Texas Commission on Environmental Quality
Interoffice Memorandum

To: Commissioners **Date:** May 3, 2013

Thru: Bridget C. Bohac, Chief Clerk
Zak Covar, Executive Director

From: Ramiro Garcia, Jr., Deputy Director
Office of Compliance and Enforcement

Subject: Consideration of a Petition for Rulemaking

Docket No.: 2013-0700-RUL

Project No.: 2013-028-PET-NR

Who Submitted the Petition:
On April 1, 2013, the Texas Commission on Environmental Quality (TCEQ) received a petition for rulemaking from 3M Company (Petitioner).

What the Petitioner Requests:
The Petitioner requests that its fire protection fluid: 3-Pentanone, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-, CAS No. 756-13-8 (hereafter C6 fluoroketone), be listed in 30 Texas Administrative Code (TAC) §101.1 (88), which would establish a reportable quantity of 5,000 pounds instead of the default reportable quantity of 100 pounds. The chemical is sold as 3M™ Novec™ 1230 Fire Protection Fluid. According to the petition, the fluid is "used to extinguish fires in high valued assets" that cannot be protected with water.

Recommended Action and Justification:
The executive director recommends the initiation of rulemaking and state implementation plan revision to increase the reporting threshold for C6 fluoroketone. In considering reportable quantities, the TCEQ considers toxicological effects, photochemical reactivity for producing ozone, and its intent of limiting upset reports to the most significant events. C6 fluoroketone is neither a criteria pollutant nor precursor of ozone, and therefore the 100-pound default for nonattainment and maintenance areas should not apply.

No signs of acute toxicity were observed in rats exposed to 100,000 parts per million (ppm) C6 fluoroketone for up to four hours. The "no observed adverse effect" level for acute toxicity in rats was 100,000 ppm or 10%. Other toxicity studies have concluded that C6 fluoroketone is only minimally irritating to the eye, non-irritating to the skin, and does not cause sensitization. There have been no complaints of adverse health effects from human experience with exposures to C6 fluoroketone. C6 fluoroketone is safe to the public when discharged in the event of a fire. C6 fluoroketone was approved by the United States Environmental Protection Agency in 2002 (67 Federal Register 77931) as an acceptable substitute for ozone-depleting substances, such as halon 1301, for use in fire suppression.

Re: Docket No. 2013-0700-RUL

Applicable Law:

- Texas Government Code, §2001.021, which establishes the procedures by which an interested person may petition a state agency for the adoption of a rule
- 30 TAC, §20.15, which provides such procedures specific to the commission
- 30 TAC, §101.1(88) Texas Clean Air Act, Texas Health and Safety Code, §§382.011, 382.012, 382.016, 382.017, 382.021, and 382.0215

Agency contacts:

Candice Garrett, Rule Project Manager, 512-239-1457
Amy Browning, Staff Attorney, 512-239-0891
Bruce McAnally, Texas Register Coordinator, 512-239-2141

Attachment

Petition

Re: Docket No. 2013-0700-RUL

cc: Chief Clerk, 2 copies
Executive Director's Office
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March 8, 2013

3M

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APR 01 2013
EXECUTIVE DIRECTOR

Mr. Zak Covar, Executive Director
Texas Commission on Environmental Quality
12100 Park 35 Circle, Building F
Austin, TX 78753

Subject: Petition for Adoption of Rules

Dear Director Covar,

In accordance with Texas Administrative Code, Title 30, Part 1, Chapter 20, Rule § 20.15 Petition for Adoption of Rules, the 3M Company respectfully petitions for an addition to Texas Commission on Environmental Quality Rules, Chapter 101 – General Air Quality Rules, Subchapter A: General Rules § 101.1 Definitions, (88) Reportable Quantity (RQ), (A)(i)(III).

According to (88)(A)(ii), the default RQ for individual air contaminant compounds released into the environment is 100 pounds unless a different reportable quantity for a specific chemical or category of chemicals is stated in (88)(A)(i)(I) 40 CFR Part 302, Table 302.4, or (88)(A)(i)(II) 40 CFR Part 355 Appendix A, or (88)(A)(i)(III). The chemical being addressed in this petition is not listed in 40 CFR Part 302 or Part 355 and, since it is not listed in (88)(A)(i)(III), by default the petition chemical then would have a RQ of 100 pounds if released to the environment in the state of Texas.

3M Company manufactures and sells the following petition chemical substance:

3-Pentanone, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-, CAS No. 756-13-8
ASHRAE nomenclature: FK-5-1-12
Synonym: C6 fluoroketone,

This chemical is sold globally as 3M™ Novec™ 1230 Fire Protection Fluid. Novec 1230 fluid is used to extinguish fires in high valued assets such as computer rooms, data centers, control rooms, telecommunications centers and archival storage (please note the accompanying article on use of Novec 1230 at The Daughters of the Republic of Texas library at the Alamo). These are all assets that cannot be protected with water because water would destroy the contents of the enclosure. Novec 1230 fluid can be used in these applications because it is very low in toxicity, does not conduct electricity, and acts as a gas, leaving no residue behind. The industry refers to an agent with these properties as a "clean agent." These agents don't protect entire buildings but, rather, they are installed only in the enclosure that is being protected and only

discharged in the event of a fire. The obvious intent is to never discharge the system except in the event of an emergency. System size will vary dependent on the size of room being protected. A 5000 pound system is a relatively large fire suppression system.

Novec 1230 fluid was approved by the U.S. Environmental Protection Agency's Significant New Alternatives Policy (SNAP) Program in 2002 as a halon replacement and has been sold commercially since 2003. At this point, approximately 25,000 systems have been installed globally. Not only has this chemical proven to be an excellent fire protection medium but, as compared to other clean agent fire suppressants, it offers several unique environmental advantages including:

- Zero ozone depletion potential (ODP)
- Global Warming Potential (GWP) = 1 (2007, IPCC, 100 year ITH)
- Atmospheric lifetime of approximately 5 days

In its approval of Novec 1230 fluid, the U.S. EPA noted,

"EPA has reviewed the potential environmental impacts of this substitute and has concluded that, by comparison to halon 1301 and other acceptable substitutes, C6-perfluoroketone significantly reduces overall risk to the environment. With no ozone-depletion potential, a global warming potential value of less than 100, and an atmospheric lifetime of less than three days, C6-perfluoroketone provides an improvement over use of halon 1301, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) in fire protection. We find that C6-perfluoroketone is acceptable because it reduces overall risk to public health and the environment in the end use listed."

Federal Register Dec. 20, 2002

3M developed Novec 1230 fluid as a replacement product for halons and HFCs in fire suppression. Halon has been phased out of production because of its potent ozone depletion potential. Hydrofluorocarbons (HFCs) currently sold into fire suppression such as HFC-227ea , HFC-125 and HFC-23, are some of the most potent greenhouse gases known. The climate impact of these gases is more than 3000 times greater than CO2. The accelerating concentration of HFC-227ea in the atmosphere was acknowledged in 2010 by Laube, et al (reference included) and the Montreal Protocol Scientific Assessment Panel has acknowledged that the fire suppression sector is the dominant sector for use of HFC-227ea. These HFCs are targeted under a proposal by the European Union that would ban their use or phase down their production starting in 2015. Similar proposals made under the Montreal Protocol would also phase down their production globally. The fire suppression market is quickly moving to substitute materials such as Novec 1230 fluid that enable greenhouse gas emissions to be reduced by more than 99 % from this sector.

Clean agents are used in areas that may be occupied so agent safety is also an important issue. Of those agents listed in NFPA 2001 (2012), Novec 1230 fluid provides the largest margin of safety. Furthermore, in new building construction, use of Novec 1230 in new fire suppression systems is consistent with LEED certification requirements.

