison by intravenous route. Eye irritant. HR = 3.
tritolylphosphate (tricresylphosphate)	$O{=}P(OC_6H_5CH_3)_3$	1330-78-5	{RTECS TD0175000} [TNP500] LD_{50} (rat, oral) = 5190 mg/kg, LD_{50} (mouse, oral) = 3900 mg/kg. Poison by ingestion. Moderately toxic by skin contact. Eye, skin irritant. HR = 3.
tri-2-tolylphosphate (tri-*o*-cresylphosphate)	$O{=}P(OC_6H_5CH_3)_3$	78-30-8	{RTECS TD0350000} [TNP750] LD_{50} (rat, oral) = 1160 mg/kg. Poison by ingestion, subcutaneous, intramuscular, intravenous, intraperitoneal. Moderately toxic by ingestion. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. "HR" denotes the SAX Hazard Rating.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (continued).

Compound	Formula	CAS No.	Observations[a]
dimethylfluorophosphate	$C_4H_{10}FO_3P$	358-74-7	{RTECS TE5600000} [DJJ400] LC_{50} (rat, inh, 10 min) = 7 g/m^3, LC_{50} (mouse, inh, 10 min) = 500 mg/m^3. Poison by inhalation, skin. HR = 3.
dimethylfluorophosphate	$C_2H_6FO_3P$	5954-50-7	{RTECS TE6125000} [DSA800] LC_{50} (rat, inh, 1 min) = 1800 mg/m^3, LC_{50} (mouse, inh, 10 min) = 290 mg/m^3. Poison by inhalation, skin contact, intravenous. HR = 3.
2-ethyl-2(hydroxymethyl)-1,3-propane-diol, cyclic phosphate (1:1)	$C_6H_{11}O_4P$	1005-83-2	{RTECS TX6475000} [ELJ500] LC_{50} (rat, inh, 1 hr) = 30 mg/m^3. Poison by ingestion, inhalation, skin contact, intraperitoneal and intravenous routes. HR = 3.
ethyl isopropyl fluorophosphonate	$C_5H_{12}FOP$	none assigned	{RTECS SZ8552000} [ELX100] LC_{50} (rat, inh, 10 min) = 260 mg/m^3, LC_{50} (mouse, inh, 5 min) = 245 mg/m^3. Poisonous by inhalation, skin contact, and subcutaneous routes. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. "HR" denotes the SAX Hazard Rating.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (concluded).

Compound	Formula	CAS No.	Observations[a]
hexamethyl phosphoramide	$C_6H_{18}N_3OP$	680-31-9	{RTECS TD0875000} [HEK000] TC_{LO} (rat, inh, 52 wk continuous) = 50 ppb, carcinogenic. An experimental carcinogen and tumorigen. Moderately poisonous by ingestion, skin contact, intraperitoneal, intravenous. Experimental reproductive effects. Human mutagenic data. HR = 3.
diisopropyl fluorophosphate	$C_6H_{14}FO_3P$	55-91-4	{RTECS TE5075000} [IKS249] LC_{50} (rat, inh, 10 min) = 360 mg/m^3, LC_{50} (mouse, inh, 10 min) = 600 mg/m^3, TC_{LO} (human, inh, 10 min) = 8200 µg/m^3 (eye and CNS). A poison by ingestion, inhalation, skin contact, subcutaneous, intravenous, intraperitoneal, ocular, and intramuscular routes. Experimental reproductive effects. HR = 3.
isopropyl methyl fluorophosphonate	$C_4H_{10}FO_2P$	107-44-8	{RTECS TA8400000} [IPX000] LD_{50} (rat, inh, 10 min) = 150 mg/m^3, LD_{50} (mouse, inh, 30 min) = 5 mg/m^3, TC_{LO} (man, inh) = 90 µg/m^3 (eyes), LC_{50} (human, inh) = 70 mg/m^3. Deadly human poison by skin contact and inhalation. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. "HR" denotes the SAX Hazard Rating.

TABLE 4. TOXICITY AND SAFETY INFORMATION FOR SELECTED PHOSPHORUS COMPOUNDS (concluded).

Compound	Formula	CAS No.	Observations[a]
mevinphos (2-carbomethoxy-1-methylvinyl dimethyl phosphate)	$C_7H_{13}O_6P$	7786-34-7	{RTECS GQ5250000} [MQR750] LC_{50} (rat, inh, 1 hr) = 14 ppm. Poison by ingestion, inh, skin contact, subcutaneous, intravenous, intraperitoneal. HR = 3.
monocrotophos (3-hydroxy-N-methyl-cis-crotonamide, dimethyl phosphate)	$C_7H_{14}NO_5P$	6923-22-4	{RTECS TC4375000} [MRH209] LC_{50} (rat, inh, 4 hr) = 63 mg/m^3. Poison by ingestion, inh, skin contact, intraperitoneal, subcutaneous, and intravenous routes. Mutagenetic data. HR = 3.
phosphine	H_3P	7803-51-2	{RTECS SY7525000} [PGY000] LC_{50} (rat, inh, 4 hr) = 11 ppm, LC_{LO} (mouse, inh, 2 hr) = 380 mg/m^3, TC_{LO} (human, inh) = 1000 ppm. A poison by inhalation. A very toxic gas. HR = 3.
1,1,1-trishydroxy-methylpropane bicyclic phosphite	$C_6H_{11}O_3P$	824-11-3	{RTECS TY6650000} [TNI750] LC_{LO} (rat, inh, 4 hr) = 10 ppm. A poison by ingestion, inhalation, skin contact, intraperitoneal, and intravenous routes. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. “HR” denotes the SAX Hazard Rating.

SECTION IV
SILICON COMPOUNDS

A review of the chemistry of silicon compounds related to compounds of interest in the development of fire suppressants is found in Reference 50. Except where noted, the information in this section is not contained in the reference cited. The conclusions are developed both from material presented here and from data presented in Reference 50.

A. ATMOSPHERIC LIFETIME, ODP, AND GWP

1. Stratospheric Ozone Depletion

Silicon, and other metalloids and metals, are known to be deposited in the upper atmosphere by meteors; however, it is believed that only the more polar metal oxides (e.g., sodium oxide) are likely to have any direct homogeneous chemical effect on atmospheric chemistry since these compounds have weak metal-oxygen bonds and can regenerate free atoms through photolysis and reactions with •O and •OH (Reference 51). (On the other hand, it must be recognized that silicon-containing particulates could play a significant role in heterogeneous atmospheric chemistry [Reference 52]). The silicon-oxygen bond is quite strong compared with the sodium-oxygen bond in the simple diatomics (Si-O, 799.6 kJ/mole; Na-O, 256.1 kJ/mole) (Reference 23). Thus, reactions proposed for ozone depletion by sodium (Reactions 16 and 17) are unlikely for ozone depletion by silicon (Reference 53). Sodium atoms generated in the atmosphere may also enhance ozone depletion by chlorine (Reference 54), although it is not known whether similar enhancement by silicon takes place. Note, however, that since approximately 40 to 300 metric tonnes of metals are deposited daily by meteorites (Reference 55), and since silicon is one of the more abundant elements in meteorites (Reference 54), it is unlikely that anthropogenic silicon would produce a significant atmospheric effect in comparison to other sources.

$$\bullet\mathrm{Na} + \mathrm{O_3} \rightarrow \bullet\mathrm{NaO} + \mathrm{O_2} \qquad (16)$$

$$\bullet\mathrm{NaO} + \bullet\mathrm{O} \rightarrow \bullet\mathrm{Na} + \mathrm{O_2} \qquad (17)$$

2. Reactions with Tropospheric •OH

Rate constants for reactions of some silicon compounds with •OH free radicals and estimated lifetimes based on those rate constants are presented in Table 5.

TABLE 5. •OH RATE CONSTANTS FOR SILICON COMPOUNDS.

Reactant	k_{OH}, cm^3/molecule-s	Atmospheric lifetime, days[a]
SiH_4[b]	12.2×10^{-12}	0.97
$Si(CH_3)H_3$[b]	34.3×10^{-12}	0.35
$Si(CH_3)_2H_2$[b]	44.8×10^{-12}	0.27
$Si(CH_3)_3H$[b]	26.7×10^{-12}	0.45
$Si(CH_3)_4$[b]	1.09×10^{-12}	10.9
SiH_4[c]	[d]$12.4 \pm 1.9 \times 10^{-12}$	0.96
$Si(C_2H_5)_4$[c]	[e]75×10^{-12}	0.16
$Si(CH_3)_4$[f]	[d]$1.00 \pm 0.09 \times 10^{-12}$	11.9
$(CH_3)_3SiOSi(CH_3)_3$[f]	[d]$1.38 \pm 0.09 \times 10^{-12}$	8.6
$[(CH_3)_2SiO]_3$[f]	[d]$5.2 \pm 1.1 \times 10^{-13}$	22.9
$[(CH_3)_2SiO]_4$[f]	[d]$1.01 \pm 0.20 \times 10^{-12}$	11.9
$[(CH_3)_2SiO]_5$[f]	[d]$1.55 \pm 0.30 \times 10^{-12}$	7.7
$(CH_3)_3SiOSi(CH_3)_2OH$[f]	[d]$1.89 \pm 0.36 \times 10^{-12}$	6.3

[a] Lifetimes estimated using globally averaged •OH model.

