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HALOCARBONS AS HALON REPLACEMENTS: TECHNOLOGY REVIEW AND INITIATION

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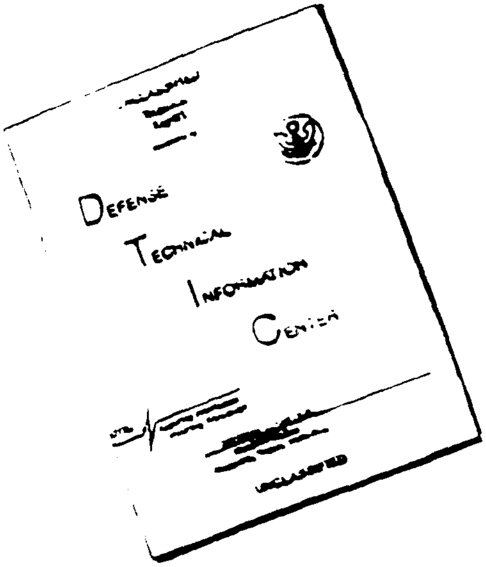
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13. ABSTRACT (Maximum 200 words)

The objective of this overall project is to develop one or more alternative clean halocarbon fire extinguishing streaming agents to replace Halon 1211. In this effort a technology review was conducted and an experimental plan was prepared. Screening criteria are presented with discussions and approaches to meeting the following criteria: cleanliness, toxicity, fire suppression, ozone depletion potentials (ODPs), global warming potentials (GWPs), physical properties, availability/manufacturability, cost, materials compatibility, and chemical stability. Lists of near-, medium-, and far-term candidate agents are presented. An algorithm was developed that enables prediction of atmospheric lifetimes of hydrogen-containing one- and two-carbon haloalkanes containing fluorine and/or chlorine. Relationships are examined among C-H bond strength, activation energy for hydrogen abstraction by OH, reaction rate constants, tropospheric lifetimes, and ODPs. A review of existing and emerging technologies for the destruction of halocarbons is included.

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the overall effort is to develop one or more alternative clean halocarbon fire extinguishing streaming agents to replace Halon 1211. The goal of this effort was to review and update all information collected during the Next-Generation Fire Extinguishing Agent project and to prepare an experimental plan for this effort.

B. BACKGROUND

The storage characteristics, effectiveness, toxicity, and environmental impact of halon replacements all need to be considered in choosing desirable alternative agents. For effective use, the material must have suitable delivery and dispersion properties, high flame suppression ability, and a residue level close to zero. For acceptable environmental impact, such factors as toxicity, ozone depletion potential (ODP), global warming potential (GWP), and physical properties related to transport, volatility, and solubility must be considered.

Large quantities of CFCs, halons, and other volatile halocarbons exist, and occasions may arise when destruction of waste, contaminated, or banked material is desirable.

C. SCOPE

The scope of this overall task involves the development of one or more halocarbon replacements for Halon 1211. Screening criteria are presented with discussions and approaches to meeting the criteria. Criteria discussed include cleanliness, toxicity, fire suppression, ODP, GWP, physical properties, availability/manufacturability, cost, materials compatibility, and chemical stability.

An algorithm was developed that enables prediction of atmospheric lifetimes of hydrogen-containing haloalkanes. Relationships are examined among C-H bond strength, activation energy for hydrogen abstraction, reaction rate constants, and atmospheric lifetimes of hydrogen-containing haloalkanes. A parametric equation based on chemical principles is presented that enables estimation of the atmospheric lifetimes for all compounds containing one or two carbon atoms, at least one hydrogen atom, and the remainder fluorine and/or chlorine atoms. The relationship between atmospheric lifetime and ODP is examined and formulas for estimating ODPs of HCFCs and CFCs are presented.

A review of existing and emerging technologies for the destruction of halocarbons including CFCs and halons is included.

D. METHODOLOGY

Screening criteria for alternative firefighting agents were developed. These criteria include cleanliness, toxicity, fire suppression, ODP, GWP, physical properties, availability/manufacturability, cost, materials compatibility, and chemical stability. The literature databases on toxicity, fire suppression, and combustion were reviewed and continuously updated. Previously developed algorithms for predicting ODPs and fire suppression concentrations were reviewed and installed. The NMERI HALOCARBON DATABASE was screened to provide lists of Group 2 (medium-term) and Group 3 (far-term) candidate agents.

An extensive literature review was conducted on hydrogen-containing haloalkanes to examine bond strengths, activation energies, and rates of reaction with OH. The relationships among these factors are described and relevant equations are presented. A new parameterization scheme based on chemical structure was developed that enables rapid estimation of atmospheric lifetimes for these compounds.

A review of existing and emerging technologies for destruction of halocarbons was conducted. The methods reviewed include many types of incineration, carbon absorption, biological treatment, supercritical water oxidation, oxidation by ozone and ultraviolet light, wet air oxidation, and chemical dehalogenation.

E. TEST DESCRIPTION

Screening criteria were developed and applied to the NMERI HALOCARBON DATABASE to obtain lists of potentially attractive Group 2 and 3 agents. An experimentation plan was developed for Phase II including small- and medium-scale testing of pure agents and blends of agents recommended in this Phase I study.

F. RESULTS

Databases of properties of halocarbons and information on toxicity, fire suppression, and combustion were updated and reviewed. Screening criteria were developed for candidate alternative firefighting agents, and application of these criteria to the chemicals in the NMERI HALOCARBON DATABASE yielded lists of candidate Group 2 and Group 3 agents. A review of destruction technologies of halocarbons was conducted and recommendations on attractive disposal methods were made.

G. CONCLUSIONS

Many candidates exist as potential Group 2 and Group 3 alternative clean firefighting agents; in some cases, several isomers of the same molecular formula warrant attention. Little is known at present about many of the properties of these compounds. Screening criteria were developed for alternative agents, and lists of potential medium- and far-term candidates were developed. An algorithm was developed that allows estimation of tropospheric lifetimes of hydrogen-containing haloalkanes of one or two carbons that contain fluorine and/or chlorine. This algorithm also makes it possible to choose which isomer among several will have the lowest tropospheric lifetime.

Proven methods for destruction of halocarbons including CFCs and halons are incineration, plasma pyrolysis, hydrolysis, catalytic dehydrohalogenation, dehalogenation by sodium naphthalenide, and oxidation. Oxidizing agents include ozone, hydrogen peroxide, supercritical water, and air with steam over a platinum catalyst.

H. RECOMMENDATIONS

Lists of Group 2 and 3 candidates should be continuously updated, and all information available on these compounds should be collected. The desired information includes toxicity, chemical and physical properties, fire suppression ability, cost, availability, manufacturability and materials compatibility. Toxicity requirements provide the most stringent screening criteria. Estimation methods for properties not reported in the literature should be developed. In particular, quantitative structure-activity relationships (QSARs) are needed to estimate toxicities of candidate agents. Laboratory testing of flame suppression and other properties of Group 2 and 3 candidate agents should be carried out as soon as they become available.

The algorithm for estimation of tropospheric lifetimes of HCFCs should be extended to brominated and 3-carbon compounds. Inclusion of brominated compounds requires some values of rigorously calculated lifetimes of HBFCs. The lifetime estimation algorithm should be extended to account for destruction by photolysis; in order to accomplish this the absorption cross sections of haloalkanes must be estimated and that information must be combined with knowledge of the solar spectrum. Once atmospheric lifetimes can be estimated accurately, the algorithm for estimating ODPs should be refined further, and an algorithm for estimating GWP should be developed.

The experimentation plan described for Phase II should be conducted on Group 2 and 3 agents both in pure form and in blends. This plan has the potential of finding alternative agents that are superior to existing halons.

PREFACE

This report was prepared by the New Mexico Engineering Research Institute (NMERI), University of New Mexico, Albuquerque, New Mexico 87131, under contract F29601-87-C-0001, for the Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403.

This report summarizes work done between December 1988 and May 1989. The HQ AFESC/RDCF Project Officers were Major E. Thomas Morehouse and Captain John R. Floden.

Dr. Mary Ann Smith of the College of Pharmacy, University of New Mexico, served as toxicology consultant on this project.

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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LIST OF ABBREVIATIONS

ALC	Approximate lethal concentration
BDE	Bond dissociation enthalpy (energy)
BFC	bromofluorocarbon
CFC	chlorofluorocarbon
CNS	central nervous system
cp	centipoise
g	gram
GWP	Global Warming Potential
HBFC	hydrobromofluorocarbon
HCC	hydrochlorocarbon
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
mL	milliliter
MSDS	Material Safety Data Sheet
ODP	Ozone Depletion Potential
PAFT	Programme for Alternative Fluorocarbon Testing
ppbv	parts per billion by volume
SCBA	self-contained breathing apparatus
TWA	Time Weighted Average

LIST OF SYMBOLS

a	a constant
A	Arrhenius pre-exponential or frequency factor
A'	Arrhenius pre-exponential or frequency factor, varying as a function of temperature
c	speed of light
c_1	a normalizing constant
c_1'	natural logarithm of c_1
c_2	a constant related to the rate of upward travel of a molecule through the troposphere
c_3	a constant describing the ratio of the effect of bromine versus chlorine on ozone destruction
c_4	a constant describing the transit time of a molecule during convective mixing in the troposphere
D	bond dissociation enthalpy (energy)
D_o	a constant
D_i	bond dissociation enthalpy of bond i at 298 K
D_{298}	bond dissociation enthalpy at 298 K
E	energy
E_a	activation energy
E'	activation energy varying as a function of temperature
E_o^i	critical energy of each C-H bond
F_r	reaction factor
F_s	fraction of molecules surviving to reach the stratosphere
h	Planck's constant
k	rate constant
k'	rate constant times hydroxyl radical concentration
k_i	rate constant for the i^{th} C-H bond
k_{298}	rate constant at 298 K
K	Kelvin
L	lifetime
$L_{1/2}$	half-life
L_{avg}	weighted average lifetime

LIST OF SYMBOLS
(CONTINUED)

L_μ	statistical mean lifetime
M	molar mass (molecular weight)
n	number of measurements
n_{Br}	number of bromine atoms
n_{Cl}	number of chlorine atoms
n_H	number of hydrogen atoms
$n_{\alpha\text{-}Cl}$	number of chlorine atoms on the alpha carbon
$n_{\alpha\text{-}F}$	number of fluorine atoms on the alpha carbon
$n_{\beta\text{-}Cl}$	number of chlorine atoms on the beta carbon
$n_{\beta\text{-}F}$	number of fluorine atoms on the beta carbon
R	gas law constant
s	standard deviation
S^i	number of effective oscillators
t	time for a molecule to migrate from the surface of the earth to the stratosphere
T	absolute temperature
$\bar{x}$	average of several measurements
x_i	an individual measurement
α_i	a constant for each substituent on the alpha carbon atom
β_i	a constant for each substituent on the beta carbon atom
β_i	the deviation of the cross section from σ_R^o for each C-H bond
γ_i	the number of equivalent hydrogen atoms of type i
λ	wavelength
ν	frequency
μ	reduced mass of the colliding particles
μ	viscosity
ρ	liquid density
σ_R	reaction radius
σ_R^o	a constant equal to about 1.5 Angstroms

SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of the overall effort is to develop one or more alternative clean halocarbon fire extinguishing streaming agents to replace Halon 1211. The goal of this Phase I effort was to review and update all information collected during the Next-Generation Fire Extinguishing Agent project and to prepare an experimental plan for this project.

B. BACKGROUND

Halon firefighting agents have been used for many years. Because of their combination of effectiveness, cleanliness, safety, and relatively low cost, there has been little incentive to develop new chemicals. Recently, however, calculations and limited experimental data indicate that halons deplete stratospheric ozone more severely, on a per-pound basis, than chlorofluorocarbons. Relative to an ozone depletion potential (ODP) of 1.0 for CFC-11, Halon 1211 has an ODP of approximately 2.7 and Halon 1301 has an ODP of approximately 10.0. The dangers posed by chlorofluorocarbons (CFCs), halons, and other volatile halocarbons to the atmosphere through both stratospheric ozone depletion and greenhouse effects are becoming increasingly evident (References 1-6). The United States Air Force has placed a high priority on the development of alternative agents to replace halon fire suppressants.

Work performed under the project "Next-Generation Fire Extinguishing Agent" has laid a foundation for the development of new firefighting agents. In Phase I of that project, the theory and technology of fire suppression was reviewed and used to establish directions for continuing agent development (Reference 7). In Phase II, selected laboratory experiments on alternative agents were performed (Reference 8).

The Phase III effort initiated work on an alternative training agent (Reference 9). The Phase IV effort provided additional test data on alternative training agents (Reference 10). The purpose of these two phases was to determine whether development of alternative training agents was a viable option and to find the most promising directed approach in such an effort. Since the Phase III and Phase IV work showed that an effort to develop an alternative training agent having a reduced ODP had a high probability for success, it was recommended that a separate project to develop and field test an optimum training agent be instituted. A separate project, "Alternative Training Agents," was, therefore, started as an independent effort.

Phase V (Reference 11) of "Next-Generation Fire Extinguishing Agents" supplied the initial versions of needed databases on candidate agents for both training and general firefighting use. These databases included information on ozone depletion, toxicity, physical properties, and availability. ODP and fire suppression prediction methodologies were also proposed and construction of a literature database was initiated. These materials will be used in the present project "Halocarbons as Halon Replacements," which has been initiated as an independent effort.

The storage characteristics, effectiveness, toxicity, and environmental impact of halon replacements all need to be considered in choosing desirable alternative agents. For confidence in long-term storage, the stability of the compound (or compounds, in a mixture), corrosion of metal surfaces, and compatibility with O-rings and valve seats must be known. For effective use, the material must have suitable delivery and dispersion properties, high flame suppression ability, and a residue level close to zero. In this context, suitable means appropriate to the particular use desired. For acceptable environmental impact, such factors as toxicity, ODP, GWP, and physical properties related to transport, volatility, and solubility must be considered.

If a fire extinguishant is to be effective, contributions of both physical and chemical mechanisms should be optimized. Physical extinguishment includes contributions from heat of vaporization, vapor heat capacity, and heats of reaction (e.g., heats of combustion and decomposition). Chemical extinguishment involves disruption of the radical chain reactions occurring in fires.

Both ODPs and GWPs depend on atmospheric lifetimes. For ODP, a longer lifetime means a greater proportion of the molecules released reaches the stratosphere, where photolysis creates the chlorine or bromine radicals that catalyze destruction of ozone. With respect to global warming, a longer lifetime means the molecules are absorbing infrared light radiated by the surface of the earth and transforming it to kinetic energy for a longer time, resulting in increased warming.

Large quantities of CFCs, halons, and other volative halocarbons exist, and destruction of banked material may be desirable when replacements become available. In addition, it is sometimes safer, easier, and more economical to destroy contaminated or waste CFCs and halons than to purify them by distillation, filtration, or other means. During the technology assessment of halocarbons, information continued to appear on destruction technologies. Since this information was acquired without additional effort, and will be of interest to the Air Force, it has been included here.

C. SCOPE

The scope of this overall task involves the development of one or more halocarbon replacements for Halon 1211. The target criteria for the replacement agents are as follows:

- The agent shall leave no residue upon evaporation.

- The ozone depletion potential (ODP) shall be 0.05 or less on either a per-molecule basis or a unit-weight basis when compared with CFC-11.*
- The estimated or reported acute toxicity shall be equal to or better than that of the halon being replaced.
- The environmental impact (other than ODP) shall be equal to or less than that of the halon being replaced.
- No major changes in Air Force equipment shall be required for storage, transfer, or delivery. This effort will be followed by field validation studies.

This effort included development of screening criteria for alternative firefighting agents. Statements of the criteria, discussions of relevant factors, and approaches to meeting the criteria are presented. Criteria discussed include cleanliness, toxicity, fire suppression, ODP, GWP, physical properties, availability/manufacturability, cost, materials compatibility, and chemical stability.

This effort also included development of an algorithm that enables prediction of atmospheric lifetimes of hydrogen-containing haloalkanes. The relationships among C-H bond strength, activation energy for hydrogen abstraction. reaction rate constants, and atmospheric lifetimes are examined for hydrogen-containing haloalkanes. A parametric equation based on chemical principles is presented that enables estimation of the atmospheric lifetimes for all compounds containing one or two carbon atoms, at least one hydrogen atom, and the remainder fluorine and/or chlorine atoms. The relationship between lifetime and ODP is examined and formulas for estimating ODPs of HCFCs and CFCs are presented. This algorithm is a step toward more accurate, theoretically supportable estimation methods for ozone depletion potentials (ODPs) and global warming potentials (GWPs). The

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*The Subtask Statement gives an ODP requirement of 0.10 or less; however, recent developments within the Air Force and the EPA indicate that an ODP of 0.05 or less is a more appropriate target.

estimates of lifetimes, ODPs, and GWPs are needed as initial screens for environmental acceptability of halogenated compounds used for firefighting and other purposes.

A review of existing and emerging technologies for the destruction of halocarbons including CFCs and halons is presented.

D. TECHNICAL APPROACH

The reports cited in the Applicable Documents Section of the Subtask Statement (References 7-9, 12) were reviewed. The literature databases on toxicity, fire suppression, and combustion initiated in earlier work plus other information sources were also reviewed. The literature databases were updated; the updating will continue throughout this project.

The previously developed candidate halocarbon database, which gives information on ODP, toxicity, availability, and physical properties was reviewed and expanded as additional data were generated experimentally and collected from the literature. These data were used for planning experiments.

Computerized ODP and fire suppression prediction algorithms developed in earlier work were reviewed and installed. Throughout this project, these prediction techniques will be upgraded and improved as needed and as new data become available. Predicted ODPs and fire suppression characteristics will be used to help plan experiments.

Screening criteria for alternative firefighting agents are presented. These criteria include cleanliness, toxicity, fire suppression, ODP, GWP, physical properties, availability/manufacturability, cost, materials compatibility, and chemical stability.

An extensive literature review was conducted on hydrogen-containing haloalkanes to examine bond strengths, activation energies, and rates of reaction with OH. The relationships among these factors are described and relevant equations are presented. Previous methods for estimating all of these items are summarized. The utility of these methods in estimating atmospheric lifetimes is assessed. A new parameterization scheme based on chemical structure is developed that enables rapid estimation of activation energies and atmospheric lifetimes for these compounds.

First, the components of the rate constants for reactions of hydroxyl radicals with hydrogen-containing halocarbons are discussed in terms of the Arrhenius rate law. These components include the pre-exponential factor, activation energy, and absolute temperature. This section is followed by a discussion of bond strengths and their relationship to activation energy. Next, a group additivity scheme for estimation of C-H bond strength in haloalkanes is described. A parameterized equation relating chemical structure directly to activation energy (and therefore rate constant and lifetime) is presented. Theoretically supportable equations relating ODPs to lifetimes for HCFCs and CFCs are presented; these match the experimental and rigorously calculated values well.

Information on existing and emerging technologies for destruction of halocarbons is included. The methods reviewed include many types of incineration, carbon adsorption, biological treatment, supercritical water oxidation, oxidation by ozone and ultraviolet light, wet air oxidation, and chemical dehalogenation.

SECTION II
THE HALON/GLOBAL CHANGE PROBLEM

A. OZONE DEPLETION AND GLOBAL WARMING

Short wavelength solar radiation causes many adverse environmental effects. This radiation (UV-B) is believed to cause skin cancer, cataracts, materials degradation, increased tropospheric oxidants, crop damage, and disruption of ecosystems (Reference 13). Fortunately, a layer of ozone in the stratosphere acts as a barrier to prevent a large percentage of solar UV-B from reaching the earth's surface. In 1974, it was pointed out that emissions of certain halogenated chemicals can deplete stratospheric ozone (Reference 14), and evidence of this threat has continued to increase. Among the chemicals implicated are chlorofluorocarbons (CFCs) and halon fire extinguishing agents.

Stratospheric ozone is depleted in a four-step process: (1) a halocarbon containing chlorine and/or bromine is released, (2) the halocarbon migrates to the stratosphere, (3) the halocarbon is photodissociated by intense stratospheric UV solar radiation, and (4) the released bromine or chlorine catalytically destroys ozone. Ozone Depletion Potentials (ODPs) are measures of the impact of a chemical on stratospheric ozone per unit weight (or per molecule) released and are determined by complex computer calculations involving transport and reaction (Reference 15). No technique currently exists by which to measure an ODP directly in the laboratory. ODPs are normalized relative to the impact of CFC-11, which is arbitrarily assigned an ODP of 1. Halon 1301 has an ODP of approximately 10 and is, therefore, 10 times more damaging to stratospheric ozone than is CFC-11 (per pound released). Halon 1211 has an ODP of about 3.

Halocarbons with low ODPs can be obtained in two ways: (1) If no bromine or chlorine is present, no damage occurs. Fluorine does not damage ozone since it reacts rapidly with methane and other materials to form HF, which is stable and is eventually lost by migration to the troposphere, where it is removed by rain and other processes. Thus FCs and HFCs (hydrofluorocarbons) have zero ODPs. (2) If the released molecule is destroyed in the troposphere before it has a chance to migrate to the stratosphere, there is no impact on stratospheric ozone. For example, compounds such as HCFCs (hydrochlorofluorocarbons) contain hydrogen atoms, which can react with trophospheric hydroxyl free radicals. If reaction occurs, the halocarbon is destroyed before it enters the stratosphere. Since some molecules may survive, the ODPs for HCFCs are not usually zero, though they are often low. Similarly, tropospheric photolysis may occur for some molecules containing chromophores. No effective mechanism exists for tropospheric destruction of fully halogenated alkanes such as the CFCs and the halons now used, and such compounds have high ODPs.

During the fall of 1989, the NASA total ozone mapping spectrometer on the Nimbus 7 satellite showed that ozone depletion over Antarctica nearly matched the record depletion of October 1987 (Reference 16). On 5 October 1987, the ozone concentration dropped to a record low of 109 Dobson units, compared with the 300 Dobson units normally expected for October. One Dobson unit corresponds to one micrometer thickness of pure ozone gas at standard temperature and pressure (Reference 17). On 5 October 1989, the observation of a concentration of less than 125 Dobson units indicates that severe ozone depletion is continuing.

The threat to the global environment has been considered sufficiently serious that, in 1987, an international treaty, the Montreal Protocol on Substances That Deplete the Ozone Layer, was established to limit the production and consumption of CFCs and halons. The Protocol has now (June 1990) been signed by 67 nations and has been ratified by 62 of those countries. The ratifiers include the U.S. and almost every other industrialized country.

To implement this protocol, the U.S. Environmental Protection Agency (EPA) has limited the consumption of halons to 1986 levels beginning in 1992. Here, "consumption" is defined as production minus exports plus imports, allowing for materials produced as intermediates. On 29 June 1990, the parties to the Protocol met in London to amend the Montreal Protocol. The Principal Investigator for this project was a member of the United Nations Environment Programme, Technical Options Committee, which prepared a report for the London meeting (Reference 18). Participation in the work of this committee permitted the determination of what new technologies might be available, the establishment of contacts with others working on alternative technologies, and the acquisition of information required to better define needed time lines for the Halocarbons as Halon Replacements project. Amendments passed at the London meeting call for a phaseout of all halons, except for essential uses, by the year 2000. Though "essential uses" must yet be defined by the Protocol parties, it is expected that no more than five percent of the present halon usage will be deemed essential, and at a meeting at Tyndall AFB, Dr. Stephen Andersen of the EPA stated that three percent for essential uses is more likely (Reference 19).