Per Rule § 20.15, our proposed text to be added to § 101.1 Definitions, (88) Reportable Quantity (RQ), (A)(i)(III), would be: '**3-pentanone, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)- (FK-5-1-12) - 5,000 pounds;**' It is noted that the names of chemicals in the (88)(A)(i)(III) list are preceded by a letter in parentheses, e.g., (-a-); the appropriate designation

for this new addition is left to TCEQ's discretion although, based on the current list, the most likely designation would appear to be **(-aaa-)**.

Per Rule § 20.15, Texas Government Code § 2001.021 establishes the procedure by which an interested party may petition a state agency for the adoption of a rule and 30 TAC § 20.15 provides such procedures specific to TCEQ.

Rule § 20.15 also requires, 'each petition shall include an allegation of injury or inequity that could result from the failure to adopt the proposed rule.'

The inequity results from the fact that the HFCs listed above have reportable quantities of 5000 pounds meaning that their release from most fire suppression systems would not require reporting. The reportable quantity for Novec 1230 fluid, by default, is 100 pounds. The disparity in these reportable quantities is driving decisions in the market. The requirement to report the discharge of a fire suppression system is enough to drive the Texas market to use potent greenhouse gases rather than replacement technology. In effect, the regulation is currently encouraging the use of potent greenhouse gases where sustainable alternative technologies are available.

The agents referred to above are listed as follows in (88)(A)(i)(III), along with their known GWP and atmospheric lifetimes (Atm.Lf.):

(-y-) 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea): GWP = 3220, Atm.Lf. = 34 years

(-ii-) pentafluoroethane (HFC-125): GWP = 3500, Atm. Lf. = 29 years

(-yy-) trifluoromethane (HFC-23): GWP = 14800, Atm. Lf = 270 years

Accompanying this letter are several documents in support of the petition chemical including:

- 3M Novec 1230 Fire Protection Fluid Product Information
- 3M Novec 1230 Fire Protection Fluid: Environmental Properties of Novec 1230
- 3M Novec 1230 Fire Protection Fluid Safety Assessment
- 3M Novec 1230 Fire Protection Fluid: BP Chooses Novec 1230 Fluid for Fire Protection
- 3M Novec 1230 Fire Protection Fluid Protects the Alamo at The Daughters of The Republic of Texas Library
- Accelerating growth of HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) in the atmosphere, J.C. Laube, et al., Atmos. Chem. Phys., 2010, 10, 5903 - 5910.
- Atmospheric Degradation of Perfluoro-2-methyl-3-pentanone: Photolysis, Hydrolysis, and Hydration, S.A. Mabury, et al., Environ. Sci. Technol., 2011, 45 (19), 8030 - 8036.
- Atmospheric Chemistry of C2F5C(O)CF(CF3)2: Photolysis and Reaction with Cl Atoms, OH Radicals, and Ozone, N. Taniguchi and T. J. Wallington, et al., J. Phys. Chem. A, 2003, 107, 2674 - 2679.
- Photolysis Study of Perfluoro-2-methyl-3-pentanone under Natural Light Conditions, C.J. Nielsen, et al., Environ. Sci. Technol., 2005, 39, 8708 - 8711.
- The large contribution of projected HFC emissions to future climate forcing, G.J.M. Velders and M. McFarland, et al., Proc. Nat. Acad. Sci., 2006, 106 (27), 10949 - 10954.

- European Commission, Press Release, Climate action: Commission proposes significant reduction in emissions of climate-warming fluorinated gases, Nov, 7, 2012
- Proposed amendment to the Montreal Protocol, HFC Phasedown Amendment Proposal, United Nations Environment Programme, May 10, 2012

For any additional information, studies, clarifications, etc., please contact 3M's chemical regulatory representative for the petition chemical:

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In summary, 3M requests amendment to General Rules § 101.1 Definitions, (88) Reportable Quantity (RQ), (A)(i)(III) that would establish a RQ of 5000 pounds for Novec 1230 Fluid.

Sincerely,

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G. Giacoletto

3M™ Novec™ 1230 Fire Protection Fluid

Introduction

3M™ Novec™ 1230 Fire Protection Fluid is a next-generation halon alternative offering outstanding performance, large margin of safety, and an excellent environmental profile.

- Zero ozone depletion potential
- 5-day atmospheric lifetime
- A global warming potential of 1
- A large margin of safety for occupied spaces

Novec 1230 Fire Protection Fluid is based on a proprietary chemical from 3M called a fluoroketone. The full chemical name for this compound is dodecafluoro-2-methylpentan-3-one. Its ASHRAE nomenclature – the way it is designated in the NFPA 2001 and ISO 14520 clean agent standards – is FK-5-1-12.

Novec 1230 fluid offers a unique combination of safety, low environmental impact and extinguishing performance, making it the first chemical halon replacement to offer a viable, long-term, sustainable technology for special hazards fire protection.

Physical Properties

Novec 1230 fluid is applied as a gas, but is liquid at room temperature. It is electrically non-conducting in both the liquid and gaseous state. The breakdown voltage of Novec 1230 fluid vapor under saturated conditions at 1 atm, 21°C over a 2.7 mm electrode gap is 15.6 kV, nearly 2.3 times that of dry nitrogen. The breakdown voltage of liquid Novec 1230 fluid under the same conditions is 48 kV.

The properties of Novec 1230 fluid are similar to many of the first generation halon alternatives with one primary exception – this compound is a liquid at ambient conditions. The boiling point of Novec 1230 fluid is 49.2°C, meaning this product has a much lower vapor pressure than other clean agents, which are gases at ambient conditions.

Novec 1230 fluid has a very low heat of vaporization, approximately 25 times less than that of water. This, along with a higher vapor pressure, causes Novec 1230 fluid to evaporate more than 50 times faster than water. This allows the agent to transition from a liquid to a gaseous state very rapidly when discharged through a nozzle. In a properly designed system, Novec 1230 fluid will rapidly vaporize and evenly distribute throughout the protected space.

Properties Description

Not for specification purposes. All values @ 25°C (77°F) unless otherwise specified.

Not for specification purposes. All values @ 25°C (77°F) unless otherwise specified.

Properties	Novec™ 1230 Fluid
Chemical Formula	$CF_3CF_2C(O)CF(CF_3)_2$
Molecular Weight	316.04
Boiling Point @ 1 atm	49.2°C (120.6°F)
Freezing Point	-108.0°C (-162.4°F)
Critical Temperature	168.7°C (335.6°F)
Critical Pressure	18.65 bar (270.44 psi)
Critical Volume	494.5 cc/mole (0.0251 ft^3/lbm)
Critical Density	639.1 kg/m^3 (39.91 lbm/ft^3)
Density, Sat. Liquid	1.60 g/ml (99.9 lbm/ft^3)
Density, Gas @ 1 atm	0.0136 g/ml (0.851 lbm/ft^3)
Specific Volume, Gas @ 1 atm	0.0733 m^3/kg (1.175 ft^3/lb)
Specific Heat, Liquid	1.103 kJ/kg°C (0.2634 BTU/lb°F)
Specific Heat, Vapor @ 1 atm	0.891 kJ/kg°C (0.2127 BTU/lb°F)
Heat of Vaporization @ boiling point	88.0 kJ/kg (37.9 BTU/lb)
Liquid Viscosity @ 0°C/25°C	0.56/0.39 centistokes
Vapor Pressure	0.404 bar (5.85 psig)
Relative Dielectric Strength, 1 atm (N_2=1.0)	2.3

3M

Physical Properties (continued)

Although 3M™ Novec™ 1230 Fire Protection Fluid is a liquid at room temperature, its vapor pressure is sufficient for the agent to readily achieve vapor extinguishing concentrations in air. At 25°C, one could form vapor concentrations with Novec 1230 fluid up to 39 volume percent prior to reaching saturation. Typical fire suppression design concentrations for most applications are in the range of 4 to 6 percent by volume of the protected space. That large differential between design and saturation concentrations dictates that condensation of vapor will not occur.