[b] Personal communication from Dr. Paul Marshall, Department of Chemistry, University of North Texas, Denton, to Dr. Robert E. Tapscott, 27 May 1997. Values are at 295 K.

[c] Reference 15

[d] 297 K

[e] 793 K

[f] Reference 31

Methane (CH_4) has a rate constant of 0.0836×10^{-12} cm^3/molecule-s at 298 K (Reference 15), a value considerably smaller than that found for silane (SiH_4). This is, however, undoubtedly due to the lower Si-H bond strength in SiH_4 (bond strengths: H-SiH_3, 384.1 kJ/mole; C-CH_3, 438.9 kJ/mole) (Reference 23). Of greater interest are rate constants for silicon-containing molecules with no Si-H bonds. 2,2-Dimethylpropane ($C(CH_3)_4$) has an •OH rate constant of 0.875 x 10^{-12} cm^3/molecule-s at 298 K, which is slightly smaller than that of tetramethylsilane ($Si(CH_3)_4$). Unfortunately, other data allowing a direct comparison between C-H bond rate constants for carbon and silicon compounds are unavailable. Thus, at this time, there appears to be no reason to assume that, in the absence of Si-H bonds, silicon compounds are inherently more reactive toward •OH than are carbon compounds.

3. Reactions with Tropospheric O_3

Maximum rate constants (no reaction observed) on the order of 10^{-21} have been determined for the reaction of O_3 with silicon-containing compounds (Reference 31). These data give minimum estimated lifetimes of the order of 2500 days, showing that there would be little, if any, removal by tropospheric ozone.

4. Other Tropospheric Removal Processes

In general, silicon compounds are considerably more unstable toward hydrolysis than are carbon compounds, and this property may provide an effective removal route for many of these materials. The Si-halogen bond hydrolyzes readily; however, the rapidity of this hydrolysis (and the resulting formation of toxic products) eliminates the consideration of compounds containing halogens bonded directly to silicon as fire suppressants (other than for basic laboratory studies). Compounds containing Si-H bonds also hydrolyze relatively easily when the pH is greater than 7, but are relatively stable in acidic solution. The alkoxy-Si bond is subject to hydrolysis and cleavage can cause condensation to higher polymers. Note, however, that this is highly dependent on the absence of steric hindrance. Alkoxy-substituted silanes with larger alkoxy groups are much more stable toward hydrolysis (Reference 56). Silanes containing only carbon bonded to silicon are relatively hydrolytically stable.

Silicon compounds are expected to be more susceptible to photolysis than are the corresponding carbon compounds. The laser-induced photodissociation of silanes is one method used for vapor deposition of silicon films in the production of microelectronics (Reference 57).

5. Lifetimes and GWPs

A few, scattered, and, in some cases, suspect lifetime and GWP data have been reported for silicon-containing compounds (Reference 50). Siloxanes have been reported to have atmospheric lifetimes of from 10 to 30 days.*

6. Conclusions

Silicon compounds are unlikely sources of stratospheric ozone depletion due to the presence of silicon only. When hydrogen atoms are present, limited data indicate effective removal by tropospheric •OH and short atmospheric lifetimes. Insufficient data are available to judge tropospheric removal and atmospheric lifetimes for silicon compounds containing no hydrogen, with one exception. Silicon compounds containing direct Si-halogen bonds will hydrolyze rapidly and give short atmospheric lifetimes; however, such compounds are unsuitable for halon substitutes due to their expected high toxicity. Photolysis may be a potential route to atmospheric removal in some cases. Of particular interest is possible photolytic "synergism" when both silicon and bromine are present; however, no data exist to evaluate such "synergism." Unfortunately, there are no atmospheric data for fully halogenated organosilicon compounds containing no Si-H or Si-halogen bonds (and, in particular, compounds containing primarily fluorine as the halogen). Such compounds are unlikely to be removed rapidly by hydrolysis, rainout, or other processes, with the possible exception of photolytic decomposition. In summary, although there is no evidence that silicon compounds will have unacceptable global atmospheric environmental properties (e.g., unacceptable ODP, GWP, or lifetime), this may not be true for fully halogenated silicon compounds containing no Si-H or Si-halogen bonds.

B. TOXICITY

1. Newly Acquired Information

The toxicity of silicon compounds is discussed in Reference 50 and, for that reason, will not be given here in any detail.

One paper not presented in Reference 50 reported that no toxic signs were found for four male rats to a single 6-hour exposure at 8000 ppm or to fifteen 6-hour exposures at 1000 ppm for tetramethylsilane, $Si(CH_3)_4$ (Reference 49). In the same study, twenty 6-hour exposures of four female rats to diphenyldimethoxysilane, $Si(C_6H_5)_2(OCH_3)_2$, at its saturation vapor pressure showed no adverse effects.

A recent EPA final action on significant new uses lists potential toxicity hazards for a number of silicon compounds (Reference 58). The final rule states that alkoxysilanes can cause lung toxicity and severe irritation to skin, eyes, and mucous membranes. Of particular interest is the finding that “Based on analogy to alkoxysilanes and perfluoro compounds,” $Si(OCH_3)_3(CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3)$ may cause lung toxicity, irritation to mucous membranes, liver toxicity, blood toxicity, immunosuppression, and reproductive toxicity. In part, this finding may be due to the analogy between the fluoroalkyl chain and some HFCs; it may have little or nothing to do with the silicon atom.

2. Conclusions

A relatively small amount of toxicity data is available for silicon compounds of primary interest here (compounds containing halogenated alkyl groups and no direct Si-halogen bonds). In general, siloxanes have moderately low toxicities. Alkoxy-containing silicon compounds could cause irritation to skin, eyes, and mucous membranes. The presence of Si-halogen bonds is expected, in all cases, to cause severe toxicity problems due to hydrolysis with formation of hydrohalic acids. Such compounds are probably unacceptable as halon substitutes.

---

*Swanson, S. P., Cull, R. A., Bryant, D., and Moore, J., “New Technologies and Cleaning Performance Based on Volatile Methyl Siloxanes,” International Conference on Ozone Protection Technologies, Washington, DC, 21-23 October 1996.

SECTION V

FLUORINATED AMINES

Some information on amines of interest as fire suppressants is presented in Reference 4. Information reported in that source will not be presented here except as noted. The conclusions are developed both from material presented here and from data presented in Reference 4.

A. ATMOSPHERIC LIFETIME, ODP, AND GWP

1. Stratospheric Ozone Depletion

The fact that nitrogen oxides could be direct depleters of stratospheric ozone through Reactions 3 through 5 (Reference 59) was actually recognized earlier than that halocarbons posed an environmental threat. The first concerns were about direct injection of nitrogen oxides into the stratosphere by high-altitude aircraft (Reference 60). Nitrogen compounds, however, play other roles in atmospheric chemistry involving ozone depletion. The ozone chemical balance depends directly on the total amount of active nitrogen species (Reference 61). Nitric oxide (NO) releases chlorine from chlorine monoxide (Reaction 18) (Reference 62). Nitrogen oxides can also decrease stratospheric ozone depletion by the formation of the chlorine nitrate ($ClONO_2$) reservoir (Reaction 19) (Reference 62) and by the removal of •OH (Reactions 20 through 22) (Reference 63). Hydroxyl free radicals convert HCl and HBr to free chlorine and bromine atoms, which are potent depleters of stratospheric ozone. Removal of nitric acid by condensation is believed to play a major role in the Antarctic ozone hole (Reference 63).

$$\bullet NO + \bullet ClO \rightarrow Cl + \bullet NO_2,\ \Delta H_r = -37\ kJ/mole,\ \Delta G_r = -28\ kJ/mole \qquad (18)$$

$$\bullet NO_2 + \bullet ClO \rightarrow ClONO_2 \qquad (19)$$

$$\bullet OH + HNO_3 \rightarrow H_2O + \bullet NO_3 \qquad (20)$$

$$\bullet NO_3 + h\nu \rightarrow \bullet NO_2 + \bullet O \qquad (21)$$

$$\bullet OH + \bullet NO_2 + M \rightarrow HNO_3 + M^*,\ \Delta H_r = -206\ kJ/mole,\ \Delta G_r = -159\ kJ/mole \qquad (22)$$

Since some highly fluorinated amines have long atmospheric lifetimes, it is possible that anthropogenic amines of interest in this research could deplete stratospheric ozone.