A major uncertainty exists regarding which chemicals will be resticted. The present Protocol restrictions are based on both ODP and amount manufactured. These criteria will probably be used for future regulatory action also. It is likely that taxes imposed on halons will limit the market for materials with higher ODP values. The Budget Reconciliation Act of 1989 enacts a halon excise tax that increased to $2.65 per pound per ODP unit beginning in 1994. Thus, beginning in 1994, Halons 1301 and 1211 will be taxed at $26.50 per pound and $7.95 per pound, respectively, if the presently accepted ODP values for these compounds continues. Even with decreased demand, it is likely that there will be increasing shortages, restrictions on use, and eventual elimination of most or all firefighting agents having high ODPs. Though several countries tried to restrict halon alternatives to an ODP of 0.1 or less at the June 1990 London meeting of the Protocol parties, this resolution was not passed. It may, however, be the basis for future amendments.

Halogenated hydrocarbons also contribute to global warming. The earth is normally in a state of thermal equilibrium. Visible and ultraviolet solar radiation strikes the earth and heats it. The heated earth then emits infrared radiation into space. Part of the outgoing infrared radiation is captured and then re-emitted by certain atmospheric gases, in particular, carbon dioxide, methane, water vapor, and nitrogen oxides. These gases are transparent to most UV/visible radiation but absorb part of the IR radiation normally lost to space. Part of this IR radiation is directed back to the earth. If it were not for this "greenhouse effect," the earth would be much cooler than it is today.

The concentrations of greenhouse gases are, however, increasing, and new greenhouse gases (in particular, halons and CFCs) are being added. The earth must therefore heat up to achieve a sufficiently high temperature that the IR energy loss is again equal to the solar energy gain. At this point, a new, higher equilibrium global average temperature will be achieved.

Like ODP, a global warming potential (GWP) can be calculated for gaseous materials. Per pound released, Halon 1301 has a temperature sensitivity factor (directly related to GWP) that is 25,000 times that of carbon dioxide (Reference 20). Though this seems very high, most gaseous organic chemicals, and all halocarbons, have GWPs much higher than that of carbon dioxide because most organic molecules are effective absorbers of IR radiation in the wavelength range emitted by the earth. Halons are not greatly different from other gaseous organic compounds. The reason that carbon dioxide causes much more global warming than do the halons and CFCs is that the carbon dioxide release rate is much larger. A decrease in atmospheric lifetime also decreases the GWP of a compound. Therefore, compounds such as HCFCs and HFCs, which contain hydrogen and can be destroyed by tropospheric hydroxyl free radicals, have reduced, though nonzero, GWPs. On the other hand, perfluorocarbons, which have longer atmospheric lifetimes, can have significant GWPs. Note, however, that any gaseous material that could be used in fire extinguishment will almost certainly have a GWP much larger than that of carbon dioxide. Moreover, it is likely that GWPs will not be an important issue in the use of alternative agents in critical applications, such as North Slope and related facilities.

At the 8 June 1990 meeting of the Halon Alternatives Research Corporation (HARC) Government Working Group in Washington, DC, EPA representatives stated that global warming potential was not likely to be an important factor for firefighting chemicals "if they are used wisely."

B. HALONS, CFCs, AND RELATED MATERIALS

Halons, CFCs, and related materials are partially or fully halogen-substituted aliphatic hydrocarbons. The halogens of interest here are fluorine, chlorine, and bromine. Chlorofluorocarbons (also know as "Freons" [duPont], and "Genetron" [Allied Signal]) are organic compounds containing only chlorine and fluorine substituents on the aliphatic carbon skeleton. Of interest in this proposal are the perfluorocarbons (FCs), which are fully fluorinated hydrocarbons. Other chemicals that have been considered for total-flood applications are the hydrofluorocarbons (HFCs), which are partially halogenated hydrocarbons, and the hydrochlorofluorocarbons (HCFCs), which are partially halogenated hydrocarbons containing both chlorine and fluorine. Since the formulas and names for these compounds are complex, they have been given simple designation numbers with the prefixes "CFC," "FC," "HFC," "HCFC," etc. The additional prefix "C" is used to denote a cyclic compound. In the refrigeration and air conditioning industry, the prefix "R" is often used. The numerical designations give the number of carbon atoms minus 1, the number of hydrogen atoms plus 1, and the number of fluorine atoms. Preceding zeros are dropped. Thus, for example, dichlorodifluoromethane, CF_2Cl_2, is CFC-12 (or R-12) and chlorodifluoromethane, $CHClF_2$, is HCFC-22 (or R-22).

An alternative numerical nomenclature system, using the prefix "Halon," is usually used for fire extinguishing halocarbons. Most halons contain bromine in addition to fluorine, and some contain chlorine substituents. Halon designations give the number of carbon, fluorine, chlorine, and bromine atoms. Thus, Halon 1301 is bromotrifluoromethane, CF_3Br, and Halon 1211 is bromochlorodifluoromethane, CF_2ClBr.

C. FIRE EXTINGUISHMENT BY HALONS

Halons exhibit two important features. First, they are clean. They leave no residue and do not harm or cause malfunction of electronic and electrical equipment. Second, halons are highly effective, particularly where a multidimensional agent is needed. Concentrations of only a few percent are necessary to effect extinguishment, and, at these low concentrations, they are relatively safe to use in occupied areas.

Halocarbons extinguish fires by both chemical and physical mechanisms. For Halons 1301 and 1211, the two most widely used halon extinguishing agents, chemical mechanisms appear to be the most important for fire extinguishment, because of the propensity for bromine to enter into catalytic chemical suppression cycles. For HCFCs, FCs, and HFCs, physical processes are very important; however, where it can be formed, CF_3 appears to provide a very important chemical suppression mechanism. These chemical and physical mechanisms are discussed in Section V.

Halon 1211 is a streaming agent; it is usually applied by discharge directed into a fire from a manually operated portable extinguisher. Replacement agents for Halon 1211 must have higher boiling points to allow streaming and, in general, would not be used to flood an area and render it inert. Since directed discharge limits exposure to personnel, streaming agents do not have toxicity requirements as stringent as those for total-flood agents.

Halon 1301 is usually used as a total-flood agent. Such agents fill an area to give the concentration needed for extinguishment and inertion. Total-flood agents, which are usually applied from non-portable systems (usually automatic, rather than manual), have very stringent toxicity requirements since they are often used in inhabited areas, where there may be extensive contact with personnel.

SECTION III

EXPANSION OF THE DATABASE

The NMERI HALOCARBON DATABASE was expanded to include all known acyclic chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons whose molecules contain one or two carbon atoms. All known three-carbon compounds of these classes having selected molecular formulas are also included. The molecular formulas used for three-carbon compounds include one to three hydrogen atoms, zero to three chlorine atoms, and three to six fluorine atoms. The reasoning used to set these parameters is that at least one hydrogen atom is required for a short atmospheric lifetime, while more than three hydrogen atoms tend to make a compound more flammable and more toxic, though some exceptions may exist. The presence of more than three chlorine atoms generally leads to increased toxicity. The presence of three or more fluorine atoms helps reduce toxicity and anesthetic properties. In addition to these compounds, all perfluorocarbons through perfluoroheptane and selected cyclic alkane derivatives have been included. The database contains 671 compounds at this time. Executable versions of the macros that allow user-friendly access to the database information were created. A search of the literature for additional chemical property information also continues.

SECTION IV

TOXICITY DATABASE EXPANSION

The toxicity portion of the database has been revised and expanded to include general toxicity information on the various chemicals as well as specific referenced and abstracted toxicity information. The General Toxicity Data fields provide summaries of important toxicological parameters, such as established or estimated occupational exposure limits (e.g., time weighted averages, TWAs), evidence of mutagenicity and/or carcinogenicity (and, if so, in what species), the stage of toxicity testing, governmental study programs and inventories the chemical is listed under, and a lethality index that allows quantitative comparisons among halocarbons. In addition, a short abstract summarizing the known health effects is provided. The Toxicity Reference Data fields provide compilations of referenced toxicity information taken from the open literature, lectures, symposia, and personal communications. This portion of the database provides a computerized means of compiling the vast amounts of information being acquired on halocarbons and is continuously updated as new data become available.

In addition to the toxicity information, a section has been added on safety information and recommendations. These records provide information on flammability and explosive limits as well as summaries of the health and safety information from the Material Safety Data Sheets (MSDS) supplied by manufacturers. With this information in the database the proper handling and storage requirements of each compound are readily available to the user.

SECTION V
FIRE EXTINGUISHMENT CALCULATION

A. CHEMICAL EXTINGUISHMENT MECHANISM

The primary chemical mechanism for halons and halon-like suppressants involves the termination of free-radical reactions that sustain combustion. Bromine-substituted compounds are particularly effective in this role. The most important chemical reaction occurring in the early stages of suppression appears to be bromine abstraction by hydrogen (Reference 21). This is shown below using Halon 1301 as an example:

$$CF_3Br + H \rightarrow CF_3 + HBr \qquad [1]$$ *

Once formed, the HBr can react with another H atom to form diatomic hydrogen (H_2), releasing a bromine atom. The atomic bromine can then form diatomic bromine (Br_2) in a three-body reaction involving nitrogen, oxygen, or some other molecule (M) to carry off energy. The Br_2 released is available for reaction with another hydrogen atom to give HBr again, and reactions can continue in a cyclic catalytic process to remove more hydrogen atoms:

$$HBr + H \rightarrow H_2 + Br \qquad [2]$$

$$Br + Br + M \rightarrow Br_2 + M \qquad [3]$$

$$Br_2 + H \rightarrow HBr + Br \qquad [4]$$

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*For the convenience of the reader, reaction numbers are placed in brackets and equation numbers are placed in parantheses.

This mechanism converts highly reactive H free radicals into much less reactive diatomic hydrogen.

Although removal of hydrogen atoms is believed to be the primary chemical mechanism for combustion suppression, removal of other free radicals also plays a role. Abstraction of bromine by fire-generated hydroxyl free radicals also occurs in the initial stages of halon/fire interactions (Reference 22). Generation of HOBr is followed by reaction with hydrogen to give water and bromine atoms again. Since OH is nearly as effective as H in sustaining combustion, this mechanism is also believed to be important in fire extinguishment, although there is some question on this (Reference 23).

$$CF_3Br + OH \rightarrow CF_3 + HOBr \qquad [5]$$

$$HOBr + H \rightarrow H_2O + Br \qquad [6]$$

Similar mechanisms appear to be effective in removing oxygen atoms from the combustion free-radical pool; however, because of their lower concentration, oxygen free radicals may not play as large a role as do hydrogen and hydroxyl free radicals.

Thermal decomposition of halons may also provide free Br and/or Br_2 for catalysis of hydrogen atom or hydroxyl free radical removal. This mechanism, which seems to be more important for large halon molecules, is shown for Halon 2402 below:

$$CF_2BrCF_2Br + M^* \rightarrow CF_2BrCF_2 + Br + M \qquad [7]$$

$$CF_2BrCF_2Br\ M^* \rightarrow CF_2CF_2 + Br_2 + M \qquad [8]$$

Reactions [1] through [8] also hold for chlorine; however, chlorine is somewhat less effective in quenching free radical reactions. Fluorine, which is even less effective than chlorine, can also participate in these reactions. Thus, compounds containing no bromine are generally less effective fire extinguishants than the bromine-containing halons used today. However, bromine-containing compounds, particularly those containing hydrogen, often have toxicity problems. Moreover, all such compounds are expected to have significant ODPs, even when hydrogen is present.

One can predict extinguishment concentrations by fitting an equation first reported by Hirst and Booth (Reference 24) to a small set of extinguishment concentrations (see below). Results from this algorithm indicate that compounds containing the CF_3 group have anomalously low extinguishing concentrations. These results and other recent work at the Naval Research Laboratory (Reference 25) indicates that the CF_3 group has a relatively high effectiveness in fire extinguishment. Thus, compounds such as FC-116 (CF_3CF_3), FC-218 ($CF_3CF_2CF_3$), and FC-125 (CHF_2CF_3) are much more effective than calculated from fire extinguishment algorithms. The following

$$CF_3 + H + M \rightarrow HCF_3 + M \qquad [9]$$

$$CF_3 + OH \rightarrow COF_2 + HF \qquad [10]$$

B. PHYSICAL MECHANISMS

Oxygen and gaseous fuel dilution appears to play only a very minor role in extinguishment by halocarbons, as can be seen in the high fire extinguishment concentration (above 20 percent) required by carbon dioxide, which operates primarily by dilution. In comparison, halocarbons usually have extinguishment concentrations well below 20 percent.

Two other physical mechanisms are important in extinguishment by halons and other halocarbons. First, the molecules can carry off energy (remove heat) by excitation of rotational, vibrational, and translational molecular motions. This energy removal occurs during both agent evaporation and agent heating. Second, the molecules can dissociate thermally, while absorbing energy. Both of these processes lower the temperature of the fire.

It has also been proposed that halons have a fire suppression mechanism that is not clearly physical or chemical. Their molecules can act as third bodies to absorb energy and facilitate free-radical recombination (Reference 23).

C. EXTINGUISHMENT CONCENTRATION PREDICTION

A computer model, PREDICT, based on the Hirst and Booth model (Reference 24), has been developed to predict the extinguishing capabilities of halocarbons. The basic prediction formula employs a parameterized fit to the molecular formula using minimization and regression techniques. The formula predicts the concentration necessary to extinguish heptane cup burner flames. Data from literature searches were used to determine a baseline of extinguishing concentrations. The model fits 11 experimental data points with $r^2 = 0.941$. When applied to other halocarbons, it predicts extinguishing concentrations that agree well with measured values in most cases. As noted above, discrepancies appear to occur when CF_3 groups can be generated. This model has been installed as part of the NMERI HALOCARBON DATABASE and will be modified as additional laboratory data are obtained.

SECTION VI
SCREENING CRITERIA

A. CLEANLINESS

1. Criterion

Alternative firefighting agents must be clean. For this purpose the definition of clean is that the agent evaporates within a few minutes leaving negligible residue.

2. Discussion

One of the major advantages of halons is their cleanliness. They can be used on electronic, electrical, or complex mechanical equipment without requiring subsequent cleanup or causing equipment malfunction.

3. Approaches

Halocarbons with low to moderate boiling points are in general expected to meet this criterion. For streaming applications, compounds with boiling points above approximately 50 °C will be ranked lower in terms of cleanliness than compounds with lower boiling points because the former will evaporate more slowly. Unless the agents have high-molecular weight or other nonvolatile impurities, the residue levels from evaporation of these organic liquids are expected to be negligible.

B. TOXICITY

1. Criterion

Measured or estimated acute toxicity of candidate agents must be comparable to or lower than that of existing halons.

2. Discussion

Human and animal research indicates several principal adverse health effects of halogenated hydrocarbons. First, they can stimulate or suppress the central nervous system (CNS) to produce symptoms ranging from lethargy and unconsciousness to convulsions and tremors (Reference 26). Second, halogenated hydrocarbons can cause cardiac arrhythmias and can sensitize the heart to epinephrine (adrenaline) (Reference 27). Serious arrhythmias are of particular concern because firefighters are exposed to these compounds while under highly stressful conditions, when their bodies have high levels of circulating epinephrine. Third, inhalation of halogenated hydrocarbons can produce bronchoconstriction, reduce pulmonary compliance, depress respiratory volume, reduce mean arterial blood pressure. and produce tachycardia (rapid heartbeat) (Reference 28). Fourth, these agents can cause organ damage due to degradative byproducts produced by metabolism (Reference 29). CNS effects, cardiac sensitization, and pulmonary disorders appear to be reversible upon termination of exposure to these chemicals. Organ toxicity, on the other hand, is a latent effect, and sequelae (delayed effects due to the compound or its metabolites) are usual.

The immediate effects of a halocarbon on the nervous system, cardiovascular system, and respiratory system appear to be caused by the compound itself. However, it is thought that the latent effects that take place in specific organs, such as the liver, kidneys, and lungs, are caused by the degradative products formed when the halocarbons enter into metabolic processes. Both the immediate effects and the latent organ damage must be considered when evaluating potential candidates for firefighting agents. Although generalization to the entire class of halocarbons would be convenient, toxicity information on each candidate must be acquired in order to assess fully its potential health hazards.

The relationship between chemical structure and toxicity has been explored in simple halogenated alkanes. Evidence indicates that the greater the number of fluorine atoms and the fewer the number of chlorine, bromine, and iodine atoms present on the molecule, the lower the toxicity of the compound. Even with the replacement of only one chlorine by fluorine (e.g., HCFC-22 versus HCFC-21), a notable reduction in toxicity as indicated by exposure limits is observed. The same trend is seen in perhalogenated methanes, where, for example, CFC-14 (CF_4) is much less toxic than CFC-10 (CCl_4). Similarly, toxicity is decreased when bromine or iodine atoms are replaced by fluorine. Also, when hydrogen is replaced with fluorine, a reduction in toxicity occurs. The same trends hold for halogenated ethanes, propanes, and butanes, in which the reduction of toxicity is a function of increasing fluorination at the expense of chlorine. In haloalkanes of two or more carbons, when four fluorine atoms are present on the molecule, the number of hydrogen atoms appears to have little or no effect on the toxicity.

It is desirable that alternative agents be less toxic than Halon 1211. For comparison purposes, a summary of the toxicity information on Halon 1211 is provided here.

The original toxicological studies on Halon 1211 were performed in 1950 by the United States Army Chemical Center (Reference 30). In these studies, laboratory rats were exposed to various concentrations of halocarbons and other fire extinguishing agents for 15 minutes and the exposure level necessary to result in death was observed. The approximate lethal concentration (ALC) of Halon 1211 was 32.4 percent. Rats exposed to this concentration of Halon 1211 became unconscious after 1 minute and showed signs of lung irritation and damage when they were examined post-mortem. Death in all cases appeared to be due to extreme CNS depression and respiratory tract irritation. Later, Underwriters' Laboratories performed similar experiments in guinea pigs (Reference 31). They exposed these animals to varying concentrations of fire extinguishing agents ranging from 0.5 to 20 percent for 5 minutes to 2 hours. On the basis of their results, the Underwriters' Laboratories established a classification of comparative hazardous agents. Halon 1211 was classified as having moderately low toxic effects, approximately similar to those of carbon dioxide. Several other research teams have investigated the toxic consequences of Halon 1211 in a variety of animal species (Reference 32). Exposure of rats, mice, guinea pigs, rabbits, and monkeys to concentrations of Halon 1211 greater than about 10 percent usually resulted in slight trembling of the extremities within 10 minutes, and if exposure to higher concentrations was prolonged, convulsions eventually occurred. Chronic exposure tests were conducted by exposing small laboratory animals for several hours per day for 15 days to varying concentrations (Reference 33). These tests revealed that no toxic effects occurred during or after the chronic exposures, other than those described for acute and subchronic experiments.

Halon 1211 has also been shown to sensitize the heart to epinephrine in dogs given intravenous injections of epinephrine and in some dogs exposed to halons in fright-producing situations (Reference 33). Since it is not easy to predict how humans will respond to exposure based upon animal experiments, several acute human exposure studies have been performed (Reference 33). Volunteers exposed to 4 to 5 percent Halon 1211 for 1 minute noted symptoms ranging from marked dizziness to tingling toes and fingers. The initial effects of exposure were a feeling of intoxication and impairment of mental and physical performance. In one subject, when exposure was continued past this point, signs of CNS dysfunction and spontaneous, transient arrhythmias became apparent. Since no effects are seen within the first 30 seconds of exposure, it appears that this amount of time is required for the body to absorb a sufficient quantity of the agent to bring about the onset of the effects. After the "threshold" level has been reached, the onset of the effects is rapid. Also, evidence suggests that the CNS results precede the heart effects. Based on this information, the maximum safe exposure limit for humans is 4 to 5 percent Halon 1211 for 1 minute.

Toxicity testing is the most time-consuming part of studies of potential firefighting agents. Under the accelerated testing schedule of the Programme for Alternative Fluorocarbon Toxicity Testing (PAFTT), thorough testing of a new compound requires six years (Reference 34).

Considerations of the short- and long-term health hazards to exposure, the relationships between chemical structure and toxic effects, and the biodegradation and production of reactive metabolites are of key importance when deciding which compounds hold potential for future use as firefighting agents.

C. FIRE SUPPRESSION

1. Criterion

The agent must be effective in suppressing three-dimensional Class A and B fires. The agent itself should not be flammable at any concentration in air.

2. Discussion

Chlorine- and bromine-containing haloalkanes are in most cases highly effective fire suppression agents. In general, the higher the percentage of hydrogen in a molecule, the more flammable it is. Halocarbons containing three or more hydrogen atoms are at risk of being flammable at some concentrations in air. For example, HCFC-141b is flammable at concentrations of 7 to 16 volume in percent in air (Reference 35). HFC-152a is flammable at concentrations of 3.9 to 16.9 volume percent in air (Reference 36). However, HFC-143a is reported to be nonflammable (Reference 37).

3. Approach

An algorithm has been developed for estimating the fire suppression concentrations of haloalkanes based on molecular formula. This algorithm is described in Reference 11 and is discussed in Section V of this report. At least one chlorine, bromine, or iodine atom is required for effective fire suppression. On the basis of potential flammability, chemicals containing less than three hydrogen atoms will be favored.

D. OZONE DEPLETION POTENTIAL

1. Criterion

The ODP should be less than 0.05 and as close to zero as possible.

2. Discussion

Present halon firefighting agents have high ODPs because they generate bromine radicals in the stratosphere (References 38-41). As a class, halons have ODPs ranging from approximately 3 to 10. Other types of fluorocarbons (CFCs, HFCs, HCFCs, and FCs) have lower ODPs because chlorine is less destructive to ozone than bromine. Moreover, those fluorocarbons containing one or more hydrogen atoms in their molecules undergo significant destruction by hydroxyl radicals in the atmosphere before they can reach the stratosphere. Perfluorocarbons have a zero ODP, since they do not generate ozone-destroying chlorine or bromine radicals. An ODP of 0.05 for an alternative agent would be 2 percent of the ODP of approximately 3 for Halon 1211.

3. Approach

Alternative agents containing at least one hydrogen atom should be developed. Another possibility is an agent that contains chlorine but not bromine. A third possibility is the development of agents that contain other functional groups (such as double bonds or geminal dibromides) that result in their rapid destruction in the troposphere.

E. GLOBAL WARMING POTENTIAL

1. Criterion

The GWP of an alternative agent should be as close to zero as possible.

2. Discussion

The greenhouse effect of halogenated hydrocarbons is receiving increasing attention (References 42 and 43). This effect may be equal in importance to ozone depletion as an environmental hazard. Existing halons and CFCs have global warming potentials (GWPs) ranging up to 25,000 times that of carbon dioxide on a per-pound basis. Approximate ranges for estimated ODPs and GWPs for various classes of fluorocarbons are shown in Table 1 (References 44-46).

The greenhouse effect is caused by the absorbance and emission of infrared light in the "atmospheric window" (the 7-14 μm, 800-1400 cm^{-1} region) by trace atmospheric components. Molecules containing carbon-to-halogen bonds (C-F, C-Cl, C-Br) absorb and re-emit infrared radiation in this region, causing energy that would otherwise have been lost into space to be redirected toward the earth. Temperature sensitivity is a measure of how much the temperature of a body of air increases for every part per billion by volume (ppbv) of an organic present. GWP takes into account both this temperature sensitivity and atmospheric lifetime. On a per-molecule basis, some halocarbons, such as $CBrF_3$ (Halon 1301) and $CClF_3$, have temperature sensitivities 25,000 times that of carbon dioxide.