Design Concentrations

Minimum design concentration based upon cup burner results × 1.3

Flammable Liquid	Design Concentration (vol%)
Acetone	5.6
Ethyl alcohol	7.2
n-heptane	5.9
Technical heptane	5.6
Diesel fuel	4.5
Methanol	8.5
Methyl ethyl ketone	5.9

Like other halocarbon halon alternatives, Novec 1230 fluid extinguishes principally by removing heat from the fire. Upon discharge, Novec 1230 fluid creates a gaseous mixture with air. This agent/air mixture has a heat capacity much larger than that of air alone. A higher heat capacity means that this gas mixture will absorb more energy (heat) for each degree of temperature change it experiences. At the system design concentration, the agent/air mixture absorbs sufficient heat to upset the conditions required for combustion to occur. The amount of heat the fire loses to the surroundings is increased by the presence of the agent. This causes the combustion zone to cool to the point that the fire extinguishes. Novec 1230 fluid has the highest heat capacity of the commercially available halon alternatives resulting in the lowest extinguishing concentrations for a given fuel. The design concentration for Class A fuels is a minimum of 4.2 vol% for designs based on UL 2166 in the USA. Different design concentrations may be required in other countries based on local approvals.

Typical Applications

Novec 1230 fluid can effectively be applied in total and localized flooding, inerting and explosion suppression applications in the following areas:

- Data Processing Centers
  - Computer Rooms
  - Data Storage Facilities
- Telecommunications
  - Cellular Sites
  - Switching Centers
- Commercial and Military Aviation
  - Engine protection
- Commercial Marine
  - Control and Paint Rooms
  - Engine Rooms
  - Storage Rooms
- Military Systems
  - Combat Vehicles
  - Marine Engine Rooms
- Oil & Gas Petrochemical Facilities
  - Pumping Facilities
  - Gas Compressor Rooms
  - Offshore Oil Exploration Rigs
- Transportation
  - Merchant Marine Vessels
  - Mass Transit Vehicles
- Recreation
  - Pleasure Craft
  - Race Cars
- Cultural Facilities
  - Museums
  - Libraries
  - Archives
- Medical Facilities
- Manufacturing Facilities
- Storage Areas

Environmental Properties

Once emitted to the environment, there are a number ways for organic compounds to be removed from the atmosphere. Studies conducted on 3M™ Novec™ 1230 Fire Protection Fluid have determined the atmospheric loss rates via these removal mechanisms and the effect on the atmospheric lifetime of this compound. The very low water solubility of Novec 1230 fluid and the low degree to which it partitions into liquid water was found to preclude atmospheric hydrolysis from being a meaningful removal mechanism. The principal atmospheric sink for Novec 1230 agent is photolysis. It exhibits strong absorption of energy at near UV wavelengths, resulting in a very short atmospheric lifetime. The rate of photolysis under atmospheric conditions and the mechanism of decomposition of this compound have been investigated by two different research groups[1,2]. The photolysis rate of the fluoroketone leads to an atmospheric lifetime of approximately 1 week, which is consistent with the 3M study that found the atmospheric lifetime of Novec 1230 fluid to be on the order of 5 days.

Ozone Depletion Potential

Novec 1230 fluid, which contains no chlorine or bromine, has an ozone depletion potential of zero.

Global Warming Potential

The Global Warming Potential (GWP) is an index that provides a relative measure of the possible climate impact due to a compound that acts as a greenhouse gas in the atmosphere. The GWP of a compound, as defined by the Intergovernmental Panel on Climate Change (IPCC), is calculated as the integrated radiative forcing due to the release of 1 kilogram of that compound relative to the warming due to 1 kilogram of CO_2.

The potential for Novec 1230 fluid to have a climate impact is limited by its very short atmospheric lifetime and low global warming potential. The GWP of Novec 1230 fluid is calculated to be 1 or less using the IPCC 2007 method and a 100-year integration time horizon[3], including both the direct effect from the agent as well as the indirect effect from decomposition products. Taniguchi et al.[1] and D'Anna et al.[2] have concluded that "the global warming potential of the compound is negligible."

Potential for Reducing GHG Emissions

The fire protection industry has made considerable progress in reducing emissions from the relatively high levels experienced during the use of halon. However, the high GWP of the HFCs used in these applications combined with their growing installed base results in continually increasing greenhouse gas emissions. A single discharge of an average sized fire protection system containing HFCs is meaningful in itself. Based upon an average sized halon 1301 system containing 200 kg, an equivalent sized system using, for example, HFC-227ea, contains approximately 347 kg of agent. A GWP of 3220 results in CO_2 equivalent emissions of 1,110,000 kg when this HFC agent is discharged. This is equivalent to the emissions from more than 240 typical automobiles in the USA driven for an entire year!

Discharge of a fire protection system using Novec 1230 fluid in place of an HFC extinguishing agent results in significantly reduced greenhouse gas emissions. Due to the dramatically lower GWP, greenhouse gas emissions from discharge of Novec 1230 fluid are reduced by more than 99.9% compared to any of the HFCs used in fire protection. As a result, Novec 1230 fluid is a low GWP alternative that can reduce emissions of greenhouse gases in fire protection applications and help to further the environmental goals of the industry.

Environmental Properties Comparison

Not for specification purposes.

All data other than those for Novec 1230 fluid were compiled from published sources.

Properties	Novec 1230	Halon 1211	Halon 1301	HFC-125	HFC-227ea
Ozone Depletion Potential (ODP)[1]	0.0	4.0	12.0	0.0	0.0
Global Warming Potential–IPCC[2]	1	1890	7140	3500	3220
Atmospheric Lifetime (years)	0.014	16	65	29	34.2
SNAP (Yes/No)	Yes	N/A	N/A	Yes	Yes

[1] World Meteorological Organization (WMO) 1998, Model-Derived Method.
[2] Intergovernmental Panel on Climate Change (IPCC) 2007 Method, 100 Year ITH.

Safety Considerations

The safety of 3M™ Novec™ 1230 Fire Protection Fluid has been thoroughly evaluated through both acute and repeat dose toxicity testing. A full series of toxicological tests has been completed using this compound. In each case, Novec 1230 fluid has been demonstrated to be very low in toxicity and to have a large margin of safety in use as a clean extinguishing agent. Key testing of Novec 1230 fluid was conducted at independent laboratories as shown in the following table.

Toxicity testing results

Properties	Novec 1230
4-hour Acute Inhalation	Practically Non-Toxic (LC_{50} >100,000 ppm)
Cardiac Sensitization	Not a Sensitizer (NOAEL = 100,000 ppm)
Acute Dermal Toxicity	Low Toxicity (LD_{50} >2000 mg/kg)
Ames Assay	Negative
Primary Skin Irritation	Non-Irritating
Primary Eye Irritation	Minimally Irritating
Acute Oral Toxicity	Low Toxicity (LD_{50} >2000 mg/kg)
Skin Sensitization	Not a Skin Sensitizer
28-Day Inhalation Study	NOAEL of this study: 4,000 ppm
Chromosomal Aberration	Negative

The no observable adverse effect level (NOAEL) for any end point of acute toxicity has been determined to be 10 volume percent (100,000 ppmv) in air. With a NOAEL of 10%, there is consensus that Novec 1230 fluid is not only safe for its intended end use but that it provides a large margin of safety relative to the typical design concentrations of fire protection systems. Typical design concentrations in the range of 4.2 to 5.9 volume percent result in safety margins of 69 to 138%.

Thermal Decomposition

Well over 90% of applications involving the use of halocarbons, like 3M™ Novec™ 1230 Fire Protection Fluid, protect Class A assets, including those related to computer and telecommunication facilities. Continuity of operation is paramount, and those types of assets, typically involving electronic switches and circuit boards, cannot tolerate even a relatively modest fire. System design, therefore, must be such that fire size be kept to a minimum.

Levels of HF produced from fires extinguished by Novec 1230 fluid are similar to those involving other physically acting halocarbon agents. Industry practice over the last decade has demonstrated that fire extinguishing systems using halogenated halon alternatives can be designed to minimize thermal decomposition product formation and avoid adding to the potential toxic threat of a fire event (the hazards created by the combustion products of the fire).