2. Reactions with Tropospheric •OH

A relatively large amount of data are available for reactions of atmospheric •OH radicals with nitrogen-containing compounds; however, little experimental data (as opposed to estimations) are available for compounds that might be useful as halon replacements, those containing fully or partially fluorinated alkyl groups (to improve toxicity and flammability characteristics). Amines containing no hydrogen atoms are expected to be inert to attack by •OH, which can be seen in the absence of reaction observed with N,N-bis(pentafluoroethyl)penta-fluoroethanamine ($N(CF_2CF_3)_3$), for which an •OH rate constant $k_2 < 6 \times 10^{-16}$ cm^3/molecule-s has been reported (Reference 64). This rate constant corresponds to an estimated atmospheric lifetime of greater than 55 years, a lifetime that is likely to be considerably higher.

A relatively large amount of data are available for hydrogen-containing, nonfluorinated amines. Nitroalkanes (RNO_2) have been relatively well studied (Reference 65), but these have little resemblance to amines, which are the most promising of the nitrogen-containing halon replacements. As a result of concerns about health impacts, the atmospheric chemistry of N-nitrosodimethylamine ($(CH_3)_2N\text{-}NO$) and dimethylnitramine ($(CH_3)_2N\text{-}NO_2$) has been examined (Reference 66). Table 6 presents rate constants for hydroxyl free radicals reactions with several nonfluorinated amines (Reference 15). Where several values are given, the first value cited at or near 298 K is used for consistency. Note that these values are calculated on or near the high pressure limit. Atmospheric lifetimes in Table 6, calculated from a globally tropospheric •OH concentration of 9.7×10^5 molecules/cm^3, are on the order of a few days or less. The reactions of all of the compounds in Table 6 probably involve hydrogen atom abstraction from the alkyl groups. Since all of these compounds are highly polar, rainout would also be an effective removal mechanism.

TABLE 6. •OH RATE CONSTANTS FOR NITROGEN-CONTAINING COMPOUNDS.

Compound	k_{OH}, cm^3/molecule-s	Temperature, K	Atmospheric lifetime, days[a]
Methylamine $NH_2(CH_3)$	$22.0 \pm 2.2 \times 10^{-12}$	299	0.5
Ethylamine $NH_2(CH_2CH_3)$	$27.7 \pm 2.8 \times 10^{-12}$	299.6	0.4
Dimethylamine $NH(CH_3)_2$	$64.5 \pm 6.6 \times 10^{-12}$	298.5	0.2
Trimethylamine $N(CH_3)_3$	$60.9 \pm 6.1 \times 10^{-12}$	298.7	0.2
Diethylhydroxylamine $N(CH_2CH_3)_2OH$	101×10^{-12}	308	0.1
2-(Dimethylamino)ethanol $CH_2(N(CH_3)_2)CH_2OH$	$47 \pm 12 \times 10^{-12}$	300 ± 2	0.3
2-Amino-2-methyl-1-propanol $CH_3C(CH_3)(NH_3)CH_2OH$	$28 \pm 5 \times 10^{-12}$	300 ± 2	0.4
N-Nitrosodimethylamine $(CH_3)_2N\text{-}NO$	$02.53 \pm 0.21 \times 10^{-12}$	298 ± 2	4.7
Dimethylnitramine $(CH_3)_2N\text{-}NO_2$	$03.84 \pm 0.15 \times 10^{-12}$	298 ± 2	3.1

[a] Based only on reaction with •OH.

3. Reactions with Tropospheric O_3

Rate constants have been compiled for gas-phase reactions of O_3 with a number of nitrogen-containing compounds (Reference 67), and the data for amines are shown in Table 7. It is obvious that the rate constants increase and lifetimes (estimated from the globally averaged tropospheric O_3 concentration) decrease with increasing alkyl substitution. This is also the direction of increasing proton affinity (-ΔH for the reaction $B + H^+ \rightarrow BH^+$, where B is a base) (Reference 68).

TABLE 7. RATE CONSTANTS FOR REACTIONS OF O_3 WITH AMINES

Compound	k_2 at 296 K, cm^3/molecule-s	Estimated tropospheric lifetime, days	Proton affinity, kJ/mole
$NH_2(CH_3)$	$2.13 \pm 0.29 \times 10^{-20}$	1087	896
$NH_2(CH_2CH_3)$	$2.76 \pm 0.34 \times 10^{-20}$	839	908
$NH(CH_3)_2$	$2.61 \pm 0.30 \times 10^{-18}$	008.9	923
$N(CH_3)_3$	$9.73 \pm 1.02 \times 10^{-18}$	002.4	938

The reactions appear to proceed by addition of O_3 to the nitrogen to give $R_3N^+\text{-O-O-O}^-$, which then decomposes by uncertain mechanisms. Data for reactions involving halogen-substituted alkyl amines have not been reported; however, it is likely that the reaction rates will decrease with increasing halogen substitution, which makes the nitrogen atom less electron rich.

Rate constants have also been reported for reaction of O_3 with pyridines (approximately 5×10^{-20} to 50×10^{-20} cm^3/molecule-s) and for unsaturated nitriles ($< 1 \times 10^{-19}$ to 1.38×10^{-19} cm^3/molecule-s for acrylonitrile ($CH_2{=}CHCN$) and 3.52×10^{-19} for methacrylonitrile ($CH_2{=}C(CH_3)CN$)) (Reference 31). Ozone is known to react with alkene derivatives, and the results for the acrylonitriles probably have little to do with the presence of nitrogen. The pyridines, which are, at best, distantly related to the amines of interest have calculated lifetimes for reaction with tropospheric ozone of approximately 1 year or less. The maximum values of the rate constants for reaction of N-nitrosodimethylamine ($(CH_3)_2N\text{-NO}$) and dimethylnitramine ($(CH_3)_2N\text{-NO}_2$) with tropospheric ozone are 1×10^{-20} and 3×10^{-21} cm^3/molecule-s (calculated lifetimes of 6 and 21 years) and could be less than this (Reference 66). Photolysis is probably the primary removal mechanism for N-nitrosodimethylamine.

4. Lifetimes and GWPs

Of particular interest are alkyl-substituted amines, with one or more alkyl groups containing bromine atoms. The primary problem is that fluorination is needed to decrease both the flammability and toxicity of amines. As fluorination increases, both the polarity and the amine flammability are expected to decrease (for different reasons). The polarity is directly related to toxicity, since highly polar amines are strong bases and therefore irritants. The polarity is, however, also directly related to the effectiveness of atmospheric removal. Nonfluorinated amines are expected to undergo significant rainout.

Reported lifetimes and GWPs are reviewed for several fluoroalkyl amines in Reference 4; however, the values are highly suspect. For example, the lifetime of $(CH_3)_2NC_2F_5$ is reported as 250 years, while that of the much less hydrogen-rich compound $(CF_3)_2NCF_2CF_2H$ is given as 2.10 years.* Moreover, the estimation or calculation methods for the lifetimes and GWPs have not been reported. Eliminating the highly questionable value of 250 years gives estimated lifetimes for hydrofluoroamines (HFAs) of around 0.3 to 3 years.*

5. Conclusions

While there is nothing inherent in nitrogen compounds that would lead to atmospheric lifetime or GWP problems, individual compounds may have significant effects. HFAs have estimated atmospheric lifetimes in the order of 0.3 to 3 years. Replacement of fluorine atoms with bromine atoms would tend to reduce these numbers by a factor of 10 in some compounds. Data indicate that for bromine-containing alkanes, each 10-year increase in the atmospheric lifetime increases the ODP by approximately a factor of 2 (Reference 4). Therefore, hydrofluorobromoamines should have low ODPs. Any impact from nitrogen on stratospheric ozone would be negligible compared to that from bromine.

B. TOXICITY

1. Hydrofluoroamines

The acute inhalation toxicities of some HFAs are given in Table 8.* These have also been reviewed in Reference 4; however, here the LC_{50} values are also given as volume percent. Although these lower bounds do not cause any concern, measurements at higher

---

*Misaki, S., and Sekiya, A., “Development of a New Refrigerant,” presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

concentrations are needed. In addition to the compounds shown in Table 8, the LC_{LO} for mouse inhalation has been reported as 0.0123 percent for 2,2,2-trifluoroethylamine ($(CF_3CH_2)NH_2$) (Reference 2), a value that appears rather low; however, this compound contains hydrogen atoms directly bonded to the nitrogen.

TABLE 8. ACUTE INHALATION TOXICITY OF HYDROFLUOROAMINES.