3. Approach

One approach to minimizing GWP is to minimize atmospheric lifetime, for example, by including hydrogen atoms or multiple bonds in the chemical structure. Another approach is to minimize absorption of infrared radiation by appropriate design of the chemical structure.

F. PHYSICAL PROPERTIES

1. Criterion

The agent should have appropriate physical properties for the application. Some properties relate to deliverability and some to extinguishing ability. These physical properties include (but are not limited to) boiling point, vapor pressure at room temperature, density, viscosity, heat of vaporization, and vapor heat capacity.

2. Discussion

The effectiveness of a fire suppression agent in real-world, large-scale fires depends upon deliverability of the agent, heat removal from the flames by the agent, and radical reactions that interfere with the combustion process.

3. Approach

An alternative streaming agent should have a boiling point comparable to existing streaming agents (approximately -10 °C to 60 °C). The vapor pressure at room temperature should be adequate to pressurize the container, but not to create a completely gaseous agent. A vapor pressure in the range of 5-40 lb/in.^2 is expected to be acceptable. For effective heat removal, an agent should have a high vapor heat capacity and high heat of vaporization. The vapor heat capacity should be greater than 0.09 cal/g-°C (compared to 0.11 cal/g-°C for both Halon 1211 and Halon 2402), and the heat of vaporization should be greater than 25 cal/g (compared to 32 cal/g for Halon 1211 and 27.6 for Halon 2402). Higher heats of vaporization are found for more polar molecules, since such molecules exhibit stronger mutual attractions.

G. AVAILABILITY/MANUFACTURABILITY

1. Criterion

The agent should be able to be manufactured in bulk.

2. Discussion

The major producers of fluorocarbons (including chlorinated and brominated fluorocarbons), with plant locations and total capacities, are listed in Table 1 (Reference 47).

The total U.S. demand for fluorocarbons in 1988 was 1130 million pounds (Reference 47). The projected demand is 1190 million pounds for 1989 and 1100 million pounds for 1992. CFC-12 and HCFC-22 each account for about 30 percent of current production, CFC-11 for 20 percent, and CFC-113 for 15 percent. The remainder includes CFC-114, CFC-115, halons, and specialty fluorocarbons.

Because of the unusual properties of fluorinated compounds, synthesis of fluoroalkanes is a specialized branch of organic chemistry. Numerous reagents and techniques exist for the synthesis of fluoroalkanes (References 48-62). As is normally the case in synthesis, certain molecules are much easier and less expensive to prepare than others.

3. Approach

Catalogs of manufacturers worldwide are monitored on an ongoing basis to track the availability of halocarbons. If attractive agents are identified that have not been manufactured in bulk, applicable synthetic methods will be reviewed to determine the feasibility of large-scale synthesis.

TABLE 1. MAJOR PRODUCERS OF FLUORINATED HALOCARBONS.

Producer	Plant Location(s)	Total Capacity, Million lbs/yr
Allied	Baton Rouge, LA Danville, IL El Segundo, CA	340
Atochem[a]	Calvert City, KY Thorofare, NJ	190
DuPont	Antioch, CA Corpus Christi, TX Deepwater, NJ Louisville, KY Montague, MI	750
Great Lakes	El Dorado, AR	b
Imperial Chemical Industries (ICI)	Dighton, MA	b
La Roche	Gramercy, LA	80
Racon	Wichita, KS	80
	Total	1,440[c]

[a] Acquired Pennwalt in 1990.

[b] Proprietary information available.

[c] Not including Great Lakes and ICI.

H. COST

1. Criterion

The agent should be able to be manufactured at acceptable cost.

2. Discussion

Acceptable cost will depend on the effectiveness and uniqueness of the agent. A highly effective agent that could be used in small quantities would be worth a higher price per pound than a moderately attractive agent that was less expensive. It should be noted that the tax on Halon 1211 will reach nearly $8 per pound in 1994.

3. Approach

Costs of available halocarbons are monitored on an ongoing basis. The review of synthetic methods will also suggest approximate costs for bulk production.

I. MATERIALS COMPATIBILITY

1. Criterion

The agent must be compatible with materials such as O-rings, valve seats, and metals used in extinguishers.

2. Discussion

Because agents are often stored for prolonged periods, long-term compatibility with O-rings and valve seats must be satisfactory. Corrosion of metal surfaces must be minimal. Compatibility with materials to which the agent is applied during fires should also be considered. For example, the agent should have low electrical conductivity to avoid shorting electrical equipment. Since organic liquids in general, and halogenated hydrocarbons in particular, have very low electrical conductivity, this is not expected to pose a problem.

3. Approach

Since it is generally expected that materials can be found that are compatible with a particular halocarbon, it is anticipated that this criterion will be applied only after a group of attractive agents has been identified, based on the criteria described previously in this section. Once attractive agents have been identified, testing for materials compatibility will be needed. These tests include such methods as those described in the ASTM tests for fluid resistance of gasket materials (ASTM F 146-84), hardness (ASTM D 1415-83), effects of liquids (ASTM D 471-479), change in length during liquid immersion (ASTM D 1460-81), and physical properties of O-rings (ASTM D 1414-78).

Corrosion tests on metals will need to be conducted at both normal and elevated temperatures and pressures, and in both the absence and presence of water. Such tests as the laboratory immersion corrosion testing of metals (ASTM G 31-72) and the examination and evaluation of pitting corrosion (ASTM G 46-76) will be required.

J. CHEMICAL STABILITY

1. Criterion

An agent must be stable in long-term storage.

2. Discussion

Since agents are often stored for long periods before use, sometimes under tropical or arctic extremes of temperature, agents must be chemically stable. Common pathways of chemical decomposition include thermal homolytic cleavage of weak carbon-to-halogen bonds (Cl, Br, I), loss of a molecular dihalide (e.g., Br_2), hydrolysis, and reaction with metals.

The high electronegativity of fluorine (the most electronegative element) causes a partial positive charge to develop on a carbon atom attached to it. This, in turn, strengthens the bond of a chlorine, bromine, or iodine atom attached to that carbon atom. In addition, carbon-fluorine bonds are very strong and unreactive compared to carbon-to-hydrogen bonds. Highly fluorinated chemicals are less likely to undergo the types of oxidative reactions that often destroy molecules containing carbon-to-hydrogen bonds. Thus the presence of fluorine atoms confers greater chemical stability, and this accounts in large part for the stability of existing halons.

3. Approach

During initial screening, agents containing particularly weak carbon-to-halogen bonds will be ranked lower than otherwise comparable agents with stronger bonds. For example, any chemicals containing carbon-to-iodine bonds, or those containing a bromine atom on a secondary or tertiary carbon atom or on a carbon not attached to fluorine, will be ranked lower for stability than otherwise comparable agents not containing those arrangements of atoms.

SECTION VII
GROUPING OF CANDIDATE AGENTS

A. DEFINITIONS OF GROUPS 1, 2, AND 3

Group 1 (near-term) candidate chemicals are defined as those that have been produced in bulk in the recent past, are now being produced, or are being developed for near-term bulk production, and for which significant toxicity studies, up to and including chronic studies, have been performed or are now in progress. For the most part, Group 1 materials are the hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (FCs) now being considered as substitutes for the fully halogenated chlorofluorocarbons (CFCs) in such applications as refrigeration and foam blowing.

Group 2 chemicals are materials that are expected to have low toxicities, but for which limited toxicity information is available. HCFCs, HFCs, and FCs other than those in Group 1 are included in this group.

Group 3 (far-term) chemicals are those expected to have very good or even superior fire extinguishment capabilities, but which are suspect for toxicity and have little or no toxicity data available. The hydrobromofluorocarbons (HBFCs) and highly chlorinated halocarbons fall into this category, as do iodine-containing, unsaturated, oxygen-containing, and aromatic compounds.

B. GROUP 1 CANDIDATES

Group 1 candidate agents are listed in Table 2. Their characteristics are discussed in detail in Reference 63.

TABLE 2. GROUP 1 CHEMICALS.

Halocarbon Number	Halon Number	Formula	Name
22	121	$CHClF_2$	chlorodifluoromethane
23	13	CHF_3	trifluoromethane
123	232	$CHCl_2CF_3$	2,2-dichloro-1,1,1-trifluoroethane
124	241	$CHClFCF_3$	2-chloro-1,1,1,2-tetrafluoroethane
134a	24	CF_3CH_2F	1,1,1,2-tetrafluoroethane
141b	212	CCl_2FCH_3	1,1-dichloro-1-fluoroethane
142b	221	$CClF_2CH_3$	1-chloro-1,1-difluoroethane
143a	23	CF_3CH_3	1,1,1-trifluoroethane
152a	22	CHF_2CH_3	1,1-difluoroethane
C318	48	cyclo-C_4F_8	octafluorocyclobutane

C. SELECTED GROUP 2 CANDIDATES

Selected Group 2 chemicals are listed in Table 3. In many cases several isomers are possible; these are marked.

TABLE 3. SELECTED GROUP 2 CHEMICALS.

Halocarbon Number	Halon Number	Formula	Name
31	111	CH_2ClF	chlorofluoromethane
32	12	CH_2F_2	difluoromethane
123a	232	$CClF_2CHClF$	1,2-dichloro-1,1,2-trifluoroethane
123b	232	CCl_2FCHF_2	1,1-dichloro-1,2,2-trifluoroethane
124a	241	$CClF_2CHF_2$	1-chloro-1,1,2,2-tetrafluoroethane
132	222	$CHClFCHClF$	1,2-dichloro-1,2-difluoroethane
132a	222	$CHCl_2CHF_2$	1,1-dichloro-2,2-difluoroethane
132c	222	CCl_2FCH_2F	1,1-dichloro-1,2-difluoroethane
133a	231	CF_3CH_2Cl	2-chloro-1,1,1-trifluoroethane
133b	231	$CClF_2CH_2F$	1-chloro-1,1,2-trifluoroethane
134	24	CHF_2CHF_2	1,1,2,2-tetrafluoroethane
141	212	$CHClFCH_2Cl$	1,2-dichloro-1-fluoroethane
142	221	CHF_2CH_2Cl	2-chloro-1,1-difluoroethane
142a	221	$CHClFCH_2F$	1-chloro-1,2-difluoroethane
143	23	CHF_2CH_2F	1,1,2-trifluoroethane
225	352	$C_3HCl_2F_5$	dichloropentafluoropropane[a]
226	361	C_3HClF_6	chlorohexafluoropropane[a]
234	342	$C_3H_2Cl_2F_4$	dichlorotetrafluoropropane[a]
235	351	$C_3H_2ClF_5$	chloropentafluoropropane[a]
236	36	$C_3H_2F_6$	hexafluoropropane[a]
243	332	$C_3H_3Cl_2F_3$	dichlorotrifluoropropane[a]
244	341	$C_3H_3ClF_4$	chlorotetrafluoropropane[a]
C325	461	C_4HClF_6	chlorohexafluorocyclobutane[a]
336	462	$C_4H_2Cl_2F_6$	dichlorohexafluorobutane[a]
337	471	$C_4H_2ClF_7$	chloroheptafluorobutane[a]

[a] Several isomers are possible.

D. SELECTED GROUP 3 CANDIDATES

Selected Group 3 chemicals are listed in Table 4. As with Group 2, in many cases several isomers are possible.

TABLE 4. SELECTED GROUP 3 CHEMICALS.

Halocarbon Number	Halon Number	Formula	Name
21B1	1111	CHBrClF	bromochlorofluoromethane
21B2	1102	$CHBr_2F$	dibromofluoromethane
21B1I1	11011	CHBrFI	bromofluoroiodomethane
21I1	11101	CHClFI	chlorofluoroiodomethane
21I2	11002	$CHFI_2$	diiodofluoromethane
22B1	1201	$CHBrF_2$	bromodifluoroethane
22I1	12001	CHF_2I	difluoroiodomethane
31B1	1101	CH_2BrF	bromofluoromethane
31I1	11001	CH_2FI	fluoroiodomethane
122	223	$CClF_2CHCl_2$	1,2,2-trichloro-1,1-difluoroethane
122a	223	$CCl_2FCHClF$	1,1,2-trichloro-1,2-difluoroethane
122b	223	CCl_3CHF_2	1,1,1-trichloro-2,2-difluoroethane
123B1	2311	$CClF_2CHBrF$	2-bromo-1-chloro-1,1,2-trifluoroethane
123aB1	2311	$CF_3CHBrCl$	2-bromo-2-chloro-1,1,1-trifluoroethane
123bB1	2311	$CBrF_2CHClF$	1-bromo-2-chloro-1,1,2-trifluoroethane
123B2	2302	$C_2HBr_2F_3$	dibromotrifluoroethane[a]
124B1	2401	C_2HBrF_4	1-bromo-1,1,2,2-tetrafluoroethane
132B1	2211	$C_2H_2BrClF_2$	bromochlorodifluoroethane[a]
132B2	2201	CHBrFCHBrF	1,2-dibromo-1,2-difluoroethane
132aB2	2201	$CBrF_2CH_2Br$	1,2-dibromo-1,1-difluoroethane
133B1	2301	$C_2H_2BrF_3$	bromotrifluoroethane[a]

TABLE 4. SELECTED GROUP 3 CHEMICALS (CONCLUDED).

Halocarbon Number	Halon Number	Formula	Name
133I1	13001	CF_3CH_2I	1,1,1-trifluoro-2-iodoethane
142B1	2201	$C_2H_3BrF_2$	bromodifluoroethane[a]
224	343	$C_3HCl_3F_4$	trichlorotetrafluoropropane[a]
225B1	3511	$C_3HBrClF_5$	bromochloropentafluoropropane[a]
225B2	3502	$C_3HBr_2F_5$	dibromopentafluoropropane[a]
226B1	3601	C_3HBrF_6	bromohexafluoropropane[a]
233	333	$C_3H_2Cl_3F_3$	trichlorotrifluoropropane[a]
234B1	3411	$C_3H_2BrClF_4$	bromochlorotetrafluoropropane[a]
235B1	3501	$C_3H_2BrF_5$	bromopentafluoropropane[a]
243B2	3302	$C_3H_3Br_2F_5$	dibromopentafluoropropane[a]
244B1	3401	$C_3H_3BrF_4$	bromotetrafluoropropane[a]
328B1	4801	C_4HBrF_8	bromooctafluorobutane[a]
336B1	4611	$C_4H_2BrClF_6$	bromochlorohexafluorobutane[a]
336B2	4602	$C_4H_2Br_2F_6$	dibromohexafluorobutane[a]
337B1	4701	$C_4H_2BrF_7$	bromoheptafluorobutane[a]

[a] Several isomers are possible.

SECTION VIII

C-H BOND STRENGTHS, RATES OF REACTION WITH OH, AND TROPOSPHERIC LIFETIMES OF HYDROGEN-CONTAINING HALOALKANES

A. INTRODUCTION

Haloalkanes containing hydrogen are gaining increasing importance as potential alternatives to fully-halogenated compounds in applications including refrigeration, foam blowing, aerosol propulsion, and firefighting. For example, HCFC-22 is already in commercial use, and HCFCs 123, 134a, 141b, 142b, and 152a are all rapidly approaching large-volume usage. It also appears likely that certain hydrogen-containing halocarbons may prove to be effective fire extinguishing agents with acceptable environmental and toxicological properties.

Compounds containing hydrogen generally have much shorter atmospheric lifetimes than fully halogenated compounds because reaction with hydroxyl radicals in the troposphere results in relatively rapid destruction. The processes of hydrogen abstraction and destruction of the resulting radicals are illustrated in Reactions [11] and [12].

$$\text{R-H} + \text{OH} \dashrightarrow H_2O + \text{R} \qquad [11]$$

$$\text{R} \dashrightarrow \text{further reactions} \qquad [12]$$

The primary mechanism for removal of hydrogen-containing halocarbons from the troposphere is reaction with hydroxyl radical (Reference 64). In order to estimate the atmospheric lifetimes of these compounds, it is therefore necessary to estimate the rates of reaction with hydroxyl radicals.

Because the slow, rate-determining step in tropospheric destruction of hydrogen-containing haloalkanes is Reaction [11], the kinetics of destruction depend on this reaction. The rate of Reaction [11] is given by Equation (1).

$$\text{Rate} = -d[RH]/dt = k[OH][RH] = k'[RH] \qquad (1)$$

The OH concentration can be included in the rate constant because the (relatively constant) average concentration of OH in the troposphere is known to be approximately 6.5 (±2) x 10^5 molecules/cm^3, which corresponds to 1.1(±0.3) x 10^{-15} moles/liter (Reference 64). The conversion factor is 1 molecule/cm^3 = 1.66 x 10^{-21} moles/liter. Once the OH concentration is considered constant and included in k', the reaction follows pseudo-first order kinetics in [RH].

The tropospheric lifetime (L) is the inverse of the rate constant (Reference 65).

$$L = 1/k' \qquad (2)$$

There is a simple relationship between this lifetime and the half-life ($L_{1/2}$). Since

$$L_{1/2} = \ln 2/k' = 0.693/k' \qquad (3)$$

it follows that

$$L_{1/2}/L = (0.693/k')/(1/k') = 0.693 \qquad (4)$$

Since rate constants are temperature-dependent, they may also be written as k_t or k'_t. For global averaging, it is necessary to estimate a global average temperature for the reaction occurring. Such an average temperature is related to the average height at which the reaction occurs. This average temperature, which may vary from compound to compound, is believed to be approximately 277 K (4°C) (Reference 64). The temperature of 277 K has given the best fit of laboratory data to observed atmospheric lifetimes.

B. COMPONENTS OF THE RATE CONSTANT

The great majority of chemical reaction rate constants can be expressed readily in the Arrhenius form given in Equation (5) (Reference 66).

$$k = A\exp(-E_a/RT) \tag{5}$$

where A is the Arrhenius preexponential or frequency factor, E_a is the activation energy, R is the gas law constant, and T is the absolute temperature. The constant A accounts for collision frequency and geometric requirements. The Boltzmann factor $\exp(-E_a/RT)$ represents the fraction of molecules possessing the critical energy E_a needed for reaction (Reference 67). Experimentally, it is found that A and E_a are constant over a small temperature range of 100 K, and that even over a temperature range of 500 K, A and E change only slightly.

Although most gas-phase rate constants can be expressed as in Equation (5), a small group of them cannot. These cases are termolecular recombinations of atoms or of atoms with diatomic molecules, for example, those shown in Reactions [13] and [14].

$$O + O + M \dashrightarrow O_2 + M \qquad [13]$$

$$O + NO + M \dashrightarrow NO_2 + M \qquad [14]$$

In Reactions [13] and [14], the third body M serves to remove excess energy. In cases such as these it may be necessary to express the rate constants in the form of a modified Arrhenius equation in which a simple temperature variation for the A factor is introduced.

$$k = A'T^n\exp(-E'/RT) \tag{6}$$

where A′, E′, and n are the new parameters. One consequence of this modified Arrhenius equation is that the A factor and E_a are now both explicitly dependent on temperature.

C. BOND STRENGTH

Bond strength, also known as bond dissociation enthalpy or energy (BDE) is the energy required to break a particular bond, measured in kcal/mole or kJ/mole. The conversion factor between these units is 1 kcal/mole equals 4.18 kJ/mole. Bonds can break either homolytically or heterolytically. In homolytic cleavage, the pair of electrons making the bond divides with one electron going to each atom previously bonded, resulting in the formation of two radical fragments from a neutral molecule. In heterolytic cleavage, both electrons of the bonding pair remain with the more electronegative atom of the two previously bonded, causing the formation of anion and cation fragments from a neutral molecule. Homolytic bond cleavage, shown in Reaction [15], is of greater relevance to atmospheric degradation of haloalkanes.

$$R\text{-}X \;\;--->\;\; R \;+\; X \qquad [15]$$

where, in the case of haloalkanes, R is an alkyl or haloalkyl group and X can be hydrogen, a halogen, or another alkyl or haloalkyl group. The energy consumed in this bond-breaking process equals the energy released when the same two radicals combine to form a new bond (Reaction [16]).

$$R \;+\; X \;\;--->\;\; R\text{-}X\cdot \qquad [16]$$

Reaction [16] is simply the reverse of Reaction [15].

Table 5 shows the ranges of strength of various classes of bonds (Reference 68).

TABLE 5. RANGES OF STRENGTH FOR CLASSES OF BONDS.

Type	Bond Strength, kcal/mol
Covalent bonds	40-110
Ionic bonds	5- 10
Ion-dipole interactions	1- 4
Dipole-dipole interactions	1- 4
Hydrogen bonds	1- 4
Charge transfer complexes	1- 2
Hydrophobic interactions	1
London forces	0.5-1

Normal ranges for strengths of various types of covalent bonds to sp^3 hybridized carbon are shown in Table 6 (Reference 48). Covalent bond strengths depend on several factors including the electronegativities of the atoms involved and the electronic and steric effects of substituents.

TABLE 6. RANGES OF STRENGTH FOR VARIOUS TYPES OF COVALENT BONDS TO SP^3 CARBON.

Bond Type	Bond Strength, kcal/mole
C-H	92-106
C-F	105-117
C-Cl	70- 86
C-Br	64- 72
C-I	48- 57
C-C	64-108

A general relationship exists between bond strength and the activation energy needed for a bond-breaking process. The stronger the bond, the more difficult it is to break and, in general, the higher the activation energy and the lower the rate constant for the reaction. Within a related series of compounds, the activation energy is approximately proportional to bond strength (Reference 69). This relationship between bond strength and activation energy for the bond-breaking reaction is described by the Polanyi-Evans theory, a theory which assumes that the activation energy of an exothermic atom-transfer reaction is a linear function of the enthalpy of reaction for a series of homologous compounds. Since the bond being formed is always the same, the enthalpy of reaction is a linear function of D(R-H), the bond dissociation enthalpy of the R-H bond. This linear function is shown in Equation (7).

$$E_a \approx a[D(R\text{-}H) - D_o] \qquad (7)$$

where E_a is the activation energy for Reaction [1] and D_o and a are constants. Values of D(R-H) at 298 K and the Arrhenius parameters for several hydrogen-containing halocarbons are given in Table 7 (Reference 70). This table includes only compounds for which the reaction involves only C-H bond cleavage, and for which all the C-H bonds have the same strength (i.e., are identical). A plot of activation energy (E_a) versus bond strength (D(R-H)) for the compounds listed in Table 7 is given in Figure 1 (Reference 70). Table 8 shows rate data at various temperatures.

Figure 1 illustrates the general trend toward higher activation energy as bond strength increases; however, the scatter of the data is too great to provide useful predictions. Some of the compounds have activation energies differing from those predicted by a simple linear fit to the data by more than 0.9 kcal/mole. This deviation would lead to an error in the rate

TABLE 7. BDEs AND RATE COEFFICIENT PARAMETERS FOR COMPOUNDS WITH EQUIVALENT REACTIVE HYDROGEN ATOMS.

Compound	D(R-H) kcal/mole	10^{11}A cm^3/s	E_a cal/mole
CH_3Cl	101.7	0.22	2269
CH_2Cl_2	99.0	0.52	2174
CF_3H	106.2	-	-
$CHCl_3$	95.9	0.47	2253
$CHCl_2F$	97.4	0.15	2345
$CHClF_2$	103.6	0.12	3310
CH_3Br	100.2	0.079	1766
CH_3CCl_3	96.9	0.195	2645

TABLE 8. RATE DATA AT VARIOUS TEMPERATURES.