Materials Compatibility

Compatibility of "O" Rings with Novec 1230 Fluid

Exposure Time: 1 Week@ 25°C, 100°C

Elastomer Type	Exposure Temperature	Change in Shore A Hardness	% Change in Weight	% Change in Volume
Neoprene	25°C	-1.8	-.06	-1.2
	100°C	-2.2	+2.3	+0.8
Butyl rubber	25°C	-2.7	+0.2	+0.1
	100°C	-4.0	+4.3	+4.2
Fluoroelastomer	25°C	-6.2	+0.7	+0.6
	100°C	-12.6	+9.5	+10.6
EPDM	25°C	-4.7	+0.6	+0.3
	100°C	-5.7	+3.3	+2.4
Silicone	25°C	N/A	+3.1	+2.8
	100°C	-5.4	+6.0	+5.1
Nitrile	25°C	-0.7	-0.3	-0.5
	100°C	+2.5	+4.6	+0.7

Effect of Novec 1230 Fluid on Various Metals

Metals	Effect
Aluminum Alloy 6262 T6511	A
Brass Alloy UNS C36000	A
AISI Type 304L stainless steel	A
AISI Type 316L stainless steel	A
Copper UNS C12200	A
ASTM A 516, Grade 70 carbon steel	A

A. No discoloration or destruction of fluid or metal at temperature indicated, 10 days minimum exposure, 48°C.

3M has extensive data on compatibility with various materials. For more information, contact your local 3M technical service representative.

Regulatory Registries

When commercializing 3M™ Novec™ 1230 Fire Protection Fluid, inclusion of the chemistry on a region's or country's chemical registry was required. For example, in Japan, a chemical must attain METI approval and, in the EU, the ELINCS approval must be in place before a chemical may be imported. Local regulatory approvals and listings on chemical registries of key countries are complete. The following table lists eight of the major chemical registry approvals.

Chemical Registry Approvals

Chemical: dodecafluoro-2-methylpentan-3-one CAS#: 756-13-8

Country/Region	Status
USA (TSCA)	Listed
Canada (CDSL)	Listed
EU (ELINCS):	EC# 436-710-6
Australia (AICS)	Listed
Japan (METI)	METI# (2)-4024
Korea (KECI)	KECI# 2002-3-2022
China (IECSC)	Listed
Philippines (PICCS)	Listed

Additionally, both the German Hygiene Institute and Swiss BUWAL approval have been attained. In the USA, Novec 1230 fluid has been approved by the EPA Significant New Alternatives Policy (SNAP) Program for use as a halon replacement in both total flooding and streaming applications.

Industry Approvals

Fire suppression systems containing Novec 1230 fluid are commercially available globally. Major system listings and approvals, with Novec 1230 fluid as a component, are included in the following table. Component recognitions have been attained from US-based Underwriters Laboratories, Inc. and FM Global, as well as EU-based LPCB, VdS and CNPP. Also, the German Amtliche Prüfstelle has approved systems using Novec 1230 fluid. While approval from the SSL in Australia is complete, other AsiaPac approvals are in progress.

Industry Listings and Approvals

Underwriters Laboratories Inc (ULI)	USA
Underwriters Laboratories CA (ULC)	Canada
FM Global (FM)	USA
Loss Prevention Certification Board (LPCB)	United Kingdom
Scientific Services Laboratories (SSL) Also called Certifire Pty Ltd	Australia
VdS Schadenverhütung (VdS)	Germany
Centre National de Prévention et de Protection (CNPP)	France
Korea Fire Institute(KFI)	Korea

Novec 1230 fluid is included in the 2008 edition of NFPA 2001, Standard on Clean Agent Fire Extinguishing Systems and the 2006 edition of ISO 14520, Gaseous Media Fire Extinguishing Systems. In each standard, it is referenced by the generic ASHRAE nomenclature FK-5-1-12.

For one specific industry, commercial marine, numerous approvals for systems using 3M™ Novec™ 1230 Fire Protection Fluid have been attained globally, and are listed below.

Global marine approvals for Novec 1230 fluid

American Bureau of Shipping (ABS)	International
Australian Maritime Safety Agency	Australia
Bureau Veritas (BV)	France
Canadian Coast Guard	Canada
Danish Maritime Authority (DMA)	Denmark
Det Norske Veritas (DNV)	Norway
Germanischer Lloyd (GL)	Denmark
Icelandic Maritime Administration	Iceland
Inland/Sea going acceptance (BZI)	Belgium
Lloyd's Register of Shipping (LR)	International
Maritime and Coastguard Agency (MCA)	UK
Marine Marchant Approval	France
Nippon Kaiji Kyokai (NK)	Japan
Polish Register of Shipping	Poland
Registro Italiano Navale (RINA)	Italy
Shipping Authority Acceptance – Inland/Sea going	Holland
United States Coast Guard (USCG)	USA
Marine Equipment Directive (MED) Module B	EU

Commercial Availability

Six independent original equipment manufacturers (OEMs) have substantially invested to gain the necessary approvals and to commercialize their total flooding systems with Novec 1230 fluid. They are:

- Firetrace International (USA)
- Minimax (DE)
- Sevo Systems (USA)
- Siemens Systems (CH)
- Tyco Fire & Security (USA)
- UTC Fire & Security (USA)

Total flooding system development has been the near term effort of these companies. All have invested heavily to test their systems against recognized test protocols and commercialize their products. Future development is expected to expand into specialty, military, and aerospace clean agent applications as well as handheld portable extinguishers.

Packaging and Availability

Novec 1230 fluid is currently available in 2425 lb. (1100 kg) intermediate bulk containers (IBCs), 661 lb. (300 kg) drums and 11 lb. (5 kg) glass sample jugs.

A cylinder containing Novec 1230 fluid superpressurized with nitrogen varies less than 150 psi (10 bar) over a temperature range of 250°F (120°C). Also, because it is packaged in IBCs and drums, it can be air freighted without the restrictions of gaseous alternatives.

Resources and Distribution

Novec 1230 fluid is supported by global sales, technical and customer service resources, with technical service laboratories in the U.S., Europe, Japan, Latin America and Southeast Asia. Users benefit from 3M's broad technology base and continuing attention to product development, performance, safety and environmental issues.

Extensive OEM policies and equipment design guidelines have been prepared for system retrofit, installers and equipment manufacturers in support of Novec 1230 fluid.

For additional technical information on Novec 1230 fluid in the United States, or for the name of a local authorized distributor, call 3M Electronics Markets Materials Division, **800 810 8513**.

For other 3M global offices, and information on additional 3M products, visit our web site at **www.3M.com/novec1230fluid**.

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The 3M™ Novec™ Brand Family The Novec brand is the hallmark for a variety of patented 3M products. Although each has its own unique formula and performance properties, all Novec products are designed in common to address the need for safe, effective, sustainable solutions in industry-specific applications. These include precision and electronics cleaning, heat transfer, fire protection, lubricant deposition and several specialty chemical applications.

3M™ Novec™ Engineered Fluids • 3M™ Novec™ Aerosol Cleaners • 3M™ Novec™ 1230 Fire Protection Fluid • 3M™ Novec™ Electronic Coatings • 3M™ Novec™ Electronic Surfactants

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98-0212-3709-8

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Technical Brief

Novec™ 1230
Fire Protection Fluid

Environmental properties of Novec 1230 Fluid

3M™ Novec™ 1230 Fire Protection Fluid was developed as an environmentally responsible extinguishing agent. This total flooding clean agent is the first halogenated halon alternative to address not only the concerns of stratospheric ozone depletion but also those related to climate change (i.e., global warming).

Definitions

When speaking of halogenated compounds, several terms relating to their environmental impact are commonly used. The following provides a brief explanation of what these terms mean.