Compound	Subject	LC_{50}, mg/L	Molecular weight	LC_{50}, %
$(CF_3)_2NCH_3$	3-hr rat	>20	113.99	>0.43
$(CF_3)_2NCF_2CF_2H$	3-hr rat	>20	253.04	>0.19
$(CF_3)_2NCFHCF_3$	3-hr rat	>20	253.04	>0.19
$(CF_3)_2NCH_2CF_3$	3-hr rat	>20	235.05	>0.21
$(CF_3)_2NCH_2CF_2H$	4-hr rat	>20	217.06	>0.23
$(CF_3)_2NCH_2CH_3$	4-hr rat	>20	181.08	>0.27

2. Other Fluorine-Containing Nitrogen Compounds

A review of Reference 2 identified inhalation toxicity data for over 120 compounds containing both nitrogen and fluorine; however, inhalation data are available for only 6 compounds (Table 9). The remaining compounds either did not reference toxicity data or the data were for oral, intravenous, or some other exposure route. Nearly every compound in this limited set is given a SAX HR of 3, signifying the worst hazard level. Note, however, that none of these compounds is closely related to amines, and most contain groups known to lead to toxicity. Many N-nitroso compounds, such as the nitrosocarbamates, are carcinogens.

TABLE 9. TOXICITY, SAFETY INFORMATION FOR SELECTED N, F COMPOUNDS.

Compound	Formula	CAS No.	Observations[a]
fluoroacetanilide	C_8H_8FNO	330-68-7	{RTECS AE2975000} [FFH000] LC_{LO} (mouse, inh, 10 min) = 480 mg/m^3. Poison by ingestion, intraperitoneal, and possible other routes. Moderately toxic by inhalation. HR = 3.
β-fluoroethyl-N-(β-chloroethyl)-N-nitrosocarbamate	$C_4H_8ClFN_2O_3$	63884-92-4	{RTECS EZ2275000} [FIH000] LC_{LO} (guinea pig, inh, 10 min) = 300 mg/m^3. Poison by inhalation. HR = 3.
2-fluoroethyl-N-methyl-N-nitrosocarbamate	$C_4H_7FN_2O_3$	63982-15-0	{RTECS FC6475000} [FIS000] LC_{LO} (guinea pig, inh, 10 min) = 100 mg/m^3, LC_{LO} (mouse, inh, 10 min) = 500 mg/m^3. Poison by inhalation. HR = 3.
3-nitrobenzotrifluoride	$C_7H_4F_3NO_2$	98-46-4	{RTECS XT3500000} [NFJ500] LC_{50} (rat, inh) = 870 mg/kg, LC_{50} (mouse, inh, 2 hr) = 880 mg/m^3. Moderately toxic by ingestion, inhalation, and subcutaneous routes. HR = 3.
(α,α,α-trifluoro-*m*-tolyl)isocyanate	$C_8H_4F_3NO$	329-01-1	{RTECS NR0200000} [TKJ250] LC_{50} (rat, inh) = 3600 mg/m^3, LC_{50} (mouse, inh) = 3300 mg/m^3. Moderately toxic by ingestion, inhalation, intraperitoneal routes. HR = 2.
2,4,6-trifluoro-s-triazine	$C_3F_3N_3$	675-14-9	{RTECS XZ1750000} [TKK000] LC_{50} (rat, inh, 4 hr) = 3.1 ppm. Poison by skin contact, inhalation. HR = 3.

[a] The SAX No. (Reference 2) is given in brackets followed by information from that reference; the RTECS No. (Reference 3) is given in braces. "HR" denotes the SAX Hazard Rating.

3. Conclusions

No generalities on the toxicity of nitrogen compounds can be made. Amines range in toxicity from poisons to only slightly toxic. In fact, fully fluorinated alkyl amines show no toxicity. Some amines are skin irritants while others are sensitizers (Reference 2). Although LC_{50} values have been determined for some hydrofluoroamines (HFA), the test levels are very low and measurements at higher concentrations are needed. One brominated compound ($(CH_3)_2NCF_2CBrF_2$) has tested negative for genotoxicity and cytotoxicity (Reference 69).

SECTION VI

FLUORINATED ETHERS

Some information on fluorinated ethers of interest as fire suppressants is derived from Reference 4. Information reported in that source will not be included here except as noted. A large amount of new material has been obtained. The conclusions are developed both from material presented here and from data in Reference 4.

A. ATMOSPHERIC LIFETIME, ODP, AND GWP

1. Reactions with Tropospheric •OH

The presence of the oxygen ether linkage increases reactivity toward hydrogen abstraction, though fluorine substitution decreases the enhancement (Reference 14). Hydrofluorocarbons show an approximately linear correlation between k_{OH} and the highest-occupied molecular orbital (HOMO) energies (Reference 16). Rate constants, many estimated, reported for reaction of hydrofluoroethers (HFE) with •OH are shown in Table 10. In the absence of a hydrogen atom, fluorinated ethers exhibit no reaction with •OH.

2. Reactions with Tropospheric O_3

Very little work has been done on reactions of ethers with ozone, primarily due to their low reactivity. The rate constants for reaction with furan (2.42×10^{-18} cm^3/molecule-s) and 2,5-dihydrofuran (1.61×10^{-17} cm^3/molecule-s) are relatively large owing to the presence of a double bond (Reference 67). For saturated ethers, however, rate constants are expected to be extremely slow, $\leq 10^{-20}$ at room temperature (Reference 67).

3. Lifetimes and GWPs

The energy of the HOMO has been used to estimate atmospheric lifetimes for a number of HFEs (Reference 70). A list of atmospheric lifetimes reported for halogenated ethers, most of which are estimated, are shown in Table 11.

TABLE 10. RATE CONSTANTS FOR HYDROFLUOROETHER REACTIONS WITH •OH.

Halocarbon No.	Formula	kOH, cm^3/molecule-s	Reference
HFE-CE225ea	-O-CF_2CHFCF_2-	[a]2.51 x 10^{-15}	14
		[a]2.4 x 10^{-15}	14
HFE-E	CH_3-O-$CF(CF_3)_2$	[a,b]1.6 x 10^{-14}	13
HFE-E	CH_3-O-$CH(CF_3)_2$	[a,b]2.2 x 10^{-13}	13
HFE-E	CHF_2-O-$CH(CF_3)_2$	[a,b]1.8 x 10^{-14}	13
HFE-E	CH_2F-O-$CH(CF_3)_2$	7.3 x 10^{-14}	71
HFE-E125	CHF_2-O-CF_3	[a]3.38 x 10^{-15}	14
		[a]3.56 x 10^{-15}	14
		[c]4.2 x 10-16	72
HFE-E134	CHF_2-O-CHF_2	[a]2.53 x 10^{-14}	14
		[a]2.41 x 10^{-14}	14
		[a,b]3 x 10^{-15}	13
		[c]2.3 x 10^{-15}	72
HFE-E143a	CH_3-O-CF_3	[a]2.14 x 10^{-14}	14
HFE-E227ca1	CHF_2-O-CF_2CF_3	[b,d]1.95 x 10^{-15}	16
HFE-E227ca2	CHF_2CF_2-O-CF_3	[b,d]4.5 x 10^{-15}	16
HFE-E227ea1	CF_3CHF-O-CF_3	[a,b]5.1 x 10^{-15}	13
		[b,d]3.5 x 10^{-15}	16
HFE-E236ca1	CHF_2-O-CF_2CHF_2	[b,d]1.15 x 10^{-14}	16
HFE-E236ca12	CHF_2-O-CF_2-O-CHF_2	1.3 x 10^{-15}	72
HFE-E236ea1	CHF_2-O-$CHFCF_3$	[a,b]9.5 x 10^{-15}	13
		[b,d]7 x 10^{-15}	16
HFE-E236ea2	CHF_2CHF-O-CF_3	[b,d]3 x 10^{-14}	16
HFE-E236mf1	CF_3CH_2-O-CF_3	[a,b]1.5 x 10^{-14}	13
HFE-E245ca2	CHF_2-O-CF_2CH_2F	[b,d]7 x 10^{-15}	16
HFE-E245cb1	CH_3-O-CF_2CF_3	[c]1.07 x 10^{-14}	73
		[a,b]4.6 x 10^{-14}	13
		[b,d]5.5 x 10^{-14}	16
HFE-E245cb2	CH_3CF_2-O-CF_3	[b,d]1.5 x 10^{-15}	16

[a] 296K

[b] Estimated from HOMO energy.

[c] 298K

[d] Average

TABLE 10. RATE CONSTANTS FOR HYDROFLUOROETHER REACTIONS WITH •OH (concluded).