	$10^{11}k(T)$, cm^3/s			$E_0 - 2RT\ln\beta$, kcal/mole		
Compound	200 K	298 K	400 K	200 K	298 K	400 K
CH_3Cl	7.3×10^{-4}	0.0048	0.013	3865	4762	5717
CH_2Cl_2	2.2×10^{-3}	1.32×10^{-2}	3.4×10^{-2}	3244	3891	4588
CHF_3	-	1.3×10^{-4}	-	-	6227	-
$CHCl_3$	1.6×10^{-3}	0.0105	0.028	3085	3602	4171
$CHCl_2F$	4.1×10^{-4}	0.0028	0.0078	3630	4390	5195
$CHClF_2$	2.9×10^{-5}	4.6×10^{-4}	1.86×10^{-3}	4689	5467	6345
CH_3Br	9.3×10^{-4}	0.0039	8.6×10^{-3}	3744	4848	5995
CH_3CCl_3	2.5×10^{-4}	2.2×10^{-3}	7.0×10^{-3}	4257	5173	6141

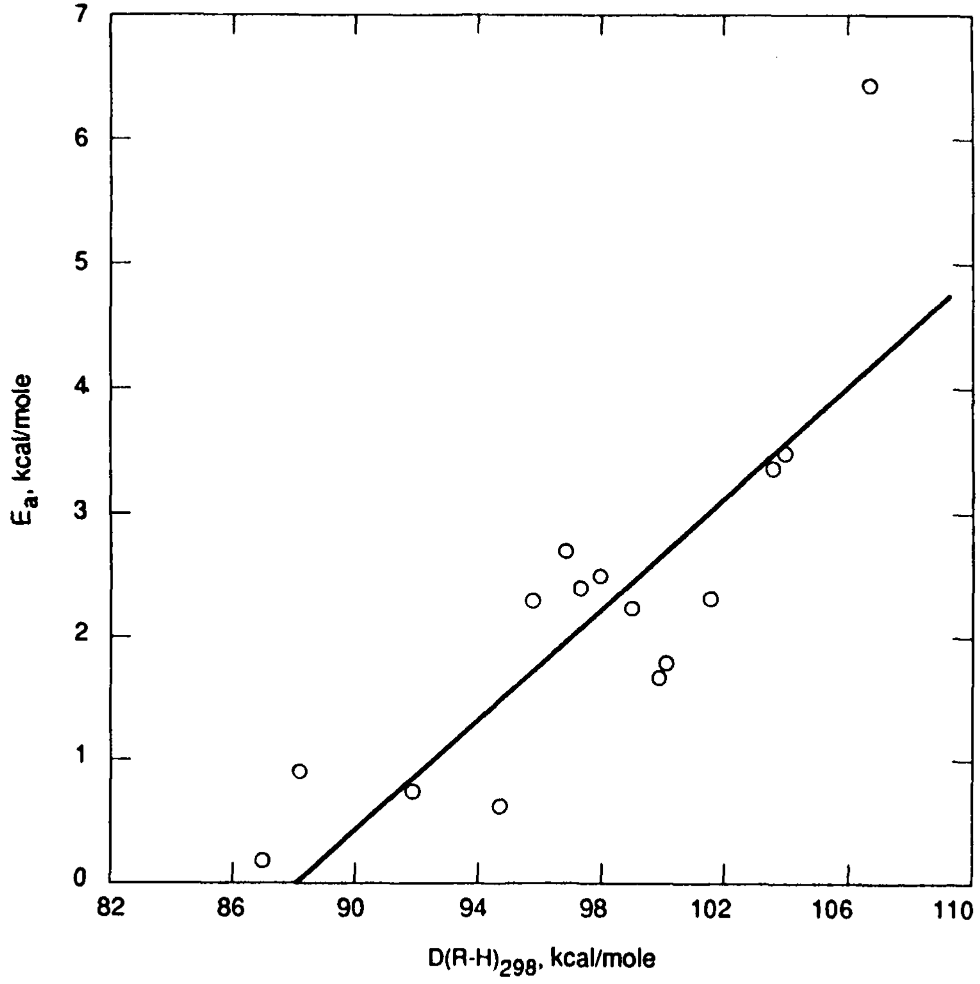


Figure 1. Activation Energy Versus Bond Strength.

coefficient of a factor of more than 4.6 at room temperature. It is clear from these results that a more sophisticated method of calculating activation energies is required. Several such methods exist.

One such method is the bond energy-bond order (BEBO) approach (References 71 and 72). In this method conservation of bond order is assumed, and bond energies are assumed to be proportional to some power of the bond order. The Morse potential parameters are needed to compute the repulsion energy between the end groups. Activation energies can be computed, though they are quite sensitive to input parameters, which must therefore be known accurately. Computed values are within 1 kcal/mole of the observed values, about the same accuracy as that obtained from Evans-Polanyi plots.

Several efforts have been made to predict rate coefficients for H atom abstraction reactions more accurately than is possible using either Evans-Polanyi plots or BEBO calculations. One method is to plot the logarithm of the rate constant for the OH abstraction reaction versus bond dissociation energies (Reference 73). Such a plot yields Equation (8).

$$\log k_{OH} = -0.136 \times D(R\text{-}H) + 1.46 \qquad (8)$$

with a value of $r = 0.82$ for 18 points. The compounds used in this plot were alkanes and some small oxygenated molecules, and the correlation should be re-examined using only haloalkanes. In addition, no correction was made for the differing number of hydrogens per molecule. More extensive studies have been conducted of rates of reaction of OH with alkanes (References 74-79) than with haloalkanes (References 80-83).

Another formula used to compute room temperature rate coefficients for Reaction [11] is

$$k_{298} = \sum_i n_i \alpha_i \beta_i k_i \qquad (9)$$

where k_{298} is the rate of reaction at 298 K, n_i is the number of equivalent hydrogen atoms of each type, α_i is a constant for each substituent on the α carbon atom, β_i is a constant for each substituent on the β carbon atom, and k_i is the rate coefficient for the i^{th} hydrogen atom, which depends on the substitution pattern on the adjacent atom and whether a vinyl or phenyl group is attached (Reference 84). The values of these parameters shown in Table 9 can be used to predict rate coefficients within about a factor of 2 in many cases.

TABLE 9. PARAMETERS FOR PREDICTING RATE CONSTANTS USING EQUATION 10.

Substituent or Group	α	β	$10^{12}k$, per H
H	1.0	1.0	
Cl, Br	2.4	0.4	
F	1.0	0.3	
C	1.3	1.0	
$-\overset{\vert}{\underset{\vert}{C}}-CX_2H$			0.065± 0.013
$(-\overset{\vert}{\underset{\vert}{C}}-)_2CXH$			0.55 ± 0.07
$(-\overset{\vert}{\underset{\vert}{C}}-)_3CH$			2.9 ± 0.6

A more general expression than Equation (9) has been developed that accounts for molecular weight and allows calculations at other temperatures (Reference 70). The line-of-centers collision reaction rate coefficient k(T) is given by Equation (10).

$$k(T) = (8\pi kT/\mu)^{1/2}\sigma_R^2(E_o/RT)^s \exp(-E_o/RT)/s! \qquad (10)$$

where k is Boltzmann's constant, T is the absolute temperature, μ is the reduced mass of the colliding particles, $\pi\sigma_R^2$ is the reaction cross section, E_o is the critical energy needed for the reaction, R is the gas constant, and s is the number of effective vibrations participating in the reaction. Equation (4) is an approximation that is only valid if $E_o > RT$. Unless the C-H bonds are equivalent, the critical energy E_o will be different for each type of C-H bond, so the total rate coefficient is the sum of the rate coefficients for each C-H bond. Equation (10) then becomes

$$k(T) = (8\pi kT/\mu)^{1/2}(\sigma_R^o)^2\sum_i\beta_i^2\gamma_i\exp(-E_o^i/RT) \qquad (11)$$

where γ_i is the number of equivalent C-H bonds of each type, $\beta_i\sigma_R^o$ is the reactive radius for each C-H bond, or

$$\beta_i\sigma_R^o = \sigma_R[(E_o^i/RT)^{s^i}/s^i!]^{1/2} \qquad (12)$$

E_o^i is their critical energy, and s^i is the number of effective oscillators. The constant σ_R^o is about 1.5 Å, *and* β_i *is a measure of the deviation of the* cross section for each C-H bond from this value.

If the quantities β_i and E_o^i are known, the rate constant k(T) can be computed. For molecules with only one type of reactive C-H bond the summation in Equation (12) can be dropped and the equation rearranged to give

$$E_o - 2RT\ln\beta = RT\ln[(8\pi kT/\mu)^{1/2}(\sigma_R^o)^2\gamma/k(T)] \qquad (13)$$

Values of $E_o - 2RT\ln\beta$ calculated from Equation (13) for temperatures of 200, 298, and 400 K are plotted versus bond dissociation energies in Figure 2 (Reference 70).

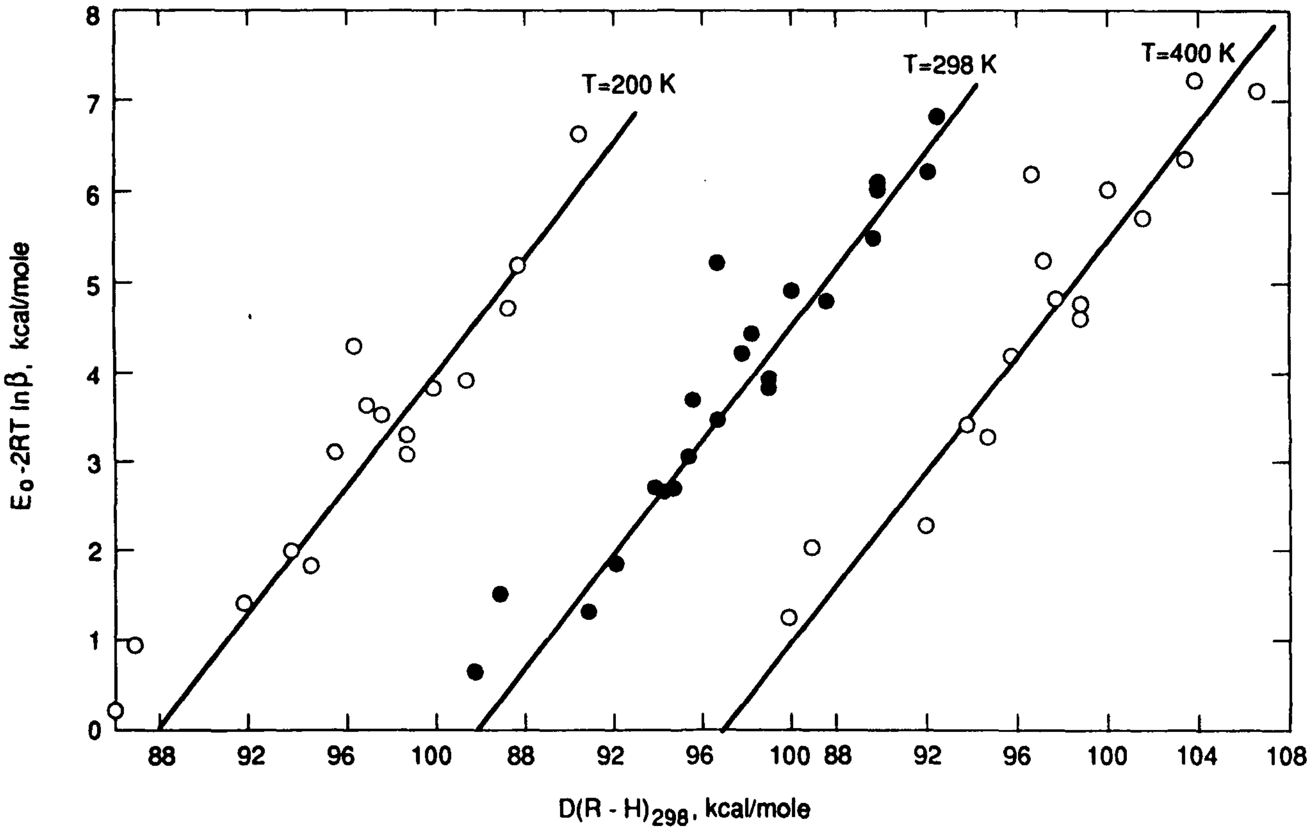


Figure 2. Plot of E_0-2RTlnβ Versus Bond Dissociation Energy.

In this plot, the data are fitted by straight lines of the same slope (0.323). These lines fit most of the points to better than 0.5 kcal/mole, which is within the range of experimental uncertainty. These lines may be expressed as

$$E_0 - 2RT\ln\beta \approx 0.323[D(R\text{-}H)_{298} - D_o] \qquad (14)$$

where D_o is the x-intercept and may be calculated by the formula

$$D_o = 1/(1.062 \times 10^{-2} + 3.52 \times 10^{-6}T) \qquad (15)$$

Combining Equations (11) and (14) gives

$$k(T) = (8\pi kT/\mu)^{1/2}(\sigma_R^o)^2\sum_i\gamma_i\exp[-a(D_i - D_o)/RT] \qquad (16)$$

where σ_R^o is 1.5 Å, a is 0.323, D_i is the bond dissociation enthalpy at 298 K, and D_o is given by Equation (15). Equation (16) permits computation of the reaction rate coefficient from knowledge of only the bond dissociation enthalpies. Conversely, if the rate constant is known, the bond strength can be calculated.

Unfortunately, bond dissociation enthalpies are often not known, and must be estimated. Several generalizations have been made about trends in bond strength with substitution pattern (Reference 85). In this article it is stated that halogen atoms (Cl, Br, and I) α to a C-H bond generally reduce both the homopolar and heteropolar BDEs. The effect on homopolar BDEs appears to be additive, largely independent of the nature of the halogen atoms, and is about 2.5 kcal/mole per α-halogen substituent. Fluorine substituents α to C-H bonds appear to have little or no effect on the homopolar or heteropolar C-H BDE. These rough observations have been refined somewhat into a still slightly crude additivity scheme for estimating C-H BDEs (Reference 65).

Rough estimates of the C-H bond strengths in halocarbons can be made using Equation (17).

$$D_{298} = 91 + \Sigma e_i \tag{17}$$

where D_{298} is the bond dissociation energy at 298 K in kcal/mole and e_i are the group additivity contributions from Table 10.

TABLE 10. GROUP ADDITIVITIES FOR ESTIMATING C-H BOND STRENGTHS IN HALOALKANES.

Substituent on Carbon	e_i
H	4.0
F	5.0
Cl	1.6
Br	3.0
I	4.0
CCl_3	2.0
CX_3 (X = Br,I)	0.0
CF_3	5.0
CF_2Cl	5.0
$CFCl_2$	2.5

Table 11 shows that the group additivity estimation method for bond strength yields estimates with an average deviation of 1.2 kcal/mole, comparable to the experimental error, though the data are limited.

Table 12 gives reported and estimated bond strengths for halomethanes having two hydrogen atoms.

TABLE 11. C-H BOND STRENGTHS IN TRIHALOMETHANES.

Substituents	C-H Bond Strength, kcal/mole Experimental	 Estimated
F F F	106.7 ± 1[a] 106[c]	106
F F Cl	101.6 ± 1[a]	102.6
F Cl Cl	98.9 ± 1.2[b]	98.2
Cl Cl Cl	95.8 ± 1.0[a] 96[c]	95.8
F F Br		104
F Br Br		102
Br Br Br	96.0 ± 1.6[a] 96[c]	100
Cl Cl Br		97.2
Cl Br Br		98.6
F Cl Br		100.6

[a] Data from Reference 86.

[b] Data from Reference 87.

[c] Data from Reference 85.

From the data in Table 12 it is apparent that the additivity scheme above can be used to predict experimental bond strengths to within an average absolute deviation of ±0.7 kcal/mole and a maximum deviation of ±1.8 kcal/mole. Since the experimental values themselves have average absolute errors of 1-2 kcal/mole, the overall errors in the predicted values are 2-3 kcal/mole.

TABLE 12. C-H BOND STRENGTHS IN DIHALOMETHANES.

	C-H Bond Strength (kcal/mole)		
Compound	Experimental	Estimated	Deviation
CH_2F_2	103.2 ± 1[a]	105	1.8
	103[b]		-0.2
CH_2Cl_2	98.4 ± 1.2[a]	98.2	-0.2
	99[b]		0.6
CH_2Br_2	99.7 ± 1.8[a]	101	1.3
CH_2I_2	103 ± 2[c]	103	0.0
CH_2ClF	100.8 ± 1.3[a]	101.6	0.8
CH_2BrF		103	
CH_2BrCl		99.6	
CH_2FI		104	
CH_2ClI		100.6	
CH_2BrI		102	

[a] Data from Reference 87.
[b] Data from Reference 85
[c] Data from Reference 48.

BDEs may also be obtained from infrared spectra (Reference 88). The observed uncoupled stretching frequencies, ν in units of cm^{-1}, are related to BDEs by Equation (18),

$$\nu = 143.3(D-c_1)^{1/2} \tag{18}$$

where ν is the observed uncoupled stretching frequency in cm^{-1}, D is the BDE in kcal/mole, and c_1 is a constant characteristic of the two bonded atoms and is not dependent on the multiplicity of the bond. Table 13 shows the values of c_1 for various combinations of atoms (Reference 89). Unfortunately, no value for c_1 for carbon-to-hydrogen bonds is given in this source.

TABLE 13. CHARACTERISTIC CONSTANT c_1 FOR BONDS TO CARBON.

Atom Bonded to C	c_1
fluorine	51.4
chlorine	42.5
bromine	40.6
carbon	39.7
nitrogen	26.7
oxygen[a]	33.8
oxygen[b]	24.2

[a] For alcohols and carbonyl groups.

[b] For alkoxy groups (e.g., ethers and esters).

Rate constants for reaction with OH and tropospheric lifetimes for haloalkanes can be estimated crudely by the following steps (Reference 65).

1. Find bond strength (bond dissociation enthalpy) for each nonequivalent C-H bond either from the literature or by estimation.

2. Calculate the rate constant with OH by summing over C-H bonds using Equation (19).

$$k_{298} = (4.66 \times 10^{-11}) \sum_i [\alpha_i \exp(38.0-0.464D_{i298})] \qquad (19)$$

where k_{298} is the rate constant at 298 k in units of cm^3 per molecule per sec, α_i is the number of equivalent C-H bonds of type i, and D_{i298} is the bond dissociation enthalpy of the i^{th} type C-H bond at 298 K.

3. Estimate the activation energy by Equation (21) (Reference 65)

$$E_a = 0.275D_{298} -24.1 \text{ kcal/mole} \qquad (20)$$

or Equation (21) (Reference 70)

$$E_a = 0.38D_{298} - 35.3 \text{ kcal/mole} \qquad (21)$$

where D_{298} is the bond enthalpy of the C-H bond contributing the largest term to the sum for the rate constant (the weakest bond).

4. Calculate the tropospheric average rate constant using Equation (22).

$$k'_t = [OH]\ k_{298}\ [1.06 \exp(-0.169E_a)] \qquad (22)$$

where the average value of [OH] is taken to be 6.5×10^5 molecules/cm^3, so

$$k'_t = (6.9 \times 10^5)\ k_{298} \exp(-0.169E_a) \ \ sec^{-1} \qquad (23)$$

The inverse of k'_t is then taken to obtain the tropospheric lifetime.

This method is useful if the BDE is known with great accuracy. Since BDEs are generally only known to within 1-2 kcal/mole, however, this method suffers some drawbacks. It is highly sensitive to errors in BDEs. Errors in BDEs are propagated in both the pre-exponential and activation energy terms. Since the correlation factor in the equation relating activation energy with BDE is approximately 0.4, an error of 2 kcal/mole in BDE leads to an error of a factor of approximately exp(0.4 x 2) = 2.2 in E_a and an error of a factor of exp(0.46 x 2) = 2.5 in k_{298}, for an overall error of a factor of 2.2 x 2.5 = 5.5. This error is unacceptably large for purposes of estimating atmospheric lifetimes. Such propagation of errors can be circumvented by estimating activation energies and rate constants directly from structural features without the use of BDEs, as described in Section IV of this report.

This algorithm can be entered at several different stages. For example, if an accurate rate constant for reaction with OH is known, Equation (23) should be used. If the BDE is known accurately, Equation (20) or (21) can be used.

D. DIRECT CORRELATION OF STRUCTURE WITH RATE CONSTANT

A reasonably successful parameterized correlation of chemical structure with rate of hydrogen abstraction by hydroxyl for haloalkanes has been reported (Reference 69). For a set of 10 halomethanes and 18 haloethanes a "universal" rate coefficient was developed that depends only on the molecular weight and the number of abstractable hydrogen atoms in the haloalkane. This rate coefficient is given in Equation (24).

$$k(T) = 10^{6.5} n_h M^{-1} T^{1.5} \exp[-(E/R - 450)/T] \qquad (24)$$

where n_h is the number of extractable hydrogen atoms of a given type, M is the molecular weight, T is the absolute temperature, and R is the gas constant. The activation energy E at 298 K is given by Equation (25).

$$E/R = 2100 - 85n_F - 51n_{Cl} - 950n_{CH_3} - 600n_{CH_2X} - 650n_{CHX_2} - 250n_{CX_3} \qquad (25)$$

where the values of n_i are the numbers of substituents of type i on the carbon bonded to the abstractable hydrogen, and X is either Cl or F. The activation energy E at 298 K can be fitted by Equation (25) with an average error of 0.3 and a maximum error of 1.1 kcal/mol. For most reagents this expression predicts experimental rate coefficients within a factor of three and can provide a useful predictive tool if no reliable data are available.

In order to assess the validity of Equations (24) and (25), a comparison was made of the rate constant functions generated by these equations with the currently best available rate constant functions (References 64 and 85). This comparison appears in Table 14.

It is apparent from Table 14 that the functions generated by Equations (24) and (25) differ markedly from the experimentally-derived functions both in the pre-exponential and activation energy terms. Although in isolated cases the match is satisfactory, in most cases the pre-exponential factor is much too low, and in general the absolute value of the activation energy is significantly too high. For this reason it was decided to modify the approach taken in Reference 69.

If the temperature is taken as 277 K, Equation (24) becomes

$$k = 1.46 \times 10^{10}(n_h/M)\exp[-(E/R-450)/277] \quad \text{liters/mole-sec} \qquad (26)$$

Conversion of Equation (26) to the units of cm^3/molecule-sec gives

$$k = 2.4 \times 10^{-11}(n_h/M)\exp[-(E/R-450)/277] \quad \text{cm}^3\text{/molecule-sec} \qquad (27)$$

If, in addition, [OH] is taken as $1.1 \times 10^{-15}\underline{M}$ (or 6.5×10^5 molecules/cm^3), either Equation (20) or (21) yields

$$k' = 1.58 \times 10^{-5}(n_h/M)\exp[-(E/R-450)/277] \quad \text{sec}^{-1} \qquad (28)$$

To convert the units of k' to inverse years, Equation (28) is multiplied by 3.15×10^7 seconds/year, yielding Equation (29).

TABLE 14. COMPARISON OF EXPERIMENTAL AND ESTIMATED RATE FUNCTIONS.