Ozone Depletion Potential (ODP)—An index that provides a relative measure of the effect a compound has on the stratospheric ozone layer. The halogens bromine and chlorine are known to cause depletion of the ozone layer. Each atom of these halogens can react with thousands of ozone molecules, collectively contributing to a thinning of the ozone layer. The halogen fluorine, however, has been shown to have no effect on the ozone layer. Novec 1230 fluid is a highly fluorinated ketone containing no chlorine or bromine. As a result, the ODP for Novec 1230 fluid is zero, meaning it has no effect on stratospheric ozone.

Global Warming Potential (GWP)— A parameter that provides a relative measure of the possible climate impact due to the presence in the atmosphere of a compound that acts as a greenhouse gas. The two primary characteristics that determine whether a compound will act as a greenhouse gas are absorption of infrared energy and persistence in the atmosphere.

All organic compounds absorb infrared energy. Compounds that contain carbon-fluorine bonds typically exhibit strong infrared absorption. If these compounds are also atmospherically long-lived, the material will have a high GWP. What sets Novec 1230 fluid apart from the first generation of halogenated halon alternatives is its extremely short atmospheric lifetime.

The previous halon replacements are long-lived in the atmosphere–taking tens, hundreds or even thousands of years to degrade after they are emitted. In contrast, Novec 1230 fluid degrades very rapidly when released to the atmosphere. Exposure to natural sunlight causes this material to break up in a matter of several days. However, this unique material remains stable in normal storage conditions as a component of a fire protection system.

How Global Warming Potential is Calculated

The GWP of a compound, as defined by the Intergovernmental Panel on Climate Change (IPCC) [1], is calculated as the integrated radiative forcing due to the release of 1 kilogram of that compound relative to the warming due to 1 kilogram of CO_2 over a specified period of time (the integration time horizon (ITH)):

$$GWP_x = \frac{\int_0^{ITH} F_x C_{xo} \exp(-t/\tau_x)\, dt}{\int_0^{ITH} F_{CO_2}\, C_{CO_2}(t)\, dt}$$

F is the radiative forcing per unit mass of a compound (the change in the flux of radiation through the atmosphere due to the IR absorbance of that compound), C is the atmospheric concentration of a compound, τ is the atmospheric lifetime of a compound, t is time and x is the compound of interest [1].

The commonly accepted ITH used for comparative purposes is 100 years, representing a compromise between short-term effects (20 years) and longer-term effects (500 years or longer). The concentration of an organic compound, x, in the atmosphere is assumed to follow pseudo first order kinetics (i.e., exponential decay). The concentration of CO_2 over that same time interval incorporates a more complex model for the exchange and removal of CO_2 from the atmosphere (the Bern carbon cycle model).

Atmospheric Lifetime of Novec 1230 Fluid

A study conducted by Taniguchi and colleagues [2] examined the atmospheric loss mechanisms for $C_2F_5C(O)CF(CF_3)_2$ commercially known as 3M™ Novec™ 1230 Fire Protection Fluid. The authors of this study determined that this compound does not react with hydroxyl radical (OH) but that substantial decay occurs when exposed to UV radiation. The authors measured the UV cross-section for Novec 1230 fluid, finding a maximum wavelength of absorbance at 306 nm. Because this compound shows significant absorbance at wavelengths above 300 nm, a wavelength higher than that required for UV light to reach the ground, photolysis in the lower atmosphere will be a significant removal mechanism or sink for this compound.

The rate of photolysis under atmospheric conditions and the mechanism of decomposition of this compound were investigated by Taniguchi, et al. The rate of photolysis of Novec 1230 fluid was measured relative to that of Acetaldehyde (CH_3CHO), which has a known atmospheric lifetime by photolysis of 3 to 4 days. The photolysis rate of the Novec 1230 fluid leads to an atmospheric lifetime of 4.5 to 15 days or "approximately 1-2 weeks". The authors of this study have concluded that their work is consistent with a previous study conducted by 3M, which found the atmospheric lifetime of Novec 1230 fluid to be on the order of 5 days or about one week [3].

Impact on Climate Change

The potential for 3M™ Novec™ 1230 fluid to have an impact on the radiative balance in the atmosphere (i.e., climate change) is limited by its very short atmospheric lifetime and low global warming potential. The quantitative IR cross-section of Novec 1230 fluid was measured in accordance with section 4.6 of the U.S. EPA FTIR Protocol [4]. The IR measurements were made with a 0.5 cm-1 spectral resolution at 293K on a MIDAC (Model I2001) FTIR spectrometer, which employs a mercury-cadmium-telluride infrared detector maintained at 77 K. The experimental setup used a nominal 4 m path length, which was calibrated using certified ethylene gas standards.

Using the measured IR cross-section and the method of Pinnock et al. [5] the instantaneous radiative forcing for Novec 1230 fluid is calculated to be 0.50 $Wm^{-2}ppbv^{-1}$. This radiative forcing value and a one-week atmospheric lifetime results in GWP values as shown below using the IPCC 2001 method [1]. The most commonly cited GWP value is that calculated using a 100-year integration time horizon.

Compound	Atmospheric lifetime (years)	Radiative Forcing (Wm-2ppbv-1)	20 year ITH	100 year ITH	500 year ITH
$C_2F_5C(O)CF(CF_3)_2$ Novec 1230 fluid	0.014	0.50	4	1	0

This GWP calculation and the method of Pinnock et al. use the assumption that the compound emitted to the atmosphere will be well mixed throughout the troposphere. A material as short lived as Novec 1230 fluid cannot reasonably meet this condition due to its rapid removal from the atmosphere. As a result, this calculation overestimates the GWP for this compound. For this reason, Taniguchi et al. have concluded that "with an atmospheric lifetime of 1-2 weeks, $CF_3CF_2C(O)CF(CF_3)_2$ will have a global warming potential that, for all practical purposes, is negligible."

Direct vs. Indirect Global Warming Potential

The GWP calculated thus far is the direct GWP, which accounts for the potential warming effects due to the parent compound released to the atmosphere. In some cases, it is possible to calculate an indirect GWP in an attempt to account for the potential warming effects due to the atmospheric degradation products from that compound. While IPCC has indicated that these indirect GWPs are much less certain [1], it is possible to estimate an indirect GWP for Novec 1230 fluid since its atmospheric chemistry is well understood.

The decomposition mechanism determined by Taniguchi et al. indicates Novec 1230 fluid produces fluorinated degradation products, which are atmospherically short-lived [6], resulting in negligible GWP. However, this decomposition mechanism indicates that one mole of Novec 1230 fluid will produce 4 moles of CO_2. Since the direct GWPs are calculated on a mass basis, the indirect GWPs need to be calculated on this basis as well. Therefore, release of 1 kg of Novec 1230 fluid to the atmosphere will produce 0.56 kg of CO_2.

$$1000 \text{ g Novec 1230 fluid}/(316 \text{ g/mol})(4 \text{ mols } CO_2/\text{mol Novec 1230 fluid})(44 \text{ g/mol}) = 556 \text{ g } CO_2$$

This results in an indirect GWP of 0.56, regardless of the time horizon chosen. Therefore, both the direct and indirect GWP for Novec 1230 fluid are less than one. Clearly, compounds with such low GWP are not of concern with respect to potential climate change.

Comparison to other Halocarbons

Highly fluorinated compounds typically have a GWP of 1000 or more, meaning that 1 kg of that compound has the same climate effect as one ton or more of CO_2. For example, the GWPs of HFC-227ea, HFC-125 and HFC-23, all first generation halon replacements, are 3500, 3400 and 12,000, respectively. Due to the exceptionally short atmospheric lifetime of Novec 1230 fluid, its GWP is extremely low – only one, the equivalent to that of CO_2. Such a low GWP is virtually unprecedented for a fluorochemical, making Novec 1230 fluid a unique and sustainable alternative technology to halon and the first generation of replacements.

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Issued: 11/04

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4916(HB)
60-5002-0067-4

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Technical Brief

Novec™ 1230
Fire Protection Fluid

Safety Assessment

The safety of 3M™ Novec™ 1230 Fire Protection Fluid has been investigated with two specific purposes in mind. First, 3M has conducted the necessary toxicity tests to establish the levels to which an individual can be safely exposed upon its release from a fire protection system. Second, 3M has also established the safe level for routine handling of the material during the manufacture of fire protection systems. Dramatic differences exist in the frequency and magnitude of exposure anticipated from these two very distinct scenarios. Exposures from fire protection systems are very high (4-6%) but occur infrequently and exposures during the manufacturing process are very low but occur regularly.