Halocarbon No.	Formula	kOH, cm^3/molecule-s	Reference
HFE-E245fa1	CHF_2-O-CH_2CF_3	[a]1.25 x 10-12	14
		[a]1.2 x 10^{-14}	14
		[a,b]3.3 x 10^{-14}	13
		[b,d]5 x 10^{-14}	16
HFE-E245fa2	CF_3-O-CH_2CHF_2	[a,b]2.5 x 10^{-14}	13
		[b,d]3.5 x 10^{-14}	17
HFE-E254cb1	CH_3-O-CF_2CHF_2	[a,b]6.5 x 10^{-14}	13
		[b,d]1.5 x 10^{-13}	17
HFE-E254cb2	CH_3CF_2-O-CHF_2	[b,d]7.5 x 10^{-15}	16
HFE-E254fa1	CHF_2-O-CH_2CHF_2	[b,d]9 x 10^{-14}	16
HFE-E254fb1	CH_2F-O-CH_2CF_3	[b,d]4 x 10^{-13}	16
HFE-E254fb2	CH_2FCH_2-O-CF_3	[b,d]6.5 x 10^{-14}	16
HFE-E263fb1	CH_3-O-CH_2CF_3	[a]6.24 x 10^{-13}	14
		[a,b]5.3 x 10^{-13}	13
		[b,d]2 x 10-12	16
HFE-E263fb2	CH_3CH_2-O-CF_3	[b]2 x 10^{-13}	16
HFE-E329p2	CHF_2CF_2-O-CF_2CF_3	[a,b]8.2 x 10^{-15}	13
HFE-E338mf2	CF_3CH_2-O-CF_2CF_3	[a,b]1.3 x 10^{-14}	13
HFE-E347pf2	CF_3CF_2-O-CH_2CHF_2	[a,b]2 x 10^{-14}	13
HFE-E347s1	CH_3-O-$CF_2CF_2CF_3$	[c]1.14 x 10^{-14}	73
		[a,b]4.4 x 10^{-14}	13
HFE-E356mec1	CH_3-O-CF_2CHFCF_3	[a,b]5.9 x 10^{-14}	13
HFE-E356pcc1	CH_3-O-$CF_2CF_2CHF_2$	[a,b]6 x 10^{-14}	13
HFE-E356pfc1	CHF_2-O-$CH_2CF_2CHF_2$	[a,b]4.4 x 10^{-14}	13
HFE-E356pfc2	CHF_2CH_2-O-CF_2CHF_2	[a,b]2.8 x 10^{-14}	13
HFE-E365mc1	CH_3-O-$CH_2CF_2CF_3$	[a,b]4.9 x 10^{-13}	13
HFE-E374pcf2	CH_3CH_2-O-CF_2CHF_2	[a,b]1.3 x 10^{-13}	13
HFE-E4-3-10pccc124	CHF_2-O-CF_2-O-CF_2CF_2-O-CHF_2	[c,d]4 x 10^{-15}	72

[a] 296K

[b] Estimated from HOMO energy.

[c] 298K

[d] Average

TABLE 11. ATMOSPHERIC LIFETIMES FOR FLUORINE-CONTAINING ETHERS.

Halocarbon No.	Formula	Atmospheric lifetime, years	Reference
FE-CE216	-O-$CF_2CF_2CF_2$-	[a]>330	14
HCFE-E235ca2	CHF_2-O-CF_2CHClF	[a]6	71
HCFE-E235da1	CHF_2-O-$CHClCF_3$	[a]5	71
HFE-CE225ea	-O-CF_2CHFCF_2-	[b,c]26	14
HFE-E	CHF_2-O-$CH(CF_3)_2$	[a]3.77	[d]
HFE-E	CH_3-O-$CF(CF_3)_2$	4.9	[d]
		[b,c]3.5	13
		4.3	74
HFE-E	CH_3-O-$CH(CF_3)_2$	[b,c]0.25	13
HFE-E	CH_2F-O-$CH(CF_3)_2$	[a]1.4	71
		[b,c]3.1	13
HFE-E	$HF_2CO(CF_2O)n(CF_2CF_2O)mCF_2H$	[e]8	[f]
HFE-E125	CHF_2-O-CF_3	82	75
		19	14
		[b,c]156	72
HFE-E134	CHF_2-O-CHF_2	8	75
		[b,c]2.6	14
		[b,c]19	13
		[b,c]35	72
HFE-E143a	CH_3-O-CF_3	[b,c]3	14
HFE-E227ca1	CHF_2-O-CF_2CF_3	[b,e,f]16.05	70
		[b,e,f]33	16

[a] Estimated

[b] For reaction with •OH only.

[c] Non-rigorous calculation.

[d] Misaki, S., and Sekiya, A., “Development of a New Refrigerant,” presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[e] Average

[f] Estimated from HOMO energy.

[g] Calculated by N. R. Jensen et al., E. U. Joint Research Centre, Ispra, Italy; personal correspondence from M. Visca, Ausimont S.p.A., to Dr. Robert E. Tapscott, 11 November 1997.

[h] Grenfell, M. W., Klink, F. W., Owens, J. G., and Yanome, H., “New Fluorinated Solvent Alternatives,” presented at Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

TABLE 11. ATMOSPHERIC LIFETIMES FOR FLUORINE-CONTAINING ETHERS (continued).

Halocarbon No.	Formula	Atmospheric lifetime, years	Reference
HFE-E227ca2	CHF_2CF_2-O-CF_3	[b,e,f]12.1	70
		[b,e,f]17.5	16
HFE-E227ea1	CF_3CHF-O-CF_3	[b,c]11	13
		20	74
		[b,e,f]23.5	16
		[b,e,f]14.9	70
HFE-E236ca1	CHF_2-O-CF_2CHF_2	[b,e,f]5.95	70
		[b,e,f]8.5	16
HFE-E236cb1	CH_2F-O-CF_2CF_3	[b,e,f]5.9	70
HFE-E236cb2	CH_2FCF_2-O-CF_3	[b,e,f]6.7	70
HFE-E236ea1	CHF_2-O-$CHFCF_3$	[a]4.04	[d]
		[b,e,f]6.5	16
		[b,e,f]7.5	70
HFE-E236ea2	CHF_2CHF-O-CF_3	[b,e,f]5.1	70
		[b,e,f]4.55	16
HFE-E236mf1	CF_3CH_2-O-CF_3	[b,c]3.7	13
		[b,e,f]4.75	70
HFE-E245ca1	CH_2F-O-CF_2CHF_2	[b,e,f]3.5	70
HFE-E245ca2	CHF_2-O-CF_2CH_2F	[a]2.18	[d]
		[b,e,f]6.5	16
		[b,e,f]4.4	70

[a] Estimated

[b] For reaction with •OH only.

[c] Non-rigorous calculation.

[d] Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[e] Average

[f] Estimated from HOMO energy.

[g] Calculated by N. R. Jensen et al., E. U. Joint Research Centre, Ispra, Italy; personal correspondence from M. Visca, Ausimont S.p.A., to Dr. Robert E. Tapscott, 11 November 1997.

[h] Grenfell, M. W., Klink, F. W., Owens, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," presented at Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

TABLE 11. ATMOSPHERIC LIFETIMES FOR FLUORINE-CONTAINING ETHERS (continued).

Halocarbon No.	Formula	Atmospheric lifetime, years	Reference
HFE-E245cb1	CH_3-O-CF_2CF_3	6.5	73
		[b,c]1.2	13
		[b,e,f]0.85	16
		[b,e,f]1.4	70
HFE-E245cb2	CH_3CF_2-O-CF_3	[b,e,f]11.2	70
		[b,e,f]27.5	16
HFE-E245ea1	CHF_2-O-$CHFCHF_2$	[b,e,f]2.75	70
HFE-E245eb1	CH_2F-O-$CHFCF_3$	[b,e,f]2.2	70
HFE-E245eb2	CH_2FCHF-O-CF_3	[b,e,f]3.35	70
HFE-E245fa1	CHF_2-O-CH_2CF_3	[b,c]5.2	14
		[b,c]1.7	13
		[b,e,f]1.15	16
		[a]4.71	[d]
		[b,f]1.9	70
HFE-E245fa2	CF_3-O-CH_2CHF_2	[c]2.2	13
		[b,e,f]1.45	16
		[b,e,f]2.65	70
HFE-E254ca1	CH_2F-O-CF_2CH_2F	[b,e,f]3.1	70
HFE-E254cb1	CH_3-O-CF_2CHF_2	[a]0.47	[d]
		[b,c]0.85	13
		[b,e,f]0.35	16
		[b,e,f]0.95	70

[a] Estimated

[b] For reaction with •OH only.

[c] Non-rigorous calculation.

[d] Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[e] Average

[f] Estimated from HOMO energy.

[g] Calculated by N. R. Jensen et al., E. U. Joint Research Centre, Ispra, Italy; personal correspondence from M. Visca, Ausimont S.p.A., to Dr. Robert E. Tapscott, 11 November 1997.

[h] Grenfell, M. W., Klink, F. W., Owens, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," presented at Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

TABLE 11. ATMOSPHERIC LIFETIMES FOR FLUORINE-CONTAINING ETHERS (continued).