Halocarbon Number	Formula	M	n_h	$A \times 10^{13}$		$-E_a/R$	
				Experimental	Estimated	Experimental	Estimated
21	$CHCl_2F$	102.9	1	12	2.4	1100	1910
22	$CHClF_2$	86.5	1	12	2.8	1650	1880
31	CH_2ClF	68.5	2	30	7.1	1250	1960
32	CH_2F_2	52.0	2	25	9.3	1650	1930
41	CH_3F	34.0	3	54	21	1700	2015
123	$CHCl_2CF_3$	152.9	1	6.4	1.6	850	1750
124	$CHClFCF_3$	136.5	1	6.6	1.8	1250	1710
125	CHF_2CF_3	120.0	1	3.8	2.0	1500	1680
132b	$CH_2ClCClF_2$	134.9	2	36	3.6	1600	1800
133	CH_2ClCF_3	118.5	2	5.2	4.1	1100	1800
134	CHF_2CHF_2	102.0	2	8.7	4.7	1500	1280
134a	CH_2FCF_3	102.0	2	17	4.7	1750	1765
140a	CH_3CCl_3	133.4	3	5.0	6.0	1800	1850
141b	CH_3CCl_2F	116.9	3	4.2	6.2	1200	1850
142b	CH_3CClF_2	100.5	3	9.6	7.2	1650	1850
143	CH_2FCHF_2	84.0	1α		2.9		1330
			2β		5.7		1365
			both	28		1500	
143a	CH_3CF_3	84.0	3	2.6	8.6	1500	1850
152	CH_2FCH_2F	66.0	4	170	15	1500	1415
152a	CH_3CHF_2	65.0	1α		3.7		980
			3β		11		1450
			both	15		1100	
161	CH_3CH_2F	48.0	2α				1500
			3β				1150
			both	130		1200	

$$k' = 498(n_h/M)\exp[-(E/R-450)/277] \quad \mathrm{yr}^{-1} \tag{29}$$

Equation (29) allows estimation of the rate constant based on number of reactive hydrogens, molecular mass, and activation energy.

E. ATMOSPHERIC LIFETIMES

The most accurately known atmospheric lifetimes for HCFCs are listed in Table 15 (References 64 and 88). These lifetimes have been calculated by three independent methods (and groups of researchers). Method 1 is based on scaling the methyl chloroform lifetime of 6.3 years by the ratio of the rate coefficients at 277 K (Reference 90). The lifetimes from Method 2 do not include stratospheric loss; those from Method 3 include small additional stratospheric losses. The lifetimes obtained by these three methods generally agree within 15 percent. The standard deviation on Methods 1 and 3 is 40 percent; for Method 2 it is 50 percent. Since the uncertainties in the three methods differ, the statistically correct method of obtaining the mean given in Equation (30) is used (Reference 91). In Equation (30), the mean lifetimes obtained by the three methods are weighted inversely to their variances, where the variance is the square of the standard deviation.

$$L_\mu = (L_1/\sigma_1^2 + L_2/\sigma_2^2 + L_3/\sigma_3^2)/(1/\sigma_1^2 + 1/\sigma_2^2 + 1/\sigma_3^2) \tag{30}$$

where L_μ is the most probable mean value of the lifetime, L_1, L_2, and L_3 are the lifetimes from Methods 1, 2, and 3, and σ_1, σ_2, and σ_3 are the standard deviations of Methods 1, 2, and 3. To calculate the standard deviation for this small sample, Equation (31) is used (Reference 92).

$$s = [\sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)]^{1/2} \tag{31}$$

where s is the standard deviation, x_i is an individual measurement, $\bar{x}$ is the average of the measurements, and n is the number of measurements.

Since Method 2 has a larger standard deviation, an approximation of the most likely mean value can be made by weighting the contribution of the value from Method 2 with a lower relative weight. The best fit (lowest sum of the squares of the deviations from the statistical means) was obtained with a weighting factor of 0.835. Thus

$$L_{avg} = (L_1 + 0.835L_2 + L_3)/2.835 \qquad (32)$$

where L_{avg} is the best available weighted average lifetime and L_1, L_2, and L_3 are the lifetimes from Methods 1, 2, and 3. Table 15 lists the atmospheric lifetimes reported for each method, plus a simple weighted average according to Equation (31) and a mean value plus standard deviation calculated according to Equations (30) and (31). For all compounds except methyl chloroform, the standard deviation uncertainties used are 40 percent for Methods 1 and 3 and 50 percent for Method 2.

As examples, consider the compound with the most accurately known lifetime (methyl chloroform) and another typical HCFC, HCFC-22. For these two compounds the data and uncertainties listed in Tables 16 and 17 are reported.

To calculate the most probable mean lifetime for methyl chloroform

$$(6.3/1.1^2 + 5/2^2 + 5.4/1.5^2)/(1/1.1^2 + 1/2^2 + 1/1.5^2) = 5.83 \text{ yrs} \qquad (33)$$

and

$$s = [(6.3 - 5.83)^2 + (5-5.83)^2 + (5.4 - 5.83)^2/2]^{1/2} = 0.74 \qquad (34)$$

Lifetime data for HCFC-22 are given in Table 17.

TABLE 15. KNOWN ATMOSPHERIC LIFETIMES FOR HALOCARBONS.

Halocarbon Number	Formula	Lifetime, yrs for method			stat. mean[a]	std. dev.[b]	wtd. avg.[c]
		(1)	(2)	(3)			
21	$CHCl_2F$	2.10	1.80	1.89	1.93	0.15	1.93
22	$CHClF_2$	15.3	13.0	14.2	14.2	1.2	1.42
23	CHF_3	310	635	289	321	97	418
31	CH_2ClF	1.44	1.26	1.33	1.35	0.09	1.34
32	CH_2F_2	7.3	6.0	6.8	6.72	0.66	6.74
41	CH_3F	4.1	3.3	3.8	3.76	0.40	3.73
123	$CHCl_2CF_3$	1.59	1.40	1.42	1.47	0.10	1.47
124	$CHClFCF_3$	6.6	5.5	6.0	6.04	0.55	6.04
125	CHF_2CF_3	28.1	25.9	26.1	26.7	1.2	26.4
132b	$CH_2ClCClF_2$	4.2	3.5	4.0	3.91	0.36	3.89
133	CH_2ClCF_3	4.8	4.1	4.4	4.45	0.35	4.44
134	CHF_2CHF_2	12.3	10.4	11.4	11.4	1.0	11.4
134a	CH_2FCF_3	15.5	13.1	14.4	14.4	1.2	14.3
140a	CH_3CCl_3	6.3	5.0	5.4	5.82	0.74	5.57
141b	CH_3CCl_2F	7.8	6.7	6.7	7.04	0.64	7.09
142b	CH_3CClF_2	19.1	16.6	17.8	17.9	1.3	17.8
143	CH_2FCHF_2	3.8	3.2	3.5	3.51	0.30	3.50
143a	CH_3CF_3	41	40	38	39.5	1.5	39.8
152	CH_2FCH_2F	0.63	0.60	0.58	0.602	0.025	0.605
152a	CH_3CHF_2	1.68	1.46	1.53	1.56	0.11	1.56
161	CH_3CH_2F	0.28	0.31	0.25	0.272	0.032	0.282

[a] Calculated using Equation (30).

[b] Calculated using Equation (31).

[c] Calculated using Equation (32).

TABLE 16. STATISTICAL ANALYSIS OF LIFETIME DATA FOR METHYL CHLOROFORM.

Quantity	Method 1	Method 2	Method 3
Life, yrs	6.3	5	5.4
Range	5.4-7.5	3-7	4-7
Upper deviation	+1.2	+2	+1.6
Lower deviation	-0.9	-2	-1.4
% upper deviation	+19	+40	+30
% lower deviation	-14	-40	-26
Implied σ	1.1	2	1.5

TABLE 17. STATISTICAL ANALYSIS OF LIFETIME DATA FOR HCFC-22.

Quantity	Method 1	Method 2	Method 3
Life, yrs	15.3	13.0	14.2
Range	9.2-21.4	6.5-19.5	8.5-19.9
Upper deviation	+6.1	+6.5	+5.7
Lower deviation	-6.1	-6.5	-5.7
% upper deviation	+40	+50	+40
% lower deviation	-40	-50	-40
Implied σ	6.1	6.5	5.7

An analysis for HCFC-22 using Equations (30) and (32) yields a mean lifetime of 14.2 years and a standard deviation of 1.2 years (8.5 percent). It is clear that by combining the three reported measurements in this way, great improvements in lowering the uncertainties are made.

The tropospheric lifetime can be found by taking the inverse of k'. Thus

$$L = 1/k' = 0.00201(M/n_h)\exp[(E/R-450)/277] \qquad (35)$$

Rearranging to solve for E/R gives

$$E/R = 277\ln(498n_hL/M) + 450 \qquad (36)$$

or

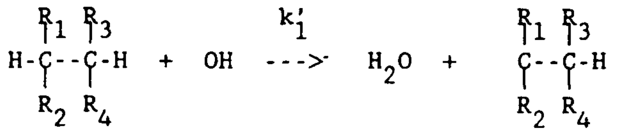
$$E/R = 450 + 277\ln(498) + 277\ln(L) + 277\ln(n_h) - 277\ln(M) \qquad (37)$$

This simplifies to

$$E/R = 2170 + 277[\ln(n_hL/M)] \qquad (38)$$

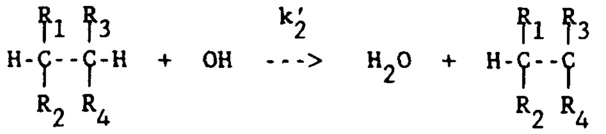
Equation (38) enables estimation of activation energies from lifetimes for those compounds that have only one type of reactive hydrogen.

If there is more than one type of reactive hydrogen in the molecule, the situation is more complex. For example, Reactions [17] and [18] illustrate the initial steps in destruction by OH of a haloalkane containing two types of reactive hydrogen, occurring by two pathways.



$$\mathrm{H{-}}\overset{R_1}{\underset{R_2}{\mathrm{C}}}{-}{-}\overset{R_3}{\underset{R_4}{\mathrm{C}}}\mathrm{{-}H} + \mathrm{OH} \xrightarrow{k'_1} \mathrm{H_2O} + \overset{R_1}{\underset{R_2}{\mathrm{C}}}{-}{-}\overset{R_3}{\underset{R_4}{\mathrm{C}}}\mathrm{{-}H}$$

[17]



$$\mathrm{H{-}}\overset{R_1}{\underset{R_2}{\mathrm{C}}}{-}{-}\overset{R_3}{\underset{R_4}{\mathrm{C}}}\mathrm{{-}H} + \mathrm{OH} \xrightarrow{k'_2} \mathrm{H_2O} + \mathrm{H{-}}\overset{R_1}{\underset{R_2}{\mathrm{C}}}{-}{-}\overset{R_3}{\underset{R_4}{\mathrm{C}}}$$

[18]

Since the rate constants k'_1 and k'_2 include the (constant) OH concentration, and these reactions are pseudo-first order in the hydrogen-containing haloalkane,

$$-d[A]/dt = k'_1[A] + k'_2[A] = (k'_1 + k'_2)[A] = k'[A] \qquad (39)$$

Therefore, the overall rate constant (k') for destruction is the sum of the individual rate constants for the processes occurring. It follows that

$$L = 1/k' = 1/(k'_1 + k'_2) \qquad (40)$$

Replacing k'_1 with $1/L_1$ and k'_2 with $1/L_2$ gives

$$L_{total} = 1/(1/L_1 + 1/L_2) \qquad (41)$$

or

$$1/L_{total} = 1/L_1 + 1/L_2 \qquad (42)$$

Table 18 gives a comparison of lifetimes obtained from Equations (25) and (30) with the best available data on atmospheric lifetimes (References 64 and 88). Equation (38) was used to calculate the required E/R to correspond to the accepted lifetime.

TABLE 18. COMPARISON OF ESTIMATED AND BEST KNOWN LIFETIMES.

Compound	M	n_h	E/R	Lifetime, yrs Estd.	 Known	Ratio	E/R Needed
CH_3F	34.0	3	2015	7.0	3.74	2.1	1841
CH_2F_2	52.0	2	1930	11.8	6.72	1.8	1773
CH_2ClF	68.5	2	1964	17.6	1.35	13.0	1252
$CHCl_2F$	102.9	1	1913	43.9	1.93	22.2	1047

TABLE 18. COMPARISON OF ESTIMATED AND BEST KNOWN LIFETIMES (CONCLUDED).

Compound	M	n_h	E/R	Lifetime, yrs		Ratio	E/R Needed
				Estd.	Known		
$CHClF_2$ (HCFC-22)	86.5	1	1879	32.7	14.25	2.3	1648
CH_3CH_2F	48.0	2α	1065	0.5		1.6	
		3β	1500	3.8			
		both		0.44	0.28	1.6	
CH_2FCH_2F	66.0	4	1415	1.2	0.604	2.0	1232
CH_3CHF_2 (HCFC-152a)	65.0	1α	980	1.0			
		3β	1450	1.7			
		both		0.63	1.68	0.38	
CH_2FCHF_2	84.0	1α	1330	3.2	3.8		
		2β	1365	3.3			
		both		1.6	3.8	0.42	
CH_3CF_3	84.0	3	1850	9.5	39.5	0.24	2244
CHF_2CHF_2	102.0	2	1280	2.2	11.40	0.19	1733
CH_2FCF_3	102.0	2	1765	12.8	14.38	0.89	1797
CHF_2CF_3 (HCFC-125)	120.0	1	1680	22.1	26.74	0.83	1732
CH_3CCl_2F (HCFC-141b)	116.9	3	1850	13.2	7.04	1.86	1674
CH_3CClF_2 (HCFC-142b)	100.5	3	1850	11.4	17.89	0.64	1974
$CH_2ClCClF_2$	134.9	2	1799	19.1	3.91	4.9	1359
CH_2ClCF_3	118.5	2	1799	16.8	4.45	3.77	1431
$CHCl_2CF_3$ (HCFC-123)	152.9	1	1748	36.0	1.48	24.4	861
$CHClFCF_3$ (HCFC-124)	136.5	1	1714	28.4	6.07	4.7	1285

It can be seen in Table 18 that the predictions made by use of Equations (24) and (30) vary widely and are not accurate enough for predictive purposes. Although good fitting with the compounds examined in Reference 58 was reported, the parameterization scheme presented therein needs to be modified to fit the more recent data in Table 15. Several modifications can be envisioned. One possibility is using the same scheme, but changing the coefficients. Such a scheme would have the form

$$E/R = A + Bn_F + Cn_{Cl} + Dn_{CH_3} + En_{CH_2X} + Fn_{CHX_2} + Gn_{CX_3} \tag{43}$$

where n_i is the number of each group of type i and X represents F or Cl. This parameterization has several theoretical drawbacks. It considers fluorines and chlorines on the beta carbon to have identical effects. This is not chemically reasonable, because of the much greater electronegativity of fluorine compared to chlorine. For example, a CF_3 group exhibits a significantly different influence from a CCl_3 group. In addition, except for the alpha fluorines and chlorines, the n values can only be zero or one. Thus the latter four n values are only 'on' or 'off' toggles, and it could be argued that this is not really parameterization. Equation (43) has a constant and six parameters, and a workable scheme may be developed using fewer parameters.

A theoretically attractive parameterization scheme would contain a term for each type of group possible in the molecule and would account for the differing effects of the first, second, and third substituent of a given type on a particular carbon. Such a scheme would take the form

$$\begin{aligned} E/R = {} & A + B(\text{for first } \alpha\text{-F}) + C(\text{for second } \alpha\text{-F}) + D(\text{for third } \alpha\text{-F}) \\ & + E(\text{for first } \alpha\text{-Cl}) + F(\text{for second } \alpha\text{-Cl}) + G(\text{for third } \alpha\text{-Cl}) + \\ & H(\text{for first } \beta\text{-F}) + I(\text{for second } \beta\text{-F}) + J(\text{for third } \beta\text{-F}) + \\ & K(\text{for first } \beta\text{-Cl}) + L(\text{for second } \beta\text{-Cl}) + M(\text{for third } \beta\text{-Cl}) + \\ & N(\text{if two carbons}) \end{aligned} \tag{44}$$

Equation (44) has one constant and 13 parameters and could be used to predict the properties of all possible one- and two-carbon haloalkanes that contain at least one hydrogen and may contain fluorine and chlorine. Since the data used to fit the parameters are only available for 17 compounds, the argument could be made that there are too many parameters to test the accuracy of the predictions with the sample size known at this time. One possible method of decreasing the number of parameters required is to assume that a halogen in the beta (or gamma) position has a fixed relationship to its effect in the alpha position. For example, in studies of anesthetic potencies of halocarbons, some researchers have obtained good correlations using the assumptions that a halogen in the beta position has one-third the effect of one in the alpha position on hydrogen bond donor ability, and that the effect diminishes to 1/9 for the gamma position (Reference 93).

Another parameterization scheme can be developed that is simpler than this ideal version, yet chemically reasonable. It has the form

$$E/R = A + Bn_{\alpha\text{-F}} + Cn_{\alpha\text{-Cl}} + D(\text{if two carbons}) + En_{\beta\text{-F}} + Fn_{\beta\text{-Cl}} \qquad (45)$$

where A, B, C, D, E, and F are constants to be fitted to the data, and n with the subscript α or β and F or Cl represents the number of alpha or beta fluorine or chlorine atoms present. This scheme considers the contributions of the first, second, and third substituent of each type to be equal. It has the advantage of only requiring six parameters.

The next step was to develop a set of linear equations to evaluate the constants for this parameterization scheme. The use of the compounds in Table 7, and for simplicity the omission of the compounds with more than one type of hydrogen, yields the equations shown in Table 19.

TABLE 19. LINEAR EQUATIONS OBTAINED FOR PARAMETERIZATION SCHEME.[a]

Compound	Eqn. No.	Equation
CH_3F	1	1841 = A + B
CH_2F_2	2	1773 = A + 2B
CH_2ClF	3	1252 = A + B + C
$CHCl_2F$	4	1047 = A + B + 2C
$CHClF_2$ (HCFC-22)	5	1648 = A + 2B + C
CH_2FCH_2F	6	1231 = A + B + D + E
CH_3CF_3	7	2244 = A + D + 3E
CHF_2CHF_2	8	1733 = A + 2B + D + 2E
CH_2FCF_3	9	1797 = A + B + D + 3E
CHF_2CF_3 (HFC-125)	10	1732 = A + 2B + D + 3E
CH_3CCl_2F (HCFC-141b	11	1674 = A + D + E + 2F
CH_3CClF_2 (HCFC-142b)	12	1974 = A + D + 2E + F
$CH_2ClCClF_2$	13	1359 = A + C + D + 2E + F
CH_2ClCF_3	14	1431 = A + C + D + 3E
$CHCl_2CF_3$ (HCFC-123)	15	861 = A + 2C + D + 3E
$CHClFCF_3$ (HCFC-124)	16	1285 = A + B + C + D + 3E
CH_3CCl_3	17	1585 = A + D + 3F

[a] Linear regression analysis of equations (1-17) in Table 19 yields the values for parameters A through F below.

A = 1983

B = -56

C = -498

D = -896

E = 289

F = 177

Table 20 shows how well these constants fit the experimental values of E/R.

TABLE 20. EVALUATION OF FITTING USING THE PARAMETERS.

Cmpd.	Parametric Equation	Exptl. E/R	Deviation
CH_3F	1983 - 56 = 1927	1841	86
CH_2F_2	1983 - 2(56) = 1871	1773	98
CH_2ClF	1983 - 56 -498 = 1429	1252	177
$CHCl_2F$	1983 - 56 + 2(-498) = 931	1047	-116
$CHClF_2$ (HCFC-22)	1983 - 2(56) - 498 = 1373	1648	-275
CH_2FCH_2F	1983 - 56 - 896 + 177 = 1208	1231	23
CH_3CF_3	1983 - 896 + 3(289) = 1954	2244	-290
CHF_2CHF_2	1983 - 2(56) - 896 +2(289) = 1553	1733	-180
CH_2FCF_3	1983 - 56 - 896 + 3(289) = 1898	1797	101
CHF_2CF_3 (HFC-125)	1983 - 2(56) - 896 + 3(289) = 1842	1732	110
CH_3CCl_2F (HCFC-141b)	1983 - 896 + 289 + 2(177) = 1730	1674	56
CH_3CClF_2 (HCFC-142b)	1983 - 896 + 2(289) + 177 = 1842	1974	-132
$CH_2ClCClF_2$	1983 - 498 -896 + 2(289) + 177 = 1344	1359	-15
CH_2ClCF_3	1983 - 498 - 896 + 3(289) = 1456	1431	25
$CHCl_2CF_3$ (HCFC-123)	1983 -2(498) -896 + 3(289) = 958	861	97
$CHClFCF_3$ (HCFC-124)	1983 - 56 - 498 -896 + 3(289) = 1400	1285	115
CH_3CCl_3	1983 - 896 + 3(177) = 1618	1585	33

Substituting the parameters from Table 19 into Equation (45) yields Equation (46).

$$E/R = 1983 - 56n_{\alpha\text{-F}} - 498n_{\alpha\text{-F}} - 896(\text{if } 2C) + 289n_{\beta\text{-F}} + 177n_{\beta\text{-Cl}} \qquad (46)$$

Substituting Equation (46) into Equation (30) to yield the lifetime gives

$$L = 0.00201(M/n_h) \times \qquad (47)$$

$$\exp[(1533 - 56n_{\alpha\text{-F}} - 498n_{\alpha\text{-Cl}} - 896(\text{if } 2C) + 289n_{\beta\text{-F}} + 177n_{\beta\text{-Cl}})/277]$$

$$L = 0.00201(M/n_h) \times \qquad (48)$$

$$\exp[5.534 - 0.202n_{\alpha\text{-F}} - 1.798n_{\alpha\text{-Cl}} - 3.235(\text{if } 2C) + 1.043n_{\beta\text{-F}} + 0.639n_{\beta\text{-Cl}}]$$

Combining the constant exponential term in Equation (48) with the initial constant (0.00201) gives

$$L = 0.509(M/n_h)\exp[-0.202n_{\alpha\text{-F}} - 1.798n_{\alpha\text{-Cl}} - 3.235(\text{if } 2C)$$

$$+1.043n_{\beta\text{-F}} + 0.639n_{\beta\text{-Cl}}] \qquad (49)$$

A comparison of known lifetimes with those predicted by Equation (49) is given in Table 21. Estimated versus known lifetimes are plotted in Figure 3.

TABLE 21. COMPARISON OF KNOWN AND ESTIMATED LIFETIMES.