Safety Assessment of Fire Protection Systems

One of the principle concerns for short term, high exposure to volatile fluorochemicals such as halons or HFCs is cardiac sensitization. Cardiac sensitization is one of the first studies conducted on Novec 1230 fluid. The purpose of the cardiac sensitization study is to identify chemicals that sensitize the heart to the effects of endogenous epinephrine and, in doing so, result in potentially fatal arrhythmias. In general, the study involves predosing restrained animals with epinephrine in order to establish a minimal effect using epinephrine alone. This first stage is then followed up with dosing Novec 1230 fluid via inhalation and challenging, again, with epinephrine. The study protocol is conservative in that it calls for dosing with epinephrine at doses far larger than normally present in the heart. The No Effect Level (NOEL) for cardiac sensitization for Novec 1230 fluid was established at 10%.

Other end points of acute toxicity were assessed using a 4 hr. acute inhalation study (rat) at 10%, a 2 hr. acute inhalation study (rat) at 10% and a 28-day inhalation study (rat) at 2.0% No signs of acute toxicity were observed in these studies. On the basis of this information, the No Effect Level (NOEL) for any end-point of acute toxicity for Novec 1230 fluid has been established at 10%.

Safety Assessment for Worker Exposure

The 28-day inhalation study was also used to establish the air concentration to which workers can be safely exposed during routine handling. The No Adverse Effect Level (NOAEL) from the 28-day inhalation study was determined to be 4000 ppm. Traditional methodologies for establishing exposure guidelines for workplace handling require that safety factors be applied to account for uncertainties in the data such as those which exist when extrapolating test results from animal to human. As a result, the 8 hr. time weighted average (TWA) exposure guideline has been established at 150 ppm. This concentration represents the concentration to which workers can be exposed for eight hrs/day, 40 hours/week without suffering adverse health effects.

Additional Background

Other toxicity studies conducted have concluded that Novec 1230 fluid is only minimally irritating to the eye, non-irritating to the skin, does not cause skin sensitization, is not mutagenic in the Ames assay and does not cause chromosomal aberrations in CHO cells.

Novec 1230 fluid is a highly fluorinated chemical with low polarizability, and, therefore, has very low water solubility. Novec 1230 fluid is also extremely volatile with a vapor pressure of 237 mmHg at 20° C. Consequently, insignificant exposure should occur through the skin and most of the material inhaled should be exhaled unchanged. The relatively small fraction

absorbed across the lung-air interface will be hydrolyzed to perfluoropropionic acid and heptafluoropropane. This process likely occurs through physical hydrolysis in biological media rather than through metabolic bioactivation. The perfluoropropionic acid is highly water soluble (5% solutions have been generated) and readily excreted in the urine. Heptafluoropropane is a gas with very low water solubility and, therefore, will be quickly exhaled. Both products of hydrolysis will have a very short half-life in the body.

Anecdotal human experience with exposures in the range of anticipated design concentrations support the observations and conclusions that have been derived from animal studies. There have not been any complaints of adverse health effects from these experiences.

Conclusions

To date, other independent assessments of the toxicity of Novec 1230 fluid include a review by the U.S. EPA, German Hygiene Institute, the U.K. Halon Alternatives Group (HAG) and an independent consulting firm, Environ. In conclusion, there is general consensus that 3M™ Novec™ 1230 Fire Protection Fluid is not only safe for its intended use but provides a large margin of safety relative to anticipated design concentrations of fire protection systems and during the manufacture of those systems.

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Issued: 10/04

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4852(HB)
60-5002-0069-0

3M News

FOR IMMEDIATE RELEASE

3M™ Novec™ 1230 Fire Protection Fluid Protects the Alamo at The Daughters of The Republic of Texas Library

3M Celebrates National Historic Preservation Month

St. Paul, Minn. – May 23, 2011 – In an effort to draw awareness to the importance of preservation, 3M is celebrating National Preservation Month by recognizing efforts by the Daughters of the Republic of Texas Library. 3M innovation is helping to protect a large part of Texas history for educators, students, history scholars and visitors.

Neatly displayed at The Daughters of The Republic of Texas Library, located in the original Alamo compound in San Antonio, are thousands of books, irreplaceable art, photographs, documents and maps representing the cultural heritage of Texas. All pieces of history are being protected by the Ansul® SAPPHIRE® Fire Suppression System utilizing 3M™ Novec™ 1230 Fire Protection Fluid. The Novec 1230 fluid is an advanced clean extinguishing agent used to protect high-value assets such as artifacts, documents, data centers, computers and other critical devices where water cannot be used.

After The Daughters of The Republic of Texas Library suffered an accidental discharge of its outdated fire suppression system, The Daughters began to look for a replacement system that minimizes collateral damage in the event of a fire, is cost-effective, works within existing historical building parameters, and is safe for both people and the environment.

"The library houses many one-of-a-kind pieces representing the cultural heritage of Texas and that are irreplaceable and vital to the education of future generations," said Leslie Stapleton, library director at The Daughters of the Republic of Texas Library. "Fire safety is always a concern in a preservation setting and 3M Novec 1230 fluid is our insurance policy that lets us breathe a little easier."

Novec 1230 fluid is a chemical agent that is stored as a liquid but is discharged as a gas that leaves no residue. The fluid has an exceptional environmental profile with zero ozone depletion potential, an atmospheric lifetime of five days, and a global warming potential of less than one. In addition, the Novec 1230 fluid offers a wide margin of safety and comes with 3M's Blue Sky℠ warranty.

"There is a lot of pending legislation and confusion surrounding continued use of hydrofluorocarbons due to the desire to reduce greenhouse gas emissions in fire suppression," states Joe Ziemba, marketing manager at 3M. "As a result, with Novec 1230 fluid, The Daughters

-more-

of the Republic of Texas and the library staff can be confident their fire suppression system is safe for both people and the environment now and into the foreseeable future."

Novec 1230 fluid is a clean extinguishing agent ideally suited for the protection of libraries, archives and document repositories. It can be discharged in rooms or spaces containing books, precious artwork, artifacts, sensitive electronics and other delicate items without causing harm. Novec 1230 fluid has also found its way into the archives of the Pennsylvania State Library to protect invaluable historical assets of the Benjamin Franklin collection.

The 3M Novec 1230 fluid technology was first developed in the 1990s as replacement fluid for ozone depleting substances. Researchers at 3M developed Novec fluids based on a sustainable technology that balances performance requirements with excellent environmental and worker safety properties. The fluid also offers an opportunity to earn innovation credits toward LEED certification.

Novec technology is also being used in a different application helping visitors at the Smithsonian's National Museum of Natural History view a 330-pound, 24-foot giant squid. The wet specimen is being safely preserved by a 3M Novec Engineered Fluid. The Novec fluid provides a clear view of the specimen, unlike alcohol, which can yellow.

To honor the preservation efforts by The Daughters of The Republic of Texas and other preservation efforts around the country, 3M is contributing to the National Trust for Historic Preservation. For more information regarding 3M Novec products log onto www.3M.com/Novec1230fluid and visit us on Facebook at www.facebook.com/#!/3MNovec1230fluid. For more information on other Novec products visit www.3M.com/Novec.

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Case Study

BP Chooses Novec 1230 Fluid for Fire Protection

Clean extinguishing agents used in modern fire protection systems are more environmentally responsible than those in use a decade or so ago, but some are still causing concern. Kurt Werner, Environmental Affairs Manager at 3M Company, examines their limitations and introduces a new agent that represents an environmentally sustainable technology.