Halocarbon No.	Formula	Atmospheric lifetime, years	Reference
HFE-E254cb2	CH_3CF_2-O-CHF_2	[b,e,f]3.85	70
		[b,e,f]6	16
HFE-E254ea1	CH_2F-O-$CHFCHF_2$	[b,e,f]1.3	70
HFE-E254ea2	CH_2FCHF-O-CHF_2	[b,e,f]1.75	70
HFE-E254eb1	CH_3-O-$CHFCF_3$	[b,f]0.5	70
HFE-E254eb2	CH_3CHF-O-CF_3	[b,e,f]2.45	70
HFE-E254fa1	CHF_2-O-CH_2CHF_2	[b,e,f]1.05	70
		[b,e,f]0.45	16
HFE-E254fb1	CH_2F-O-CH_2CF_3	[b,f]0.5	70
		[b,e,f]0.15	16
HFE-E254fb2	CH_2FCH_2-O-CF_3	[b,e,f]1.6	70
		[b,e,f]0.7	16
HFE-E263fb1	CH_3-O-CH_2CF_3	[b,c]0.1	14
		[b,f]<0.1	16
		[b,c]0.1	13
HFE-E263fb2	CH_3CH_2-O-CF_3	[b,f]0.3	16
HFE-E329p2	CHF_2CF_2-O-CF_2CF_3	[b,c]6.8	13
HFE-E338mf2	CF_3CH_2-O-CF_2CF_3	[b,c]4.3	13
HFE-E347pf1	CHF_2-O-$CH_2CF_2CF_3$	[a]1.62	[d]
HFE-E347pf2	CF_3CF_2-O-CH_2CHF_2	[b,c]2.8	13
HFE-E347s1	CH_3-O-$CF_2CF_2CF_3$	6.4	73
		[b,c]1.3	13
		5.6	74

[a] Estimated

[b] For reaction with •OH only.

[c] Non-rigorous calculation.

[d] Misaki, S., and Sekiya, A., “Development of a New Refrigerant,” presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[e] Average

[f] Estimated from HOMO energy.

[g] Calculated by N. R. Jensen et al., E. U. Joint Research Centre, Ispra, Italy; personal correspondence from M. Visca, Ausimont S.p.A., to Dr. Robert E. Tapscott, 11 November 1997.

[h] Grenfell, M. W., Klink, F. W., Owens, J. G., and Yanome, H., “New Fluorinated Solvent Alternatives,” presented at Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

TABLE 11. ATMOSPHERIC LIFETIMES FOR FLUORINE-CONTAINING ETHERS (concluded).

Halocarbon No.	Formula	Atmospheric lifetime, years	Reference
HFE-E356mcf2	CF_3CH_2-O-CF_2CH_2F	[a]1.84	[d]
HFE-E356mec1	CH_3-O-CF_2CHFCF_3	[b,c]0.94	13
HFE-E356mff2	CF_3CH_2-O-CH_2CF_3	[a]0.5	[d]
HFE-E356pcc1	CH_3-O-$CF_2CF_2CHF_2$	[b,c]0.93	13
HFE-E356pfc1	CHF_2-O-$CH_2CF_2CHF_2$	[b,c]1.3	13
HFE-E356pfc2	CHF_2CH_2-O-CF_2CHF_2	[b,c]2	13
HFE-E365mc1	CH_3-O-$CH_2CF_2CF_3$	[b,c]0.11	13
HFE-E365sf2	CH_3CH_2-O-CF_2CF_3	[a]0.3	[d]
HFE-E374pcf2	CH_3CH_2-O-CF_2CHF_2	[b,c]0.43	13
HFE-E4-3-10pccc124	CHF_2-O-CF_2-O-CF_2CF_2-O-CHF_2	[b,c]7	72
HFE-E449s1	$CF_3CF_2CF_2CF_2$-O-CH_3	4.1	76
HFE-E569sf2	$CF_3CF_2CF_2CF_2$-O-CH_2CH_3	1.2	[h]

[a] Estimated

[b] For reaction with •OH only.

[c] Non-rigorous calculation.

[d] Misaki, S., and Sekiya, A., “Development of a New Refrigerant,” presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

[e] Average

[f] Estimated from HOMO energy.

[g] Calculated by N. R. Jensen et al., E. U. Joint Research Centre, Ispra, Italy; personal correspondence from M. Visca, Ausimont S.p.A., to Dr. Robert E. Tapscott, 11 November 1997.

[h] Grenfell, M. W., Klink, F. W., Owens, J. G., and Yanome, H., “New Fluorinated Solvent Alternatives,” presented at Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

4. Hydrofluoroethers

Hydrofluoropolyethers (HFPE) are starting to be commercialized, and the environmental characteristics appear relatively good (Reference 72). The degradation products resulting from the alkoxy radicals formed after initial hydrogen atom abstraction from hydrofluoropolyethers (HFPE) have been studied (Reference 77). Chlorine-atom initiated photooxidations of the HFPEs in air ($HCF_2OCF_2OCF_2OCF_2H$, $HCF_2OCF_2CF_2OCF_2H$ and $HCF_2OCF_2OCF_2H$) produced $C(O)F_2$ as the only carbon-containing product, with observed average $C(O)F_2$ molar formation yields of 4.73, 3.77, and 2.82, respectively. In the early stages of the reaction, the $C(O)F_2$ molar formation yields are close to the number of carbon atoms in each parent HFPE. Based on current knowledge of degradation pathways of hydrofluorocarbons (HFC) and hydrochlorofluorocarbons (HCFC), it is expected that $C(O)F_2$ will also be produced with near-unit yield per carbon atom from the above HFPEs in the troposphere, where loss processes would be initiated primarily by reaction with •OH radicals.

5. Conclusions

There is no indication that the ether linkage provides any significant contribution to rainout. The polarity is too small. Perfluorinated saturated ethers are expected to have atmospheric lifetimes similar to those of the perfluorinated alkanes, a property that makes their use as halon replacements questionable. The atmospheric lifetimes for partially fluorinated ethers are much shorter. Even in this case, however, the lifetimes appear to be sufficiently long that ODPs for bromine-substituted ethers would be unacceptable.

B. TOXICITY

The toxicity of ethers has been discussed in Reference 4. The low reactivity of the ether linkage causes ethers to be relatively biologically benign, though, of course, there are many exceptions; anesthesia is a problem in some cases.

SECTION VII
RESULTS AND CONCLUSIONS

A. PHOSPHORUS COMPOUNDS

It is highly unlikely that phosphorus compounds will create any global environmental problems. Atmospheric lifetimes are expected to be sufficiently short that global warming and ozone depletion (even with bromine substitution) would be negligible.

The large variability in toxicity of phosphorus compounds and the possibility of cholinesterase inhibition causes toxicity concerns with these compounds. It appears that toxicity tends to decrease as the oxidation state of the phosphorus decreases (i.e., phosphines are generally the most toxic and phosphates are the least toxic). Phosphonitriles appear to have relatively low toxicities, but mutagenicity may be of concern. Compounds with P-halogen bonds are probably unacceptable as halon substitutes.

B. SILICON COMPOUNDS

Silicon compounds are expected to have few if any global atmospheric impacts. This may be the case even when bromine is present. There is, however, a real need for studies of the photochemistry of bromine-containing silicon compounds.

Little toxicity data are available on silicon compounds of interest as halon substitutes. On the other hand, many silicon compounds, particularly esters and siloxanes, are expected to have low toxicity. As in the case of phosphorus, compounds containing Si-halogen bonds are probably unacceptable as halon substitutes.

C. FLUORINATED AMINES

Totally fluorinated amines could cause atmospheric lifetime and global warming problems. On the other hand, amines with partial fluorination are likely to have relatively short atmospheric lifetimes. It is difficult, however, to determine whether the lifetime would be sufficiently short to allow bromine substitution.

Simple alkyl-substituted amines range from nontoxic in the case of totally fluorinated compounds to highly toxic for nonfluorinated materials. A major question is how the toxicity varies with partial fluorine substitution.

D. FLUORINATED ETHERS

The ether linkage enhances reactivity toward hydroxyl free radicals and, therefore, leads to lower atmospheric lifetimes. On the other hand, this is somewhat offset by fluorine substitution. It is possible that bromine substitution would be allowable; however, ethers are not as easily removed from the atmosphere as are amines, for example, and bromine substitution may lead to unacceptable ozone depletion potentials.

The toxicity of ethers is relatively low compared to other materials evaluated in this report. The ether linkage has a relatively low biological and chemical reactivity.

(The reverse of this page is intentionally left blank.)