Halocarbon Number	Formula	M	n_H	Lifetime, yrs Known	Estimated
21	$CHCl_2F$	102.9	1	1.93	1.18
22	$CHClF_2$	86.5	1	14.2	4.87
31	CH_2ClF	68.5	2	1.35	2.35
32	CH_2F_2	52.0	2	6.72	8.83
41	CH_3F	34.0	3	3.74	4.71
123	$CHCl_2CF_3$	152.9	1	1.47	1.92
124	$CHClFCF_3$	136.5	1	6.04	8.45
125	CHF_2CF_3	120.0	1	26.7	36.7
132b	$CH_2ClCClF_2$	134.9	2	3.91	3.41
133	CH_2ClCF_3	118.5	2	4.45	4.49
134	CHF_2CHF_2	102.0	2	11.4	5.49
134a	CH_2FCF_3	102.0	2	14.4	19.1
140a	CH_3CCl_3	133.4	3	5.82	6.05
141b	CH_3CCl_2F	116.9	3	7.04	7.96
142b	CH_3CClF_2	100.5	3	17.9	10.2
143a	CH_3CF_3	84.0	3	39.5	12.8
152	CH_2FCH_2F	66.0	4	0.60	0.77

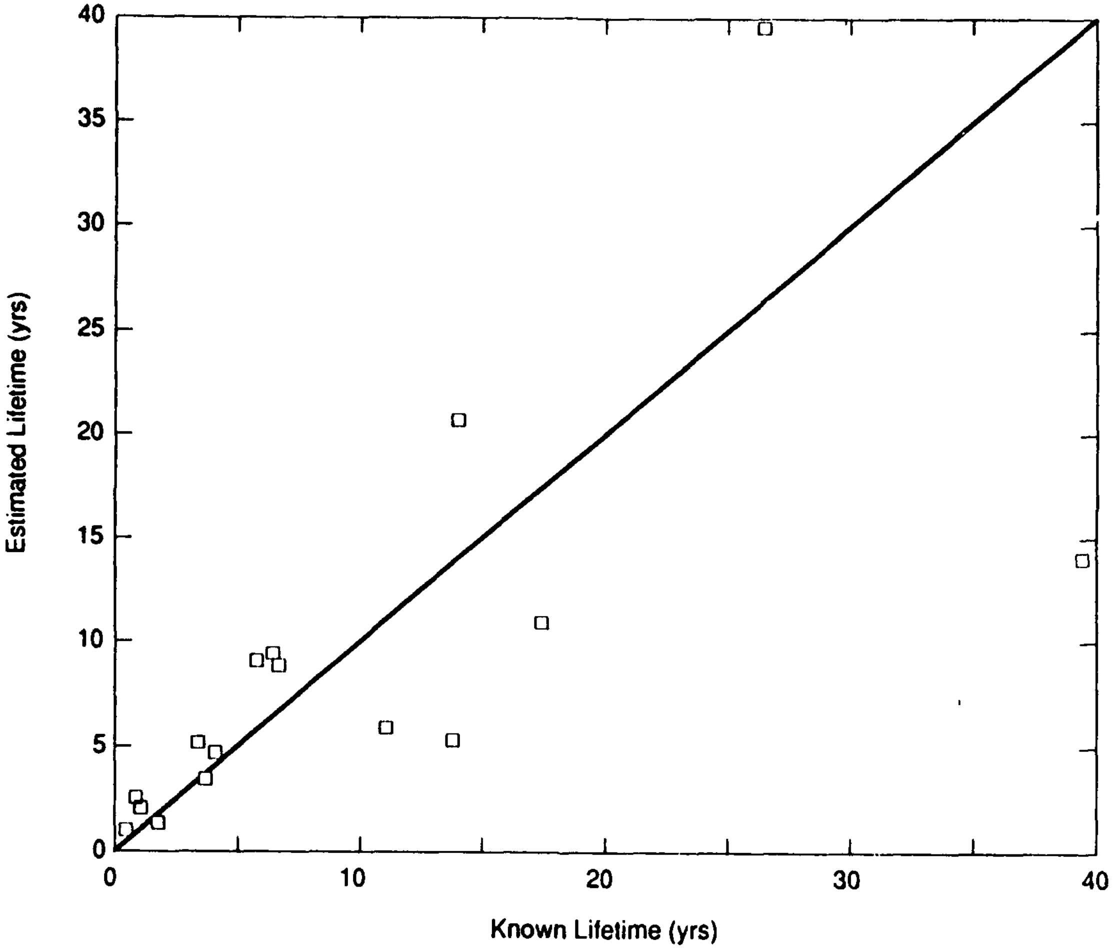


Figure 3. Comparison of Known and Estimated Lifetimes.

As an additional check on the accuracy of this algorithm, lifetimes were computed for the haloalkanes that each contain two types of reactive hydrogens. A lifetime was calculated for each type of hydrogen separately, then the two results were combined into an overall lifetime according to Equation (42). The results are shown in Table 22. This value is compared to the mean lifetimes taken from Table 15. In Table 22, column A refers to the lifetime if only the most abundant type of hydrogen in the molecule reacts; column B refers to the lifetime if only the least abundant type of hydrogen reacts.

TABLE 22. COMPARISON OF ALGORITHM WITH EXPERIMENTAL RESULTS FOR HALOCARBONS CONTAINING TWO TYPES OF REACTIVE HYDROGEN.

Halocarbon Number	Formula	M	n_h(A)	n_h(B)	Estd. Life, yrs A only	Estd. Life, yrs B only	Estd. Life, yrs Overall	Exptl. life, yrs
152	CH_2FCHF_2	84.0	2	1	5.95	3.38	2.15	3.52
152a	CH_3CHF_2	65.0	3	1	3.72	0.90	0.72	1.56
161	CH_3CH_2F	48.0	3	2	0.94	0.40	0.28	0.278

The fact that the estimated overall lifetimes for these compounds are within a factor of 2.2 of the experimental lifetimes supports the validity of the algorithm.

SECTION IX

ESTIMATION OF ODPs BASED ON ATMOSPHERIC LIFETIMES

Work continued on developing an improved ODP calculation based on first principles. This effort included the continued addition of information into the literature database. This database contains full citations and keywords for numerous papers published on ozone depletion, photolysis of halogenated compounds, stratospheric chemistry, and the greenhouse effect. The reading and interpretation of current literature is an ongoing effort.

A rapid and inexpensive algorithm is needed to give a first approximation of the ozone depletion potentials (ODPs) of halocarbons for screening purposes. Such an algorithm should match as closely as possible the rigorously calculated results (Reference 64), and the equations involved should be based on a valid theoretical foundation. This section presents such an algorithm, one which is intended only for initial screening of halocarbons, and many simplifying assumptions are made. Comparison of the results of this algorithm with rigorously calculated and experimental results will give an indication of its usefulness.

Several approaches are possible for estimating the ODPs of halocarbons. Theoretical approaches can be pursued, which involve such factors as rates of reactions and photolytic cross sections. These approaches often require experimental data that are not available for many compounds. A more empirical approach is also possible, correlating rigorously calculated lifetimes and ODPs with such factors as chemical structure, molecular weight, boiling point, bond strength, and weight percent chlorine or bromine (or, equivalently, number of chlorine or bromine atoms per molecule divided by the molecular weight). This method combines theoretical and empirical approaches.

The ODP of a compound is directly proportional to the fraction of molecules surviving to enter the stratosphere (F_s). It is also directly proportional to the numbers of chlorine and bromine radicals generated by each molecule reaching the stratosphere; this can be called the reaction term (F_r). If A is a normalizing constant, F_s is the fraction of molecules released surviving to reach the stratosphere, and F_r is the reaction term, the equation for estimation of ODP becomes

$$ODP = A \times F_s \times F_r \tag{50}$$

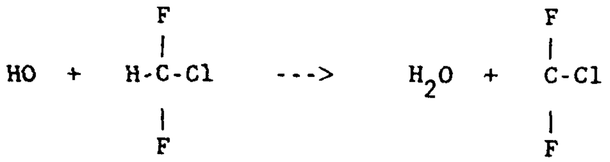
The normalizing constant (A) is used to normalize the ODP relative to the standard of CFC-11 = 1.0.

The survival term (F_s) depends on many factors. Potential sinks that would reduce the amounts of a halocarbon reaching the stratosphere include washing out, photolysis in the troposphere, and reaction with hydroxyl radicals. Washing out in rainfall and dissolution in the oceans or other bodies of water depends on the volatility of a compound, as measured by such interrelated factors as boiling point, vapor pressure, water solubility, and Henry's law constant. For the highly volatile, relatively nonpolar halocarbons under consideration in this study, the boiling points are low, vapor pressures are high, water solubilities are low, and Henry's law constants are high. As a result, the quantities of halocarbons removed by this sink are relatively small, and can, to a first approximation, be neglected (Reference 65).

Some halocarbon molecules will be destroyed by photolysis in the troposphere, before reaching the stratosphere. However, considering the greatly decreased intensity of the ultraviolet light capable of bond breaking in the troposphere compared to the stratosphere, this sink can also be neglected, to a first approximation (Reference 65). For compounds containing weaker bonds, such as alkenes and aromatics, tropospheric photolysis may be significant. Evidence is increasing that sinks exist for

CFCs and halons that have not yet been accounted for in models. Recent work has indicated that the soil on the earth's surface can remove CFCs from the atmosphere (Reference 94).

However, the major and, to a first approximation, only sink for hydrogen-containing aliphatic halocarbons in the troposphere is reaction with hydroxyl radicals. In this reaction, a hydroxyl radical removes a hydrogen atom from the halocarbon molecule to form water and a halocarbon radical that undergoes further reactions. An example of this reaction (for HCFC-22) is shown in Reaction [19].



$$HO + H\text{-}\underset{F}{\overset{F}{C}}\text{-}Cl \;\text{--->}\; H_2O + \underset{F}{\overset{F}{C}}\text{-}Cl \qquad [19]$$

or, in general,

$$HO + HCX_3 \;\text{--->}\; H_2O + CX_3 \qquad [20]$$

where the three X groups may be any combination of F, Cl, and Br.

Little is known about the reaction pathways and ultimate products of the halomethyl radicals formed in Reaction [20]. However, the generalization can be made that the haloalkyl radicals formed in Reaction [20] will likely react by several pathways, most of which will lead to significantly less volatile products than the initial halocarbon. These products would then be washed out of the troposphere without causing appreciable ozone destruction. One can speculate that one likely reaction pathway involves reaction of the radical with molecular oxygen to form a hydroperoxy radical, as shown in Reaction [21].

$$X_3C + O_2 \;\text{--->}\; X_3C\text{-}O\text{-}O \qquad [21]$$

The hydroperoxy radical could abstract hydrogen from a donor such as water

$$X_3C\text{-}O\text{-}O \ + \ H\text{-}OH \ \text{--->} \ X_3C\text{-}O\text{-}OH \ + \ OH \qquad [22]$$

Hydroperoxides contain very weak oxygen-oxygen bonds (approximate bond strengths 35-45 kcal/mole) (Reference 47) and often undergo homolytic cleavage. This cleavage would yield a haloalkoxy radical and a hydroxyl radical.

$$X_3C\text{-}O\text{-}OH \ \text{--->} \ X_3C\text{-}O \ + \ OH \qquad [23]$$

Alkoxy radicals often abstract hydrogen atoms from sources such as water. This reaction would yield a trihalomethanol, plus another hydroxyl radical.

$$X_3C\text{-}O \ + \ H_2O \ \text{--->} \ X_3C\text{-}OH \ + \ OH \qquad [24]$$

Trifluoromethanol (CF_3OH) is a reasonably stable molecule (References 95-101). However, if there is a chlorine or bromine atom on the carbon, the molecule is a halohydrin. Halohydrins are (with rare exceptions) unstable, losing HCl or HBr spontaneously to form carbonyl compounds.

$$CX_3OH \ \text{--->} \ HX \ + \ COX_2 \qquad [25]$$

The carbonyl halides formed (COF_2, $COCl_2$, $COBr_2$, COClF, COBrF, COBrCl) are highly toxic, but they also have very short environmental half-lives since they react rapidly with water, ultimately forming hydrohalic acids (HX), carbon dioxide, and water.

$$COX_2 \ + \ H_2O \ \text{--->} \ HX \ + \ HOCOX \qquad [26]$$

$$HOCOX \ + \ H_2O \ \text{--->} \ H_2CO_3 \ + \ HX \qquad [27]$$

$$H_2CO_3 \ \text{--->} \ H_2O \ + \ CO_2 \qquad [28]$$

Note that in Reactions [20]-[28] two net moles of hydroxyl radical per mole of halocarbon are produced. To a minor extent, then, this pathway would lead to accelerated destruction of remaining hydrohalocarbon molecules.

If the original halomethane contained two hydrogen atoms, one would remain after hydrogen abstraction.

$$CH_2X_2 + OH \text{ ---> } CHX_2 + H_2O \qquad [29]$$

Reactions of the dihalomethyl radical (CHX_2) similar to Reactions [20]-[28] above would be

$$CHX_2 + O_2 \text{ ---> } X_2CH\text{-}O\text{-}O \qquad [30]$$

$$X_2CH\text{-}O\text{-}O + H\text{-}OH \text{ ---> } X_2CH\text{-}O\text{-}OH + OH \qquad [31]$$

$$X_2CH\text{-}O\text{-}OH \text{ ---> } X_2CH\text{-}O + OH \qquad [32]$$

$$X_2CH\text{-}OH \text{ ---> } HX + HCOX \qquad [33]$$

Hydrolysis of the formyl halides produced in Reaction [33] would lead to formic acid (HCOOH) and hydrohalic acids (HX).

$$HCOX + H\text{-}OH \text{ ---> } HCOOH + HX \qquad [34]$$

Formic acid, though corrosive and toxic in large quantities, is relatively harmless in minute concentrations, and would be metabolized quickly by microorganisms to carbon dioxide and water.

It is also possible that halomethyl radicals would combine directly with hydroxyl radicals to form halogenated alcohols.

$$X_3C + OH \text{ ---> } X_3C\text{-}OH \qquad [35]$$

This alcohol would then be expected to undergo Reactions [33] and [34], giving the same overall products as reaction of the halomethyl radical with molecular oxygen, but with net consumption of two moles of hydroxyl radical per mole of halocarbon.

Since the principal mechanisms for the destruction of fully halogenated halocarbon and those containing hydrogen differ, predictive algorithms for estimating the ODPs and atmospheric lifetimes of these two classes of chemicals will differ as well. For hydrogen-containing halocarbons, the lifetimes are determined primarily by the rates of reaction with OH radicals. For fully halogenated halocarbons, virtually 100 percent reach the stratosphere, and photolysis in the stratosphere is the main mechanism of destruction.

The rate of reaction of hydroxyl radicals with aliphatic halocarbons not containing C-H bonds is negligible (less than 5×10^{-16} cm^3 per molecule per second) (Reference 65). The rate of reaction of hydroxyl radicals with a hydrogen-containing halocarbon (and therefore the atmospheric lifetime or half-life) can be estimated from the structure of the molecule, as described in Section VIII of this report.

Since reaction with OH is the major sink, knowledge of that rate of reaction enables estimation of the tropospheric lifetime. An estimated tropospheric lifetime, coupled with knowledge of the time required for a halocarbon molecule to reach the stratosphere, enables estimation of the fraction surviving to enter the stratosphere.

To calculate the fraction reaching the stratosphere, the lifetime must be compared to the rate of upward travel. For example, if the time to reach the stratosphere is the same as the half-life, then half the molecules reach the stratosphere. If the time to reach stratosphere is twice the half-life, one fourth reaches stratosphere. If the time required to reach stratosphere is much less than the half-life, virtually all the molecules reach the stratosphere.

Since the OH concentration is assumed to be constant, the fraction of molecules entering the stratosphere can be estimated using first-order kinetics.

$$F_s = N/N_o = \exp(-kt) \tag{51}$$

where k is the rate constant for reaction with OH and t is the time to diffuse up to the stratosphere. This can also be expressed as

$$F_s = \exp(-t/L) \tag{52}$$

or

$$F_s = \exp(-0.693t/L_{1/2}) \tag{53}$$

To use these expressions, one needs to know t, the average time required for a molecule to migrate upward to the stratosphere. Such information is not readily available. However, if it is assumed that this migration is, to a first approximation, a diffusion process, the transit time is proportional to the square root of the molecular weight.

$$t = cM^{1/2} \tag{54}$$

where t is transit time, c is a constant of proportionality, and M is molecular mass. Since in reality transport through the atmosphere involves both diffusion and convection, a more accurate equation would be

$$t = cM^{1/2} + c_4 \tag{55}$$

where c_4 is the average time spent in convective mixing. The quantity c' is expected to be relatively constant and independent of the nature of the molecule. However, c_4 introduces another variable, and if diffusion is the major transport mechanism, Equation (55) may be unnecessary to a first approximation.

Substituting Equation (54) into Equation (52) gives

$$F_s = \exp(-t/L) = \exp[-cM^{1/2}/L] \qquad (56)$$

The reaction term (F_r) describes the total number of chlorine and bromine radicals generated per molecule and includes a proportionality factor to account for the greater reactivity with ozone of bromine compared to chlorine. Once a halocarbon molecule reaches the stratosphere, it is a virtual certainty that photolysis will occur. The quantum yield is 1.0 and is independent of the carbon-halogen bond strength for chlorinated and brominated compounds. Carbon-to-bromine bonds in these compounds range in strength from approximately 64 to 72 kcal/mole.

The equation relating wavelength of light to its energy is

$$E = h\nu = hc/\lambda \qquad (57)$$

where E is energy, h is Planck's constant (6.63×10^{-34} J-s or 1.58×10^{-37} kcal-s), c is the speed of light (3.00×10^{8} m/s), and λ (lambda) is the wavelength on a per-molecule basis. Converting to a per-mole basis, leaving E variable, and solving for λ gives

$$\lambda = hcN_o/E = 2.86 \times 10^{-5} \text{ kcal-m}/E = 28{,}600 \text{ kcal-nm}/E \qquad (58)$$

Substituting a bond strength (in kcal) for E gives the corresponding wavelength of light (in nm) having sufficient energy to break that bond. A bond strength of 64 kcal/mole corresponds to light of wavelength 450 nm, and of 72 kcal/mole to 400 nm. Therefore a photon of wavelength less than 400 nm possesses enough energy to break virtually any C-Br bond. Similarly, carbon-to-chlorine bonds range in strength from approximately 70 to 86 kcal/mole, corresponding to light of wavelength 410 to 330 nm.

The rate of generation of halogen radicals depends on the absorption cross section, but the total number of halogen radicals generated does not.

For this simple algorithm, only the total quantities of halogen radicals generated in the stratosphere are considered, not the rates of generation.

Once the initial photolysis has occurred, the remaining haloalkyl radical can undergo loss of one or more additional halogen radicals. In fact, it is likely that virtually all the halogen atoms in the molecule will become halogen radicals. This allows the simplifying assumption that all of the chlorine and bromine atoms in a molecule form the corresponding radicals.

If n_{Cl} is the number of chlorine radicals generated per molecule, n_{Br} is the number of bromine radicals generated, and c_3 is the proportional effect on ozone of bromine relative to chlorine, the expression for F_r becomes

$$F_r = (n_{Cl} + c_3 \times n_{Br}) \tag{59}$$

A more sophisticated algorithm might account for the differing reactivities of the first, second, third, and subsequent halogens in a molecule. It is less likely that the last halogen on a molecule will form a free radical than the first halogen, because intervening reactions could lead to products that are washed out before all the halogens have formed radicals. For example, one could evaluate the contribution of the second, third, and subsequent chlorines or bromines relative to the first.

$$n_{Cl} = 1 \text{ (if a first Cl is present)} + c'\text{(if a second Cl is present)}$$

$$+ c'' \text{ (if a third Cl is present)} + \ldots \tag{60}$$

where the constants c_2 and c_3 have values less than one, to account for losses of intervening radicals.

A similar treatment could be carried out for bromine.

Combining Equations 50, 56, and 59 gives

$$ODP = A \times F_s \times F_r = c_1 \exp[-c_2 M^{1/2}/L] \times (n_{Cl} + c_3 n_{Br}) \tag{61}$$

where c_1, c_2, and c_3 are constants to be evaluated by curve fitting using rigorously calculated ODPs and lifetimes.

The constant c_1 is used to normalize the results relative to CFC-11 = 1.0. The constant c_3 represents the proportional effect of a bromine radical compared to a chlorine radical on stratospheric ozone. This constant has an approximate value of 32, as determined in version 1 of this algorithm (Reference 11).

To evaluate the constant c_2, the ratios of rigorously calculated ODPs can be used. For two compounds (designated by the subscripts 1 and 2) with rigorously calculated ODPs,

$$\frac{ODP_2}{ODP_1} = \frac{c_1 \exp(-c_2 M_2{}^{1/2}/L_2) \times (n_{Cl} + c_3 n_{Br})_2}{c_1 \exp(-c_2 M_1{}^{1/2}/L_1) \times (n_{Cl} + c_3 n_{Br})_1} \tag{62}$$

The ODP values are known, the c_1 cancels, and the molecular weights and formulas (including numbers of chlorines and bromines) are known. If c_3 is known at this point and

$$k_1 = M_1{}^{1/2}/L_1 \tag{63}$$

$$k_2 = M_2{}^{1/2}/L_2 \tag{64}$$

the expression becomes

$$\exp(-c_2k_2)/\exp(-c_2k_1) = \text{a constant} \tag{65}$$

This reduces to

$$\exp[(k_1 - k_2)c_2] = C \tag{66}$$

Taking natural logarithms of both sides gives

$$(k_1 - k_2)c_2 = \ln C = C' \tag{67}$$

Dividing both sides by $(k_1 - k_2)$ gives

$$c_2 = C'/(k_1 - k_2) \tag{68}$$

Solving Equation (62) for c_2 gives

$$c_2 = \frac{1}{M_1^{1/2}/L_1 - M_2^{1/2}/L_2} \times \ln \frac{ODP_2 + (n_{Cl} + c_3 \times n_{Br})_2}{ODP_1 + (n_{Cl} + c_3 \times n_{Br})_1} \tag{69}$$

Taking natural logarithms of Equation (61) gives

$$\ln(ODP) = \ln(c_1) - c_2M^{1/2}/L + \ln(n_{Cl} + c_3n_{Br}) \tag{70}$$

Equation (70) was used for non-brominated compounds ($c_3 = 0$) to evaluate constants c_1 and c_2 by linear regression. The resulting equation was

$$\ln(ODP/n_{Cl}) = \ln(c_1) - c_2M^{1/2}/L \tag{71}$$

or

$$ODP = c_1 n_{Cl} \exp(-c_2 M^{1/2}/L) \qquad (72)$$

In order to evaluate the constants c_1 and c_2, a plot of $\ln(ODP/n_{Cl})$ versus $M^{1/2}/L$ was made; this is shown in Figure 4.

Figure 4 shows that some correlation was obtained with this equation. There is, however, curvature visible on the graph. For this reason the equations were reexamined.

Rigorously calculated ODPs are the steady-state depletion in total column ozone. A one-shot release of a halocarbon leads to a decrease in total column ozone, followed by recovery as ozone is reformed by photolysis of O_2 and recombination of the oxygen atoms with O_2, as shown in Reactions [36] and [37].

$$O_2 \text{ ---> } 2\ O \qquad [36]$$

$$O + O_2 \text{ ---> } O_3 \qquad [37]$$

The ODP calculated by Equation (61) is related to the total quantity of ozone destroyed. This corresponds to the area of the curve shown in Figure 5.