BP, one of the world's biggest energy companies and a committed champion of environmental protection, has selected 3M™ Novec™ 1230 Fire Protection Fluid for use in its prestigious new commodities trading building in Houston, Texas. The selection of this environmentally responsible fire protection product complements the building's achievement of Platinum Certification in the LEED (Leadership in Energy and Environmental Design) scheme operated by the US Green Building Council.

"To protect the valuable assets within the building, we needed an extinguishing agent that was clean, efficient and safe, yet would have minimal environmental impact," said Kevin Westwood, Worldwide Group Fire Advisor for BP. "We looked at many options, including HFCs and even CO_2 but, in the final analysis, Novec 1230 fluid was by far the best match for our selection criteria."

Important issues for BP were the ozone depletion and global warming potentials for the extinguishing agents under consideration. Like the widely used HFCs, Novec 1230 fluid has an ozone depletion potential of zero, but when it comes to a consideration of global warming potentials, the contrast between HFCs and Novec 1230 fluid could hardly be more clear.

The global warming potential of the HFC most widely used in fire protection is 3,220 times that of the most common greenhouse gas, which is CO_2 (2007 IPCC assessment for HFC-227ea). The environmental footprint of HFCs is, therefore, substantial and not in concert with BP's exacting requirements.

In fact, the high global warming potential and atmospheric persistence of HFCs are already leading to concerns about whether their use will continue to be permitted. It is entirely possible that HFCs may follow the halon extinguishing agents that were so popular until the 1980s, by being restricted or even banned.

The first steps toward this can already be seen in the F-Gas Regulations that have recently been introduced in Europe. While these regulations stop short of banning the use of HFCs, they do impose requirements specific to HFCs for technician training, inspections, testing, and reporting.

Measures addressing the use of HFCs are also being drafted in the USA. An early action identified under the California Global Warming Solutions Act of 2006 includes a consideration that, from 2012, all new fire protections systems in California must use an agent with a global warming potential below a minimum threshold level.

The California Air Resources Board (CARB) proposal reflects the regulators' concern that, while emissions from this sector are currently low, emissions are growing quickly and the emission potential of an ever growing installed base represents a significant future liability. The only meaningful way to limit this future liability is to reduce the use of HFCs.

These issues were an important concern for BP since, if restrictions on the use of HFCs were introduced in the future, these would almost certainly mean that a fire protection system based on their use would either have to be replaced in its entirety, or at least very substantially modified. This would involve considerable expense, and a high risk of disrupting the critical operations carried out within the trading building.

The BP team therefore set about comparing the environmental characteristics of HFCs with those of 3M™ Novec™ 1230 Fire Protection Fluid. As already mentioned, Novec 1230 fluid's ozone depletion potential is zero, and its global warming potential is just one – a huge reduction compared with the typical figure of 3,220 for the most common HFC. In addition, the Novec 1230 fluid has an atmospheric lifetime of only five days, compared with about 30 years for HFCs.

The BP team also took into account the toxicity of the agents, as it was possible – although not planned – that an automatically initiated discharge could take place in an area while staff were present. This immediately ruled out the use of CO_2, which is noted for its high toxicity. Once again, Novec 1230 fluid was well clear of the other contenders on this issue.

It has a very wide margin of safety for use in occupied areas, which makes it entirely suitable for areas frequented by staff. "Margin of safety" reflects the difference between the design concentrations necessary to put out a fire and the threshold concentration recognized by approval bodies as suitable for use in occupied spaces. In the BP application, it is used at a concentration of 4.2%, but it is acceptable for use up to 10%. Therefore, its safety margin for this application is 138% - the largest margin for safety for any halon replacement. From the

3M

environmental and life safety standpoints, Novec 1230 fluid met or exceeded all of BP's requirements. These were not the only factors, however, which favored its adoption for this high-profile project.

Unlike most other extinguishing agents, Novec 1230 fluid is stored in bulk as a liquid in non-pressure rated containers, which results in unique benefits in storage and handling; Novec 1230 fluid can safely be stored over a wider range in temperatures and can easily be transported in bulk – even by air. Yet, Novec 1230 fluid is delivered as a gas from a properly designed system, similar to halon systems in the past or other halocarbon systems today.

Further, refilling a system after discharge is much simpler than working with bulk pressurized gas supplies as well as being faster and much more convenient than sending the cylinders off site. Finally, the number of cylinders required for Novec 1230 fluid is fewer, and therefore they occupy significantly less space than cylinders of CO_2 or inert gas.

Novec 1230 fluid is electrically non-conducting, an important consideration for the BP project, where the installation was required to protect electrical and electronic equipment. It is also a clean agent that leaves no residue after a discharge, minimizing the amount of clean up work needed and thereby reducing the time needed to return equipment to service.

Kevin Westwood concludes: "Novec 1230 fluid meets our needs so well that we're already using it in other applications, such as the protection of utility modules in the Alaska North Slope oil field, and to protect cables in our drilling installations in the Caspian Sea. In short, it's an excellent product."

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Environmental Science & Technology

ARTICLE

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Atmospheric Degradation of Perfluoro-2-methyl-3-pentanone: Photolysis, Hydrolysis and Hydration

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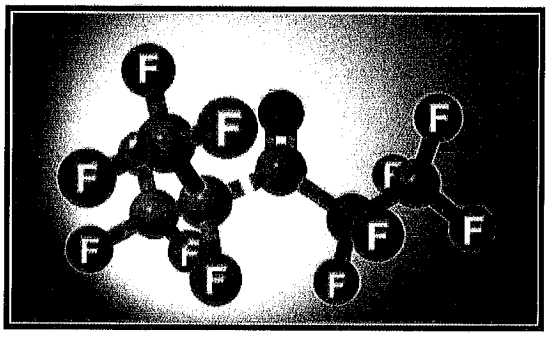
S Supporting Information



ABSTRACT: Perfluorinated carboxylic acids are widely distributed in the environment, including remote regions, but their sources are not well understood. Perfluoropropionic acid (PFPrA, $CF_3CF_2C(O)OH$) has been observed in rainwater but the observed amounts can not be explained by currently known degradation pathways. Smog chamber studies were performed to assess the potential of photolysis of perfluoro-2-methyl-3-pentanone (PFMP, $CF_3CF_2C(O)CF(CF_3)_2$), a commonly used fire-fighting fluid, to contribute to the observed PFPrA loadings. The photolysis of PFMP gives $CF_3CF_2C\cdot(O)$ and $\cdot CF(CF_3)_2$ radicals. A small (0.6%) but discernible yield of PFPrA was observed in smog chamber experiments by liquid chromatography−mass spectrometry offline chamber samples. The Tropospheric Ultraviolet−Visible (TUV) model was used to estimate an atmospheric lifetime of PFMP with respect to photolysis of 4−14 days depending on latitude and time of year. PFMP can undergo hydrolysis to produce PFPrA and CF_3CFHCF_3 (HFC-227ea) in a manner analogous to the Haloform reaction. The rate of hydrolysis was measured using ^{19}F NMR at two different pHs and was too slow to be of importance in the atmosphere. Hydration of PFMP to give a geminal diol was investigated computationally using density functional theory. It was determined that hydration is not an important environmental fate of PFMP. The atmospheric fate of PFMP seems to be direct photolysis which, under low NO_x conditions, gives PFPrA in a small yield. PFMP degradation contributes to, but does not appear to be the major source of, PFPrA observed in rainwater.

■ INTRODUCTION

Perfluorinated carboxylic acids (PFCAs) are ubiquitous in biotic[1] and abiotic environments.[2,3] Longer-chain (>C_8) PFCAs are bioaccumulative[4] and have attracted substantial research interest. Precipitation measurements by Scott et al.[3] have demonstrated that short-chain PFCAs, notably trifluoroacetic acid (TFA) and perfluoropropionic acid (PFPrA), dominate the PFCA profile. Although these smaller compounds are not expected to bioaccumulate and are not believed to represent a threat to ecosystems, their source is unclear and requires study. Thermolysis of fluoropolymers has been suggested as a potential source of TFA observed in rainwater.[5] Other sources of TFA include the atmospheric oxidation of hydrofluorocarbons[6,7] and polyfluorinated compounds.[8,9] Small yields of PFPrA have been proposed from thermolysis of fluoropolymers and atmospheric oxidation of fluorotelomer alcohols[5,8,9] but do not explain the levels of PFPrA observed in precipitation.