REFERENCES

1. Tapscott, R. E., Mather, J. D., Heinonen, E. W., Lifke, J. L., and Moore, T. A., *Identification and Proof Testing of New Total Flooding Agents: Combustion Suppression Chemistry and Cup-Burner Testing*, Final Report, NMERI 97/6/33010, U. S. Department of Defense, Strategic Environmental Research and Development Program and Defense Advance Research Projects Agency, Arlington, Virginia, March 1998.

2. Sax, N. I., and Lewis, R. J., Sr., *Dangerous Properties of Industrial Materials*, Vol. 1-3, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

3. *Registry of Toxic Effects of Chemical Substances*, Report Number DHHS (NIOSH) 87-114, Vols. 1-5, Sweet, D. V., editor, U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health, Washington, DC, April 1987.

4. Heinonen, E. W., Lifke, J. L., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume IV: Tropodegradable Halocarbons*, Vol. 4 of 5, NMERI 96/4/32540, Wright Laboratories (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

5. Skaggs, S. R., and Nimitz, J. S., "Estimating Tropospheric Lifetimes and Ozone-Depletion Potentials of One- and Two-Carbon Hydrofluorocarbons and Hydrochlorofluorocarbons," *Environmental Science and Technology*, Vol. 26, pp. 739-744, 1992.

6. Iikubo, Y., and Robin, M. L., "Fire Extinguishing Methods and Blends Utilizing Hydrofluorocarbons," USA, Patent Number 5,124,053, 23 June 1992. Assigned to Great Lakes Chemical Corporation.

7. *Scientific Assessment of Ozone Depletion: 1994*, Report No. 37, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, United Nations Environment Programme, and World Meteorological Organization, February 1995.

8. *Risk Screen on the Use of Substitutes for Class I Ozone-Depleting Substances: Fire Suppression and Explosion Protection (Halon Substitutes)*, SNAP Technical Background Document, U.S. Environmental Protection Agency, Washington, DC, March 1994.

9. "Protection of Stratospheric Ozone : Final Rule," *Federal Register*, Vol. 60, No. 113, pp. 31092-31107, 13 June 1995.

10. Prinn, R., Weiss, R. F., Miller, B. R., Huang, J., Alyea, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E., and Simmonds, P. G., "Atmospheric Trends and Lifetime of CH_3CCl_3 and Global OH Concentrations," *Science*, Vol. 269, No. 5221, pp. 187-192, 1995.

11. Wuebbles, D. J., and Connell, P. S., *A Screening Methodology for Assessing the Potential Impact of Surface Releases of Chlorinated Halocarbons on Stratospheric Ozone*, UCID-19233, Lawrence Livermore Laboratory, Livermore, California, November 1981.

12. Prather, M. J., and Spivakovsky, C. M., "Tropospheric OH and the Lifetimes of Hydrochlorofluorocarbons," *Journal of Geophysical Research*, Vol. 95, pp. 18723-18729, 1990.

13. Imasu, R., Suga, A., and Matsuno, T., "Radiative Effects and Halocarbon Global Warming Potentials of Replacement Compounds for Chlorofluorocarbons," *Journal of the Meterological Society of Japan*, Vol. 73, No. 6, pp. 1123-1136, 1995.

14. Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E., "Rate Constants for the Reactions of the Hydroxyl Radical with Several Partially Fluorinated Ethers," *Journal of Physical Chemistry*, Vol. 96, pp. 9301-9304, 1992.

15. Atkinson, R., "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," *Journal of Physical and Chemical Reference Data, Monograph No. 1*, American Chemical Society, Washington, DC, and American Institute of Physics, Woodbury, New York, 1989.

16. Cooper, D. L., Cunningham, T. P., Allan, N. L., and McCulloch, A., "Potential CFC Replacements: Tropospheric Lifetimes of C3 Hydrofluorocarbons and Hydrofluoroethers," *Atmospheric Environment*, Vol. 27A, No. 1, pp. 117-119, 1993.

17. Junge, C. E., "Basic Considerations About Trace Constituents in the Atmosphere as Related to the Fate of Global Pollutants," in *Fate of Pollutants in the Air and Water Environments, Part I, Mechanism of Interaction Between Environments and Mathematical Modeling and the Physical Fate of Pollutants*, I. H. Suffet, editor, John Wiley and Sons, New York, New York, pp. 7-25, 1977.

18. Kaizerman, J. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume III: Phosphorus Compounds*, Vol. 3 of 5, NMERI 96/5/32540, Wright Laboratory (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

19. Boodaghians, R. B., Canosa-Mas, C. E., Carpenter, P. J., and Wayne, R. P., "The Reactions of NO3 with OH and H," *Journal of the Chemical Society, Faraday Transactions 2*, Vol. 84, No. 7, pp. 931-948, 1988.

20. Rowland, F. S., "Statospheric Ozone Depletion," in *Annual Review of Physical Chemistry*, Vol. 42, Strauss, H. L., Babcock, G. T., and Leone, S. R., editors, Annual Reviews, Inc., Palo Alto, California, pp. 731-766, 1991.

21. Chase, M. W., Davies, C. A., Downey, J. R., Frurip, D. J., McDonald, R. A., and Syverud, A. N., *JANAF Thermochemical Tables*, 3rd Edition, *Journal of Physical and Chemical Reference Data*, Vol. 14, Supplement 1, 1985.

22. Stedman, D. H., and Fraser, M. E., "Spectroscopy and Mechanism of Chemiluminescent Reaction Between Group V Hydrides and Ozone," *Journal of the Chemical Society, Faraday Transactions 1*, Vol. 79, pp. 527-542, 1983.

23. *CRC Handbook of Chemistry and Physics*, 78th Edition, Lide, D. R., and Frederikse, H. P. R., editors, CRC Press, Inc., Boca Raton, Florida, 1997.

24. McElroy, M. B., Salwitch, R. J., Wofsy, S. C., and Logan, J. A., "Reductions of Antarctic Ozone Due to Synergistic Interactions of Chlorine and Bromine," *Nature*, Vol. 321, pp. 759-762, 1986.

25. Boville, B. W., "Environmental Aspects of Stratospheric Ozone Depletion," UNEP Ozone Meeting, Washington, DC, March 1977.

26. Wofsy, S. C., "Temporal and Latitudinal Variations of Stratospheric Trace Gases: A Critical Comparison Between Theory and Experiment," *Journal of Geophysical Research*, Vol. 83, pp. 364-378, 1978.

27. Anderson, J. G., "The Absolute Concentration of $O(^3P)$ in the Earth's Stratosphere," *Geophysical Research Letters*, Vol. 2, pp. 231-234, 1975.

28. Heicklen, J., "The Correlation of Rate Coefficients for H-Atom Abstraction by HO Radicals with C-H Bond Dissociation Enthalpies," *International Journal of Chemical Kinetics*, Vol. 13, pp. 651-665, 1981.

29. Atkinson, R., "Estimations of OH Radical Rate Constants from H-Atom Abstraction from C-H and O-H Bonds Over the Temperature Range 250-1000 K," *International Journal of Chemical Kinetics*, Vol. 18, pp. 555-568, 1986.

30. Tuazon, E. C., Atkinson, R., Aschmann, S. M., Arey, J., Winer, A. M., and Pitts, J. N., Jr., "Atmospheric Loss Processes of 1,2-Dibromo-3-Chloropropane and Trimethyl Phosphate," *Environmental Science and Technology*, Vol. 20, No. 10, pp. 1043-1046, 1986.

31. Atkinson, R., "Gas Phase Tropospheric Chemistry of Organic Compounds," *Journal of Physical and Chemical Reference Data, Monograph No. 2*, American Chemical Society, Washington, DC, and American Institute of Physics, Woodbury, New York, 1994.

32. Wolfe, R. E., Ellis, D. H., Leahy, H. F., Vinegar, A., and Sharma, S., *Acute Oral Toxicity Evaluation and Genotoxicity Testing of Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene, a Replacement Candidate for Ozone Depleting Substances*, AL/ OE-TR-1997-0054, Armstrong Laboratory, Occupational and Environmental Health Directorate, Toxicology Division, Human Health Systems Center, Air Force Materiel Command, Wright-Patterson AFB, Ohio, ManTech - GEO-CENTERS Joint Venture, Toxic Hazards Research, Dayton, Ohio, May 1997.

33. Weir, P., Activity of 3899-A Chlorophosphazene in IN VITRO Mammalian Cell Transformation Assay, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

34. Weir, P., Activity of 3899-B Chlorophosphazene in IN VITRO Mammalian Cell Transformation Assay, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

35. Weir, P., Activity of T1352A in IN VITRO Mammalian Cell Transformation Assay in the Presence of Exogenous Metabolic Activation, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

36. Weir, P., Activity of T1356A in IN VITRO Mammalian Cell Transformation Assay in the Presence of Exogenous Metabolic Activation, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

37. Weir, P., Activity of T1350 in the IN VIVO Cytogenetic Assay in Rodents for Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, 1979.