This curve may be approximated as an inverted triangle, with the height corresponding to the rigorously calculated ODP and the base proportional to the lifetime of the halocarbon. Since, for a triangle, area = 1/2 base x height and integrated column ozone depletion equals a constant times lifetime times rigorously calculated ODP, or

$$\text{Area} = c \times L \times ODP \qquad (73)$$

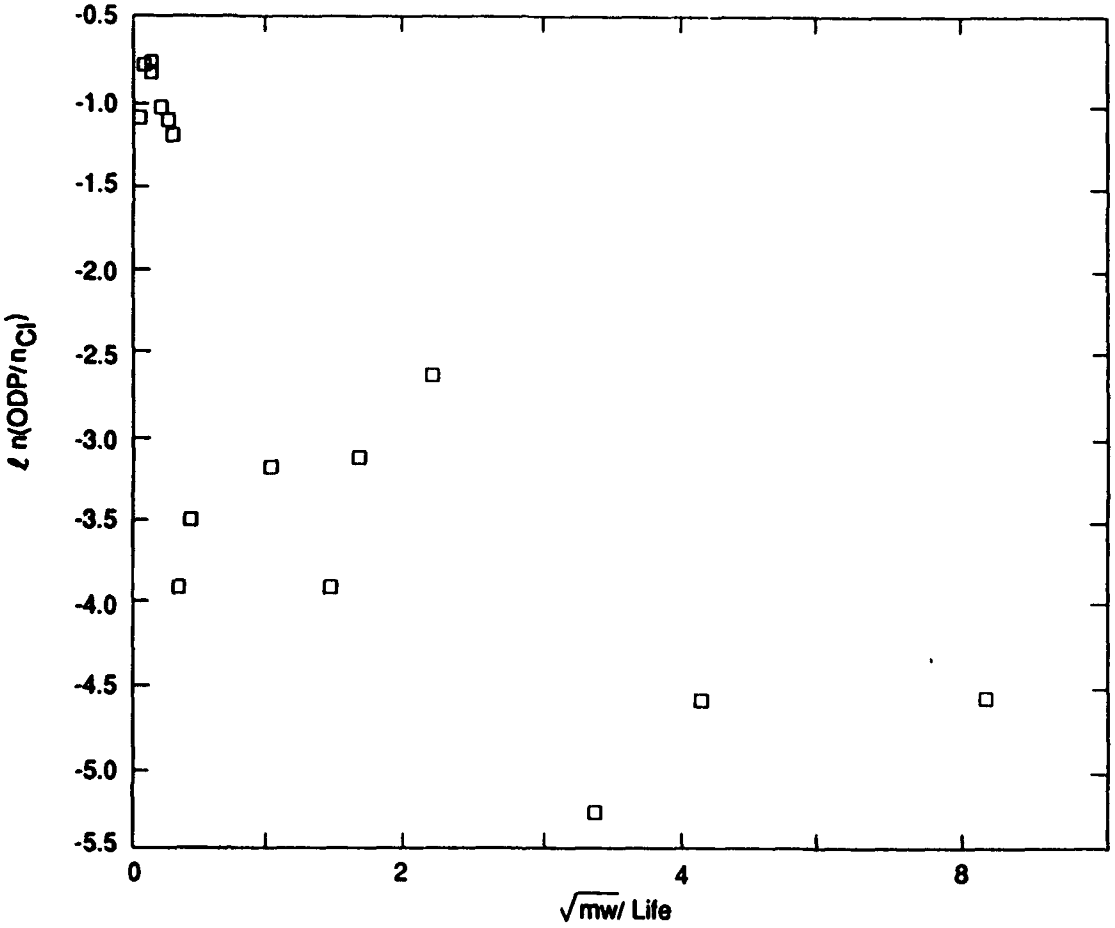


Figure 4. Plot of ODP Versus Square Root of Molecular Weight Divided by Lifetime for HFCs, HCFCs, and CFCs.

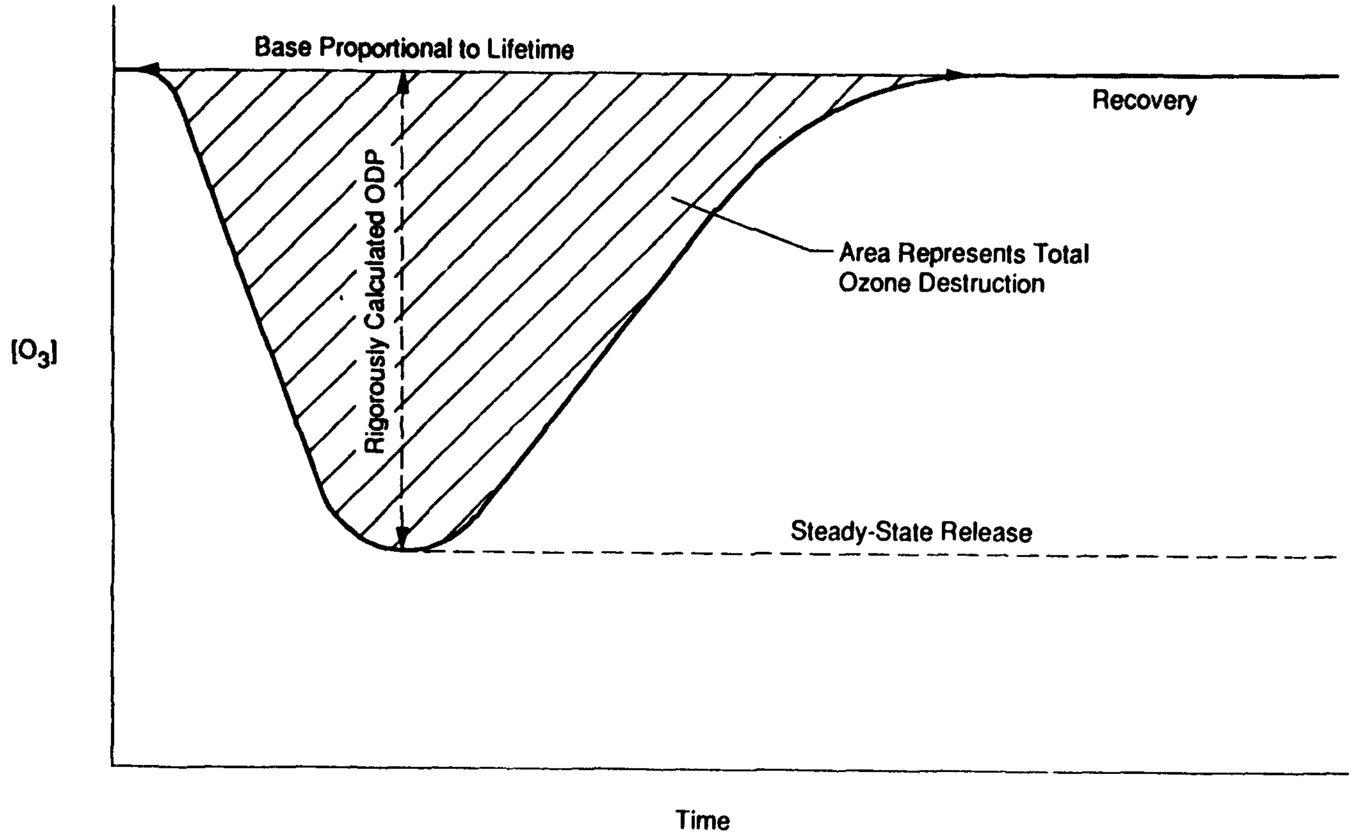


Figure 5. Integrated Column Ozone Destruction and Rigorously Calculated ODP.

Combining the constant into the constant c_1 gives

$$\mathrm{ODP} \times L = c_1 \exp[-c_2 M^{1/2}/L](n_{Cl} + c_3 n_{Br}) \tag{74}$$

or

$$\mathrm{ODP} = (c_1/L)\exp[-c_2 M^{1/2}/L](n_{Cl} + c_3 n_{Br}) \tag{75}$$

In the case that $c_3 = 0$ (no bromine is present), Equation (76) becomes

$$\ln(\mathrm{ODP} \times L/n_{Cl}) = \ln(c_1) - c_2 M^{1/2}/L \tag{76}$$

$$\text{if } \ln(c_1) = c_1' \tag{77}$$

$$\ln(\mathrm{ODP} \times L/n_{Cl}) = c_1' - c_2 M^{1/2}/L \tag{78}$$

Equation (78) has the form $y = mx + b$, where $y = \ln(\mathrm{ODP} \times L/n_{Cl})$, $m = -M^{1/2}/L$, and $b = c_1'$. Therefore, a plot of $\ln(\mathrm{ODP} \times L/n_{Cl})$ versus $M^{1/2}/L$ should have a slope of $-c_2$ and a y-intercept of c_1' (or $\ln(c_1)$). Such a plot for the six HCFCs with rigorously calculated ODPs is shown in Figure 6. The least-squares line through these points gives $c_1 = 0.677$ and $c_2 = 0.496$. The quality of the fit is $r^2 = 0.88$ for 6 points (4 degrees of freedom). For HCFCs, then, Equation (76) becomes

$$\mathrm{ODP} = (0.677 n_{Cl}/L)\exp(-0.496 M^{1/2}/L) \tag{79}$$

The corresponding plot for fully halogenated compounds is shown in Figure 7. The least-squares fit for these compounds gives $c_1 = 194$ and $c_2 = 12.0$, with $r^2 = 0.93$ for 6 points (4 degrees of freedom) so Equation (75) for CFCs becomes

$$\mathrm{ODP} = (194 n_{Cl}/L)\exp(-12.0 M^{1/2}/L) \tag{80}$$

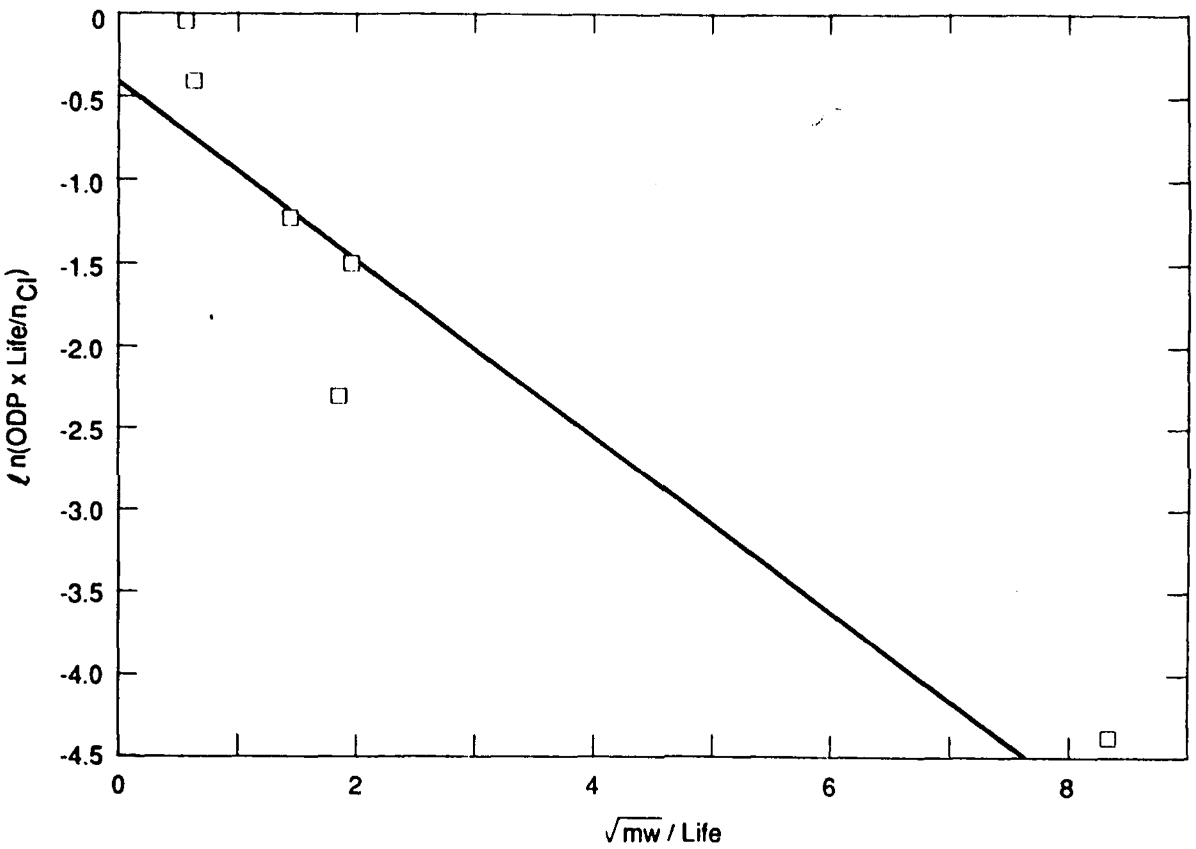


Figure 6. Plot for HCFCs of the Natural Logarithm of the Quantity ODP Times Lifetime Divided by Number of Chlorine Atoms Versus Square Root of Molecular Weight Divided by Lifetime.

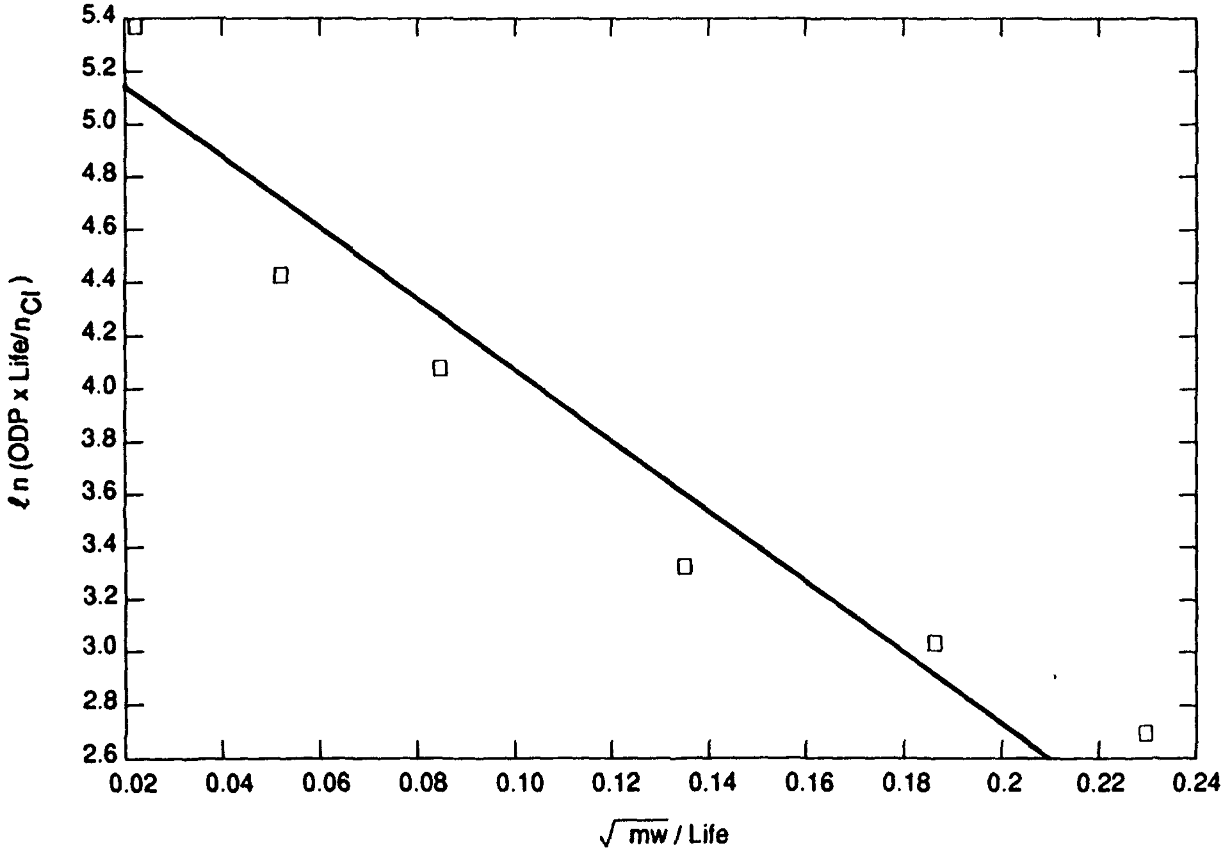


Figure 7. Plot for CFCs of the Natural Logarithm of the Quantity ODP Times Lifetime Divided by Number of Chlorine Atoms Versus Square Root of Molecular Weight Divided by Lifetime.

Several modifications to the above treatment of ODPs are possible. In Equation (54) it was assumed that transport to the stratosphere was purely a diffusion process. In reality, the process involves both diffusion and convection. For the diffusion portion, the time required is proportional to the square root of the molecular weight. Convective mixing, on the other hand, will occur at approximately equal rates for all molecules under consideration.

If c_4 is the transit time during convective mixing, Equation (55) becomes

$$t = c_2M^{1/2} + c_4 \tag{81}$$

Substituting this expression into Equation (62) gives

$$ODP \times L = c_1\exp[-(c_2M^{1/2} + c_4)](n_{Cl} + c_3n_{Br}) \tag{82}$$

Considering only chlorinated compounds ($n_{Br} = 0$), dividing both sides by n_{Cl}, and taking the natural logarithm of both sides gives

$$\ln(ODP \times L/n_{Cl}) = \ln(c_1) - (c_2M^{1/2} + c_4)/L$$

$$= \ln(c_1) - c_4/L - c_2M^{1/2}/L$$

$$= c_1' - c_2M^{1/2}/L - c_4/L \tag{83}$$

If it is desired to account for convective mixing and to introduce another variable, Equation (83) could be fitted to the experimental data.

For fully halogenated compounds, the atmospheric lifetimes may well correlate with refractive indexes, since both properties are related to interaction with light. Unfortunately, information on refractive index for most of the compounds of interest is not readily available. However, the refractive index itself can be estimated quite accurately. Refractive index shows good empirical correlation with other physical properties, including density, boiling point, vapor pressure, gas heat capacity, and heat of formation. If, in a series of related compounds, refractive indexes are known for several of the compounds, the missing values can be predicted by plotting refractive index versus the other properties just mentioned, fitting a curve, and interpolating or extrapolating the missing values of refractive index.

SECTION X
DESTRUCTION TECHNOLOGIES FOR OZONE-DEPLETING HALOCARBONS

A. INTRODUCTION

Waste halocarbons are sometimes released to the environment because no effective, low-cost disposal methods are readily available. Substantial banks of halocarbons have accumulated and some of these materials may need to be destroyed when environmentally safer alternatives become available. Occasions may also arise when it is safer, easier, and more economical to destroy waste or contaminated halocarbons than to purify them by distillation, filtration, or other means. During the acquisition of information on the chemistry and physics of halocarbons, information on destruction technologies was obtained as a byproduct. This information is collected and discussed here.

Numerous methods exist for disposing of organic chemical wastes. Treatment methods for nonsolvent halogenated organics have been reviewed (Reference 102), as have destruction technologies for CFCs (References 103 and 104).

Table 23 shows treatment alternatives of established and emerging technologies for both pure organic liquids and for aqueous streams containing small concentrations of organic compounds.

These methods are expected to also apply to solvents and the low-boiling CFCs and halons as long as their high volatility is taken into account. Destruction of halocarbons by incineration, pyrolysis, hydrolysis, catalytic dehydrohalogenation, dehalogenation by sodium naphthalenide, and oxidation will be discussed in turn.

TABLE 23. TREATABILITY OF HALOGENATED NONSOLVENT WASTES.

Treatment Alternative	Organic Liquids	Aqueous Streams
Established Technologies		
Rotary kiln incineration	X	
Fluidized-bed incineration	X	
Liquid injection incineration	X	X
Lime/cement kiln coincineration	X	
Carbon adsorption		X
Biological treatment		X
Distillation	X	
Solvent extraction	X	
Emerging Technologies		
Molten salt incineration	X	
Plasma arc incineration (pyrolysis)	X	
High temperature fluid wall destruction	X	
Supercritical water oxidation		X
UV/ozone treatment		X
Wet air oxidation		X
Chemical dechlorination	X	
Chlorinolysis	X	

B. INCINERATION

Incineration has proven useful for many years for disposal of various types of waste materials (References 105-109). From an environmental standpoint incineration is, in many cases, the best method known for disposing of hazardous wastes. In incineration, a compound undergoes thermal decomposition and oxidation and is converted to less bulky, less toxic, or less noxious materials. It has been stated that a waste compound must be combustible for incineration to be an effective disposal means (Reference 110). If this were true, incineration of some CFCs and halons would be impossible; however, it is known that several fully halogenated CFCs are candidates for incineration (Reference 105).

Few examples of deliberate destruction of CFCs or halons by incineration are reported in the literature. Accidental incineration of 240 pounds of Halon 1301 during a test of the halon fire suppression system at the Department of Energy's Savannah River incineration plant has been reported (Reference 111). The Halon 1301 was accidentally drawn into the incinerator, where it decomposed thermally to give hydrogen fluoride and bromine gases. These gases were not scrubbed out, and several employees were exposed to the highly irritating fumes. It is also reported that 255 kilograms of CFC-113 were successfully incinerated in a cement kiln over a 3-hour period at 1050 °C using a retention time of 4 seconds (Reference 103). The flue gas contained 15 milligrams of unreacted CFC per kilogram of CFC feed. In a similar test at a municipal waste combustion plant, the emission was 800-4300 milligrams/kilogram.

The most important factors considered in determining the suitability of wastes for incineration include the btu content, viscosity, water content, halogen content, and ash content (Reference 105). The minimum acceptable btu content is about 5000 btu/pound, since this heat content allows incineration to be self-sustaining without added fuels. Highly chlorinated organic compounds have a btu content of approximately 4000 btu/pound

(Reference 102). The reaction of CFC-12 with oxygen, shown in Reaction [38], if it occurred, would be endothermic by 19.9 kcal/mole (Reference 103).

$$CCl_2F_2 + O_2 \rightarrow CO_2 + Cl_2 + F_2 \qquad [38]$$

Addition of a hydrocarbon fuel (such as methane) causes the reaction to become exothermic, in this case by 229.9 kcal/mole (Reaction [39]).

$$CCl_2F_2 + 2O_2 + CH_4 \rightarrow 2CO_2 + 2HCl + 2HF \qquad [39]$$

Many halogenated compounds are listed as potential (not good or poor, but intermediate) candidates for destruction by liquid injection, rotary kiln, and fluidized bed incineration (Reference 105). These compounds include the spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, the chlorinated fluorocarbons, trichlorofluoromethane, sludges from the recovery of these solvents in degreasing operations, and still bottoms from solvent recovery.

Table 24 shows the common incineration processes and their typical operating ranges. Table 25 shows the applicability of these incineration processes to various types of hazardous waste.

EPA regulations (under the Resource Conservation and Recovery Act) for incineration of hazardous waste requires that particulate emissions be no more than 180 kilograms/m^3 and that removal efficiency for HCl from the exhaust gas be at least 99 percent. Gaseous pollutants generated during incineration of halogen containing hazardous wastes include HCl, Cl_2, Br_2, HBr, and HF, of which HCl is the most commonly found. Removal of these gases is usually accomplished by packed bed or plate-tower scrubbers. In some cases Venturi scrubbers are used for simultaneous removal of

TABLE 24. COMMON INCINERATION PROCESSES AND TYPICAL OPERATING RANGES.

Process	Temperature Range, °C	Residence Time
Rotary kiln	820 - 1600	Seconds for gases and liquids
Liquid injection	650 - 1600	0.1 to 2 seconds
Fluidized bed	450 - 980	Seconds for gases and liquids
Multiple hearth	Drying zone 320 - 540	0.25 to 1.5 hours
	Incineration 760 - 980	
Coincineration	150 - 1600	Seconds to hours
Starved air pyrolysis	480 - 820	0.1 seconds to several hours

TABLE 25. APPLICABILITY OF INCINERATION PROCESSES TO INCINERATION OF DIFFERENT TYPES OF HAZARDOUS WASTE.

Disposal Method	Organic Vapor Laden Gases	Organic Liquids or High Organic Aqueous Wastes, Often Toxic
Rotary kiln[a]	[b]X	[c]X
Liquid injection	[b]X	X
Fluidized bed[a]	[b]X	X
Multiple hearth	[b]X	
Coincineration	[b]X	X
Starved air pyrolysis	[b]X	

[a] Suitable for pyrolysis operation.

[b] If properly presented to the incinerator.

[c] If equipped with auxiliary liquid injection nozzles.

particulates and gaseous pollutants. For gases, such as HCl or HF, which are highly water soluble, water can be used in packed bed or plate-tower scrubbers to lower emissions to acceptable levels. When water is used as the scrubbing liquor, the blowdown stream is acidic and must be neutralized before discharge. The maximum concentration of HCl in the scrubbing liquor is kept in the range of 1-2 percent by adjusting blowdown rates and makeup water. Because of these acidic conditions, the scrubber must be lined with an acid-resistant material.

A highly basic (caustic) solution, usually 18-20 weight percent NaOH in water, can also be used to control HCl and HF emissions from packed-bed and plate-tower scrubbers. The NaOH reacts with and, in sufficient quantity, neutralizes the acids. Caustic scrubbing also achieves a high HBr removal efficiency, which is not obtained with water alone.

Incineration of bromine containing compounds gives HBr and Br_2 in the exhaust gases. Hydrogen bromide can be removed by scrubbing with NaOH, but the technology for controlling Br_2 emissions is not well developed. Potential scrubbing methods for Br_2 include absorption in (1) ammonia solution, to give ammonia bromide; (2) NaOH solution, to give $NaBrO_3$ and NaBr; and (3) $Ca(OH)_2$ slurry to give $CaBr_2$ and $Ca(BrO_3)_2$.

Highly halogenated compounds, including hexachlorocyclopentadiene and kepone, have been successfully incinerated using liquid injection with alkali scrubbing (Reference 102).

In any incineration process, the possible formation of highly toxic polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) must be considered (References 112 through 115). Both PCDDs and PCDFs are common byproducts of incineration. Municipal waste incinerators, coal and fossil fuel plants, chemical waste burners, fireplaces, wood stoves, gasoline and diesel combustion engines, and cigarette smoke are all sources of these compounds. Municipal incinerators are probably the greatest combustion sources of PCDD and PCDF.

These compounds arise through condensation reactions of polychlorinated phenols and polychlorinated biphenyls (PCBs). The combustion of CFCs and halons in the presence of material containing aromatic rings (e.g., benzene, paper, wood, coal) could conceivably result in some chlorination of the aromatic rings and reaction to form PCDDs and/or PCDFs. Pyrolysis of materials containing linear carbon chains of six or more atoms can also form aromatic products.

Formation of these products would be a multistep process: formation of Cl_2, multiple chlorination of an aromatic ring, and condensation. Such a multistep process is unlikely to occur to a great extent in the presence of competing reactions such as combustion. Still, since combustion of haloalkanes would cause high concentrations of halogen radicals, hydrohalic acids, and molecular halogens, it is recommended that haloalkanes not be incinerated in the presence of large quantities of phenols or other aromatic compounds until tests determine that it is safe to do so. If a fuel is needed for coincineration, a saturated hydrocarbon (e.g., methane, propane, heavy oil, etc.) appears preferable to such fuels as paper, wood, coal, or gasoline.

C. PYROLYSIS

A plasma reactor destroys wastes using temperatures of up to 10,000 K in a continuous flow of an inert gas such as argon, nitrogen, or oxygen under atmospheric pressure. Gases, liquids, and solids are all easy to place in the plasma reactor. The Japanese National Research Institute for Pollution and Resources has confirmed the effectiveness of a plasma reactor for the destruction of CFCs (Reference 103). In fact, CFCs were decomposed efficiently even in the presence of other materials. Thermal plasma, therefore, appears applicable to CFC wastes that are mixed with other materials. When a mixture of 1.25 percent CFC-11 and 2.5 percent water in an argon stream was fed continuously to a plasma torch at a flow rate of 40 liters per minute, a virtual 100 percent conversion of CFC-11 to CO_2, HCl, and HF was attained at above 10 kW of input power. The overall reaction appeared to be

$$CCl_3F + 2H_2O \rightarrow CO_2 + 3HCl + HF \qquad [40]$$

Trace amounts of the disproportionation products CF_4, CCl_2F_2, CCl_3F, and CCl_4 were observed, as were traces of two- and three-carbon CFCs, presumably formed by polymerization. Destruction efficiencies exceeding 99.99 percent have been obtained for PCBs and CCl_4 by plasma pyrolysis (Reference 116). Platinum catalysts on solid supports have attained destruction levels of 85-95 percent for PCDDs at 300-450 °C. The catalyst lowers the temperatures needed for oxidation by air and steam by about 400 °C compared to the temperatures required without a catalyst. Similar treatment of CFC-113 in a stream of 1000 ppm at 500 °C gave close to 100 percent destruction (Reference 103). Since this method is very similar to that currently used for treatment of exhaust gases, the technology is fairly well developed and may be relatively inexpensive to modify.

D. HYDROLYSIS

Many haloalkanes undergo hydrolysis (replacement of a halide by a hydroxyl group in the presence of water or hydroxide ion). This is the major degradative pathway for many halogenated contaminants in ground water (References 117 and 118). The rate of hydrolysis depends on the nature of the haloalkane. The general trend in ease of hydrolysis is bromide > chloride > fluoride. Certain bacteria catalyze hydrolysis of halogenated hydrocarbons using dehalogenase enzymes (Reference 119).

A study has been conducted of the hydrolysis of CH_2ClF (HCFC-31) in pure water at 20-35 °C (Reference 120). The results show that the reaction is first order with respect to the haloalkane and independent of pH. The proposed mechanism is

$$CH_2ClF \rightarrow CH_2F^+ + Cl^- \text{ (slow)} \qquad [41]$$

$$CH_2F^+ + H_2O \rightarrow CH_2FOH + H^+ \text{ (fast)} \qquad [42]$$

$$CH_2FOH \rightarrow HCHO + HF \text{ (fast)} \qquad [43]$$

The temperature dependence of the rate constant k_1 (in hr^{-1}) can be expressed as

$$\log_{10} k_1 = 11.1124 - 5688.65/T + 1.18655 \log_{10}T \qquad (84)$$

where T is the absolute temperature in Kelvins.

Hydrolysis of CFC-114 ($C_2Cl_2F_4$) is first order with a rate constant of 4.46×10^{-7} hr^{-1} at 25 °C (Reference 121). In this report a theoretical calculation of hydrolysis rate constants for halocarbons is also presented.

The half-lives of several other haloalkanes in water at 25 °C have been studied (Reference 122). The results are shown in Table 26.

E. CATALYTIC DEHYDROHALOGENATION

Catalytic dehydrohalogenation shows some promise for destruction of halogenated compounds (Reference 123). The compounds CCl_4, $CHCl_3$, CH_2Cl_2,

TABLE 26. HALF-LIVES AND PRODUCTS OF BROMOALKANE HYDROLYSIS.

Haloalkane	Half-life, Days	Product
1,2-dibromoethane	2.5	vinyl bromide + HBr
1,2-dibromopropane	320	bromopropenes + HBr
1,3-dibromopropane	48	alcohols
1-bromoheptane	29	1-heptanol
1-bromo-3-phenylpropane	290	3-phenyl-1-propanol

and $C_2H_4Br_2$ react with NaOH and KOH mixed with polyethylene glycol (PEG) to give halide salts, water, and elimination compounds. One drawback of this system is that some of these elimination compounds are regulated wastes.

F. DEHALOGENATION USING SODIUM NAPHTHALENIDE

Sodium naphthalenide (formed by dissolving metallic sodium in naphthalene-containing tetrahydrofuran) has been used for the destruction of many halogenated hydrocarbons, including PCBs, 2,4,5-T, PCDDs, and chlorinated polymers (References 103 and 124-126). The removal of chlorine from these materials to form NaCl is greater than 98 percent in 10 minutes. Fluorine is also removed and converted to NaF. CFCs 12, 22, and 113 have been successfully destroyed in tests using this method. The conditions used were 1.5 equivalents of sodium naphthalenide in THF for 50 minutes at 15 °C in the presence of 10 volume percent tetraethylene glycol dimethyl ether.

G. OXIDATION

Another approach for destruction would be to dissolve the compounds in an enclosed stream of water and use a treatment method that has been proven effective in dilute aqueous solutions. In dilute aqueous solution, CFCs and halons can be destroyed by any two or all three of the following: ozone, H_2O_2, and UV light (References 127-132). CFC 113 was successfully oxidized to below 0.3 percent of its original concentration of 1.0 ppm in water by 2 percent ozone and UV light in 30 minutes.* Many organic compounds can also be oxidized with UV light and a TiO_2 catalyst slurry (References 103 and 133).

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*Personal communication, Jack Zeff, Ultrox International, Santa Ana, CA; (714 545-5557).

The MODAR process oxidizes wastes using water above its critical point of 647 K (374 °C) and 22.1 MPa (218 atmospheres) (Reference 134). This process of oxidation by supercritical water has the advantages that (1) CFCs are decomposed at relatively modest temperatures and (2) hazardous products, such as HCl and HF, are trapped in water and can be neutralized easily with alkali after cooling. The presence of water prevents formation of Cl_2 or Br_2. Approximately 20 tons of water must be heated and pressurized to destroy one ton of CFCs. This destruction is potentially highly economical.

All of these methods appear to be highly effective in converting halogenated compounds in dilute aqueous solution to CO_2 and HX (X = Cl, Br, F). With further testing, one or more of these methods could be applicable to organic compounds in a more concentrated (or pure) state.

SECTION XI

CONCLUSIONS AND RECOMMENDATIONS

It is apparent from Table 24 that the algorithm described in Equation (38) can estimate activation energies with an average absolute deviation of 139 units and a maximum deviation of -290 units of E/R. The average deviation corresponds to an error in rate constant (and lifetime) of a factor of exp(139/277) or 1.7, and the maximum deviation corresponds to an error of a factor of exp(290/277) or 2.8. Thus Equation (41) appears to be a useful method for estimation of tropospheric lifetimes of hydrogen-containing haloalkanes of one or two carbons that contain fluorine and/or chlorine.

Equations (38) and (41) also make it possible to choose which isomer among several will have the lowest atmospheric lifetime. Activation energies (and lifetimes) are decreased by chlorine atoms in the alpha positions and by the presence of a second carbon. They are increased by the presence of fluorine or (to a lesser extent) chlorine atoms on the beta carbon.

The method could be extended to bromine-containing compounds by modifying Equation (38) with the addition of two terms for bromine atoms on the alpha and beta positions.

$$E/R = A + Bn_{\alpha\text{-F}} + Cn_{\alpha\text{-Cl}} + Dn_{\alpha\text{-Br}}$$

$$+ \; E(\text{if two carbons}) + Fn_{\beta\text{-F}} + Gn_{\beta\text{-Cl}} + Hn_{\beta\text{-Br}} \qquad (85)$$

To extend the scheme to three carbons, an additional term for a third carbon plus terms for gamma substituents can be added (if the hydrogen is on a terminal carbon). If the hydrogen in question is on the central carbon, all substituents on the two adjacent (terminal) carbons are beta substituents. For three carbon compounds (including brominated) the corresponding equation is

$$\begin{aligned}&E/R = A + Bn_{\alpha\text{-F}} + Cn_{\alpha\text{-Cl}} + Dn_{\alpha\text{-Br}} + \\ &E \text{ (if 2 carbons)} + Fn_{\beta\text{-f}} + Gn_{\beta\text{-Cl}} + Hn_{\beta\text{-Br}} \\ &+ I \text{ (if 3 carbons)} + Jn_{\gamma\text{-f}} + Kn_{\gamma\text{-Cl}} + Ln_{\gamma\text{-Br}} \qquad (86)\end{aligned}$$

Among the proven methods for destruction of halocarbons including CFCs and halons are incineration, plasma pyrolysis, hydrolysis, catalytic dehydrohalogenation, dehalogenation by sodium naphthalenide, and oxidation. Oxidizing agents include ozone, hydrogen peroxide, supercritical water, and air and steam over a platinum catalyst. Incineration generally requires an added hydrocarbon fuel, such as methane, because many halocarbons are not flammable. Since HF, HCl, HBr, Cl_2, and Br_2 may be formed during incineration or plasma pyrolysis, effective alkali scrubbing of the exhaust gases from these processes is essential.

Incineration and plasma pyrolysis have been demonstrated on a larger scale than the other methods. These two methods, plus oxidation by supercritical water, appear the closest to large-scale application and may be the most economical means for destruction of halocarbons. Further development and testing of all methods on a larger scale is needed, with examination of costs and destruction efficiencies for a broad range of compounds.

In conclusion, several promising technologies exist for destruction of CFCs and halons. Plasma pyrolysis and incineration with alkali scrubbing have been proven effective. Since many CFCs and halons are fire extinguishing agents, incineration must be carried out in low concentrations with added hydrocarbon fuel. Also, since HF, HCl, HBr, Cl_2, and Br_2 may evolve, effective alkali scrubbing of incinerator exhaust gases is essential. Hydrolysis has potential for destruction of CFCs and halons, but has not yet been tested on a large scale. Oxidation by supercritical water or by air and steam over a platinum catalyst are also effective destructive techniques. At this stage, further development and testing of these methods on a larger scale is needed, with examination of costs and destruction efficiencies for a broad range of compounds.

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APPENDIX A
EXPERIMENTATION PLAN FOR PHASE II

A. INTRODUCTION

The Phase II plan (Volume 2) includes laboratory-scale testing of pure agents and blends recommended in this Phase I report. Emphasis will be placed on testing Group 1 agents and blends, and both cup burner and laboratory discharge apparatuses will be used.

B. MATERIALS

The extinguishants used in this testing will include HCFC-123, -124, -141b, -142b, HFC-134a, and FC-C318, both in pure form and in selected blends. The cup burners and laboratory discharge apparatus will use n-heptane fuel.

C. EQUIPMENT

The apparatuses to be used include the NMERI cup burners (one or more of the full-, 5/8-, or 2/5-scale apparatuses) and the laboratory discharge setup. The full-scale NMERI cup burner is shown in Figure A-1. Each NMERI cup burner consists of a glass chimney containing a small glass cup (flame cup) in the center of the chimney, which is connected to a clear plastic tube fed through the stoppered chimney bottom to a sidearm flask filled with n-heptane. The bottom of the chimney contains glass beads. These beads provide even dispersion of the gases flowing into the chimney. A small glass mixing chamber (for mixing of air and extinguishing agent) is connected to the bottom of the chimney through the stopper. The extinguishing agent enters the mixing chamber through a side arm. Air is introduced into the mixing chamber via another side arm with an interior attachment that channels the air to the bottom of the chamber. The full-scale apparatus has a chimney with an ID of 83 mm and a height of 714 mm.

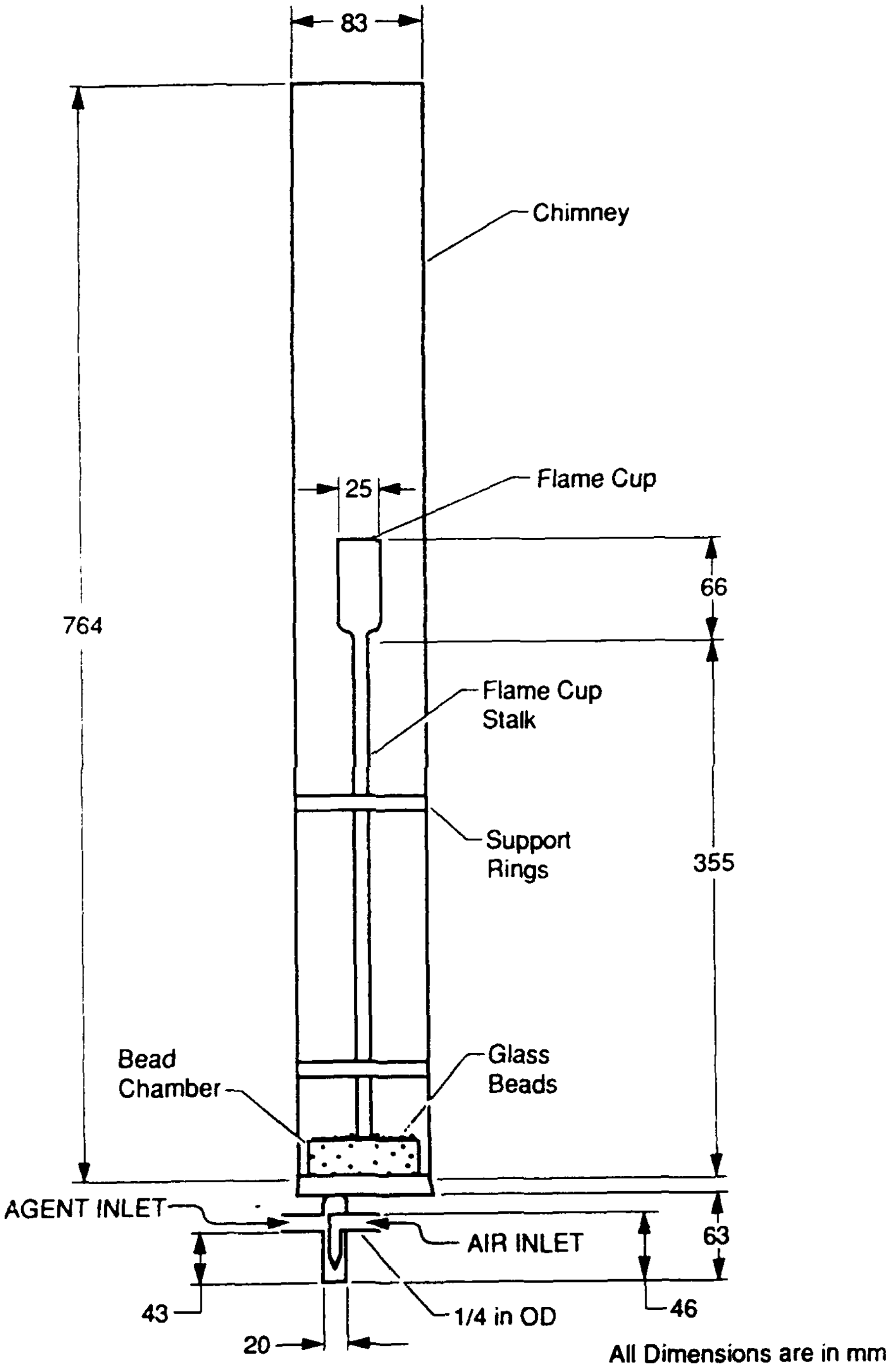

Figure A-1. NMERI Cup Burner (Full-Scale).

The flame cup has an ID of 25 mm and a height of 371 mm and runs up through the center of the chimney. The 5/8-scale apparatus has a chimney with an ID of 52 mm and a height of 470 mm. The design of the 5/8-scale cup burner was modified to include four side ports for easier access to the thermocouple and flame cup (for ignition). The flame cup is 39 mm high and is introduced through a port in the side of the chimney. It is 133 mm long, but is only inserted to a length of 26 mm, placing it in the center of the chimney. The 2/5-scale cup burner has an ID of 32 mm and a height of 308 mm. The flame cup also enters through a port in the side and has an ID of 9 mm and a total length of 108 mm.

The laboratory discharge apparatus (shown in Figure A-2) consists of a 1-liter gas sample cylinder fitted with a gas inlet valve at one end for introducting agents. For agent delivery, an outlet valve, pressure gauge, solenoid, metal tubing, and nozzle are attached at the other end. The solenoid is connected to a switch that allows rapid control of agent delivery. A selection of small nozzles controls the spray angle and pattern (flat, conical rim, or conical full). The metal tubing permits adjustment of delivery direction. The apparatus is clamped to a ring stand with the nozzle directed at a fire pan, 1 inch high and 8 inches in diameter. The cup is surrounded on three sides by fire bricks stacked two high. The entire apparatus is set up in a fume hood. Full details on construction, calibration, and use of both cup burner and laboratory discharge apparatuses will be provided in the Phase II report.

D. PROCEDURES

For cup burner testing, the desired apparatus configuration (for either gases or liquids) is chosen and set up in an explosion-proof fume hood. Gaseous agents are directed through a flow meter; liquid agents are placed in a syringe driven by a syringe pump. Mixing of air and agent (and vaporization of liquid agent) occurs in the mixing chamber. Complete mixing of agent and air is accomplished as the mixture travels past glass beads at the bottom of the chimney. Once past the beads, the vaporized mixture

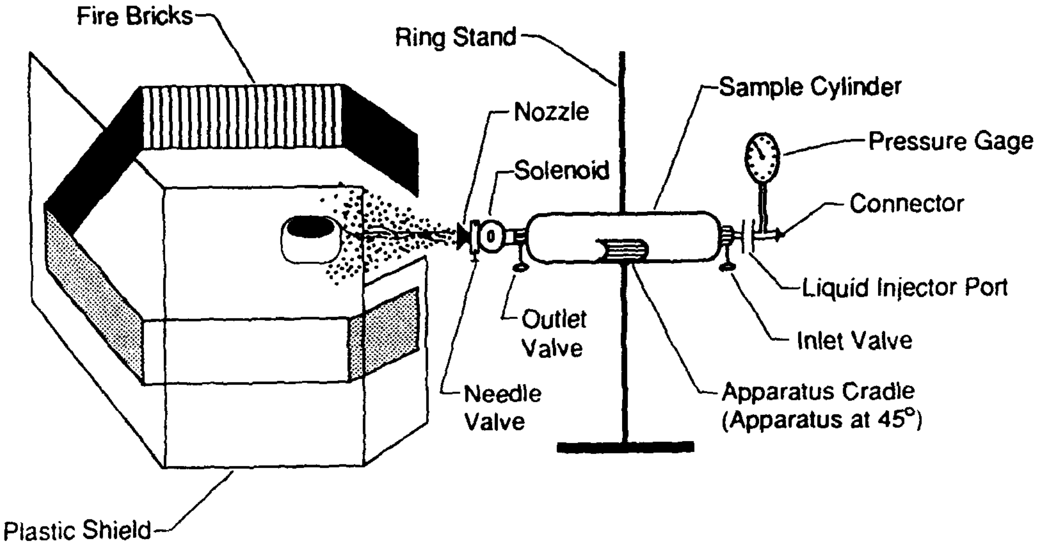

Figure A-2. Laboratory Discharge Apparatus.

continues upward through the chimney past the flame. Flow rates of air and agent are recorded and the flow rate of the agent is increased in small steps until the flame is extinguished. The extinguishing concentration can then be calculated.

Laboratory discharge tests are conducted using a 50 in^2, 8-inch diameter, 1-inch deep fire pan with _n_-heptane fuel (25 mL) floating on water. The agent is delivered from a stainless steel cylinder, the weight of which is monitored to determine agent flow rates during fire extinguishment. Before testing, the tubing and nozzle are detached from the main apparatus and clamped in the correct position on the ring stand. The cylinder is filled with agent, weighed, attached to the tubing and nozzle, and clamped to the ring stand. The cylinder delivery valve is then opened. The fuel in the fire pan is ignited and allowed to burn for 15 seconds. The solenoid is activated to deliver the agent. At extinguishment, the solenoid switch and stop watch are turned off simultaneously. The apparatus is detached from the support and weighed. The extinguishment time and weight of agent used are recorded, and the flow rate is calculated.

E. DOCUMENTATION

All test results from both the cup burner and laboratory discharge apparatus are entered into a computer database to allow rapid access for data analysis and presentation.

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