38. Weir, P., Activity of T1355 in the IN VIVO Cytogenetic Assay in Rodents for Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, 1979.

39. Weir, P., Activity of T1351A in IN VITRO Mammalian Cell Point Mutation Assay in the Presence of Exogenous Metabolic Activation, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

40. Weir, P., Activity of T1357A in IN VITRO Mammalian Cell Point Mutation Assay in the Presence of Exogenous Metabolic Activation, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

41. Weir, P., Activity of T1350 in the IN VIVO Cytogenetic Assay in Rodents for Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, 1979.

42. Weir, P., Activity of T1350 in the IN VIVO Cytogenetic Assay in Rodents for Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, 1979.

43. Weir, P., Activity of 3899-A-CPP in the SALMONELLA/Microsomal Assay for Bacterial Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

44. Weir, P., Activity of 3899-B-CPP in the SALMONELLA/Microsomal Assay for Bacterial Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

45. Weir, P., Activity of 3899-A Chlorophosphazene in a Test for Differential Inhibition of Repair Deficient and Repair Competent Strains of ESCHERICHIA COLI: DNA Repair, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, September 1978.

46. Weir, P., Activity of 3899-B Chlorophosphazene in a Test for Differential Inhibition of Repair Deficient and Repair Competent Strains of ESCHERICHIA COLI: DNA Repair, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, September 1978.

47. Weir, P., Activity of T1349 in the Dominant Lethal Assay in Rodents for Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, January 1979.

48. Weir, P., Activity of T1354 in the Dominant Lethal Assay in Rodents for Mutagenicity, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, January 1979.

49. Gage, J. C., “The Subacute Inhalation Toxicity of 109 Industrial Chemicals,” *British Journal of Industrial Medicine*, Vol. 27, pp. 1-18, 1970.

50. Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development*, *Volume I: Silicon Compounds*, Vol. 1 of 5, NMERI 96/1/32540, Wright Laboratory (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

51. Kurylo, M. J., Kaye, J. A., Hampson, R. F., and Schmoltner, A. M., *Present State of Knowledge of the Upper Atmosphere 1993: An Assessment Report*, NASA RP-1337, NASA Office of Mission to Planet Earth Science Division, National Aeronautics and Space Administration, Washington, DC, January 1994.

52. “Atmospheric Chemistry: Measurements, Mechanisms and Models: General Discussion,” *Faraday Discussions*, Vol. 100, pp. 441-457, 1995.

53. Watson, R. T., Prather, M. J., and Kurylo, M. J., *Present State of Knowledge of the Upper Atmosphere 1988: An Assessment Report*, NASA Reference Publication 1208, National Aeronautics and Space Administration, Washington, DC, August 1988.

54. Plane, J. M. C., “The Chemistry of Meteoric Metals in the Earth's Upper Atmosphere,” *International Reviews in Physical Chemistry*, Vol. 10, No. 1, pp. 55-106, 1991.

55. Plane, J. M. C., and Helmer, M., “Laboratory Studies of the Chemistry of Meteoric Metals,” in *Research in Chemical Kinetics*, Vol. 2, Compton, R. G., and Hancock, G., editors, Elsevier Scientific Publishing Company, Amsterdam, pp. 313-367, 1994.

56. *Silicones*, S. Fordham, ed., Philosophical Library Inc., New York, NY, p. 32, 1960.

57. Y. Sawado, T. Akiyama, T. Ueno, K. Kamisako, K. Kuroiwa, and Y. Tarui, “Contributions of Silicon- Hydride Radicals to Hydrogenated Amorphous Silicon Film Formation in Windowless Photochemical Vapor Deposition System,” *Japanese Journal of Applied Physics*, Vol. 33, pp. 950-955, 1994.

58. “Significant New Uses of Certain Chemical Substances: Final Rule,” *Federal Register*, Vol. 63, No. 41, pp. 3393-3441, 22 January 1998.

59. McElroy, M. B., Wofsy, S. C., Penner, J. E., and McConnell, J. C., “Atmospheric Ozone: Possible Impact of Stratospheric Aviation,” *Journal of the Atmospheric Sciences*, Vol. 31, p. 287, 1974.

60. Johnston, H. S., Kinnison, D. S., and Wuebbles, D. J., “Nitrogen Oxides from High Altitude Aircraft: An Update of Potential Effects on Ozone,” *Journal of Geophysical Research*, Vol. 94, pp. 16351-16363, 1989.

61. Guy B., and De Rudder, A., “The Potential Impact on Atmospheric Ozone and Temperature of Increasing Trace Gas Concentrations,” *Journal of Geophysical Research*, Vol. 92, pp. 10903-10920, 1987.

62. Miller, C., Steed, J. M., Filkin, D. L., and Jesson, J. P., “The Fluorocarbon Ozone Theory-VII. One-Dimensional Modeling-an Assessment of Anthropogenic Perturbations,” *Atmospheric Environment*, Vol. 15, pp. 729-742, 1981.

63. Crutzen, P. J., and Arnold, F., “Nitric Acid Cloud Formation in the Cold Antarctic Stratosphere: A Major Cause for the Springtime 'Ozone Hole',” *Nature*, Vol. 324, pp. 651-655, 1986.

64. Inoue, G., Izumi, K., and Lozovsky, V. A., “OH Reaction Rate of Halon and CFC Substitutes,” in *Development and Evaluation of Countermeasure Technologies for the Stratospheric Ozone Depletion*, Mizuno, K., and Igarashi, M., editors, Environment Agency of Japan, pp. 192-193, 1996.

65. Nielsen, O. J., Sidebotton, H. W., O'Farrell, D. J., Donlon, M., and Treacy, J., “Rate Constants for the Gas-Phase Reactions of OH Radicals and Cl Atoms with $CH_3CH_2NO_2$, CH_3CH_2NO2, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$,” *Chemical Physics Letters*, Vol. 156, No. 4, pp. 312-318, 1989.

66. Tuazon, E. C., Carter, W. P. L.., Atkinson, R., Winer, A. M., and Pitts, J. N., Jr., “Atmospheric Reactions of N-Nitrosodimethylamine and Dimethylnitramine,” *Environmental Science and Technology*, Vol. 18, pp. 49-54, 1984.

67. Atkinson, R., and Carter, W. P. L., “Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions,” *Chemical Reviews*, Vol. 84, pp. 437-470, 1984.

68. Huheey, J. E., *Inorganic Chemistry*, 3rd Edition, Harper & Row, New York, New York, p. 301, 1983.

69. Yasuhara, A., Kaya, K., and Shiraishi, F., “Human Impact of Halon Alternatives,” in *Development and Evaluation of Countermeasure Technologies for the Stratospheric Ozone Depletion*, Mizuno, K., and Igarashi, M., editors, Environment Agency of Japan, pp. 190-191, 1996.

70. Suga, A., Mochizuki, Y., Gotoh, Y., Ito, H., Takahashi, M., Yamashita, M., Aoyagi, M., Sekiya, A., Kondo, S., and Hakuta, T., “Estimated Lifetimes of Fluorinated Ethyl Methyl Ethers in Atmosphere,” *Chemistry Express*, Vol. 8, No. 4, pp. 205-208, 1993.

71. Brown, A. C., Canosa-Mas, C. E., Parr, A. D., Pierce, J. M. T., and Wayne, R. P., “Tropospheric Lifetimes of Halogenated Anaesthetics,” *Nature*, Vol. 341, pp. 635-637, 19 October 1989.

72. Visca, M., Silvani, R., and Marchionni, G., “Hydrofluoropolyethers: Another Alternative to CFCs,” *Chemtech*, Vol. 27, No. 2, pp. 33-37, February 1997.

73. Misaki, S., and Sekiya, A., “Update on Fluorinated Ethers as Alternatives to CFC Refrigerants,” *Proceedings, International Conference on Ozone Protection Technologies*, Washington, D.C., 21-23 October 1996, pp. 65-70.

74. Sekiya, A., and Misaki, S., “Development of Hydrofluoroethers as Alternative Refrigerants and Other Applications,” *Proceedings, International Conference on Ozone Protection Technologies*, Baltimore, Maryland, 12-13 November 1997, pp. 26-33.

75. *Climate Change 1995, The Science of Climate Change*, Houghton, J. T., Meira Filho, L. G., Callander, B. A., Harris, N., Kattenberg, A., and Maskell, K., editors, Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, England, 1996.

76. “Protection of Stratospheric Ozone: Notice of Acceptability,” *Federal Register*, Vol. 61, No. 173, pp. 47012-47018, 5 September 1996.

77. Tuazon, E. C., “Tropospheric Degradation Products of Novel Hydrofluoropolyethers,” *Environmental Science and Technology*, Vol. 31, pp. 1817-1821, 1997.