Perfluoro-2-methyl-3-pentanone (PFMP) is a fire protection fluid, marketed as Novec 1230 by 3M. It is a replacement for chlorofluorocarbons (CFCs) and Halons, which deplete stratospheric ozone. The atmospheric lifetime of PFMP from previous work seems to be determined by photolysis and is approximately 1 week.[10,11] PFMP does not contribute to stratospheric ozone depletion and has a negligible global warming potential.[10,11] The major photolysis products are $CF_3C(O)F$ and COF_2.[10] The atmospheric fate of $CF_3C(O)F$ is hydrolysis to yield TFA. It is possible that chemistry in remote environments following the photolysis of PFMP would give small yields of PFPrA or isoperfluorobutanoic acid (*i*-PFBA) via reactions of the corresponding perfluoroacyl radicals with HO_2 radicals.[12,13]

In addition to photolysis, hydration or abiotic hydrolysis may be a significant sink of PFMP in the environment. In the hydration reaction, PFMP would react either reversibly or irreversibly with water to form a geminal diol which would shut down the photolysis pathway. Ketones are typically unreactive toward hydrolysis because the leaving group after nucleophilic attack is an aliphatic carbanion. Carbanions are highly basic and are not good leaving groups. However, hydrolysis of PFMP gives

Special Issue: Perfluoroalkyl Acid

Received: December 28, 2010
Accepted: March 25, 2011
Revised: March 15, 2011

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a perfluorinated carbanion which, because the fluorine atoms stabilize the departing carbanion through hyperconjugation, is a much better leaving group. This effect is the basis of the well-known Haloform reaction, one of the oldest organic reactions known.[14]

Applying the Haloform reaction mechanism to hydrolysis of PFMP should give PFPrA and CF_3CFHCF_3 (HFC-227ea). HFC-227ea is a long-lived greenhouse gas and its formation would be problematic. A detailed understanding of the rate and products of PFMP hydrolysis under environmentally relevant conditions is clearly desirable.

The present work had three goals: (i) to confirm the rate of atmospheric photolysis of PFMP and to investigate the possible formation of PFPrA, (ii) to determine whether hydrolysis of PFMP is of significance in the environment, and (iii) to investigate whether hydration is an environmental fate of PFMP.

■ EXPERIMENTAL DETAILS

Measurements of UV Spectra and Calculations of Photolysis Rates. UV spectra of PFMP in the region 200−400 nm were recorded in a 6-cm cell using a Perkin-Elmer UV/vis spectrometer with a resolution of 1 nm, a slit width of 0.25 nm, and a scan speed of 15 nm min^{-1}. Photolysis rates were estimated using the Tropospheric Ultraviolet−Visible (TUV 4.2) package.[15] All rates were calculated for 0.5 km above the surface. The quantum yield was assumed to be 0.043, as measured by D'Anna et al.[11]

Smog Chamber Methods. Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The reactor was surrounded by 10 fluorescent blacklamps (GE F15T8-BL, maximum emission 360 nm) and 12 sunlamps (GE-FS40, maximum emission 310 nm), which were used to photolyze PFMP. The spectral overlap of the emission of blacklamps and sunlamps and the absorption by PFMP has been discussed by Taniguichi et al.[10] All reagents were obtained from commercial sources. Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27 m. Photolysis experiments were performed using mixtures containing 0.49−0.62 Torr of PFMP in 50 Torr of oxygen. We chose a diluent pressure of 50 Torr for the photolysis experiments as Taniguichi et al.[10] have established that the photolysis proceeds more rapidly at lower total pressures. After photolysis the reaction mixtures were pressurized to 750 Torr with air and sampled as described below.

The experimental conditions employed in the smog chamber experiments (296 K, 50 Torr total pressure of O_2 diluent, in the absence of water vapor, NO_x, and other important atmospheric constituents) are not the same as the range of conditions in the real atmosphere. However, the chemical processes studied in the chamber are very similar to those which will occur in the real atmosphere. Photolysis of PFMP in the chamber will occur via the same mechanism, the fate of the radicals formed (decomposition and addition of O_2) will be similar, and subsequent reactions of the peroxy radicals are similar to those in the real atmosphere. Hence, the results from such smog chamber experiments shed important light on the behavior of PFMP in the real atmosphere.

Offline Sample Collection and Analysis. Offline samples were collected by bubbling approximately 5 L of chamber air through 10 mL of sodium carbonate solution (pH 11) after dilution of the chamber contents with air (P_T = 750 Torr). Triplicate samples were collected following 45 min of irradiation. Sodium carbonate solutions were acidified to pH 4 using HCl and analyzed using a Waters 616 LC pump and 600 controller with detection by a Micromass Quattro Micro MS/MS detector. Analytes were separated on a Genesis C8 column (2.1 mm × 50 mm × 4 μm) using a 5-min isocratic run of 40% methanol and 60% water, both containing 10 mM ammonium acetate. Triplicate 10 μL injections were made using a Waters 717 autosampler. PFCAs were analyzed using a cone voltage of 17 V and collision energy of 9 eV and the following transitions were monitored: PFBA 213 > 169, PFPrA 163 > 119, and TFA 113 > 69. Analytes were quantified using external calibration.

Hydrolysis Kinetic Experiments. To quantify the rate of PFMP hydrolysis and identify the final products of hydrolysis, ^{19}F NMR was used. The rates of hydrolysis were measured at pH values of 5.6 anad 8.5 to simulate the upper and lower boundaries of realistic environmental pH conditions. To achieve this, either 50 mM potassium hydrogen phthalate (pH 5.6) or 50 mM sodium borate (pH 8.5) buffer was used. A Varian 400 spectrometer equipped with an ATB8123-400 autoswitchable probe tuned to ^{19}F (376.14 MHz) was used. Reaction solutions were composed of 600 μL of buffer solution and 200 μL of D_2O in a 5-mm NMR tube. Immediately prior to sample insertion, 20 μL of PFMP was added to the NMR tube followed by inversion. Reaction kinetics were followed by acquiring NMR spectra using a preacquisition delay program such that one complete spectrum was obtained every 20−30 min. Each spectrum consisted of 12 scans with an acquisition time of 1 s. To ensure quantitive results, a standard of PFPrA under the same reaction conditions as PFMP hydrolysis was subject to a pulse inversion−recovery T_1 relaxation experiment to determine a suitable relaxation delay time for PFMP. In this case, a delay time of 20 s for PFMP was chosen. After acquisition, data analysis was performed using the VnmrJ software (Agilent Technologies) as it possesses a built-in kinetic analysis module. Each arrayed spectrum was Fourier transformed with a line broadening apodization of 6 Hz to improve its signal-to-noise ratio. Kinetic data were obtained by fitting an exponential growth or decay function to the fluorinated signals in the NMR spectra (see Figure S5, Supporting Information). All hydrolysis experiments were performed at 25 °C.

Computational Method. Calculations to determine the significance of PFMP hydration were performed using the *Gaussian 03* program[16] with the WebMO interface. All computations were performed using Density Functional Theory (DFT) with B3LYP functionals using the 6-311G(d,p) basis set. Computations were carried out for both the gas phase and the aqueous phase using a polarizable continuum solvent model (PCM).[17] Equilibrium constants for hydration were computed using the relative method of Gomez-Bombarelli et al.[18] and using a training set calibration of fluoroacetone, trifluoroacetone, and hexafluoroacetone (see SI for details).

Reagents. All chemicals were used as received. PFMP was purchased from Synquest Laboratories (Alachua, FL). Disodium tetraborate and potassium hydrogen phthalate were purchased from BDH (Toronto, ON). Trifluoroacetic acid and heptafluoropropionic acid (PFPrA) were purchased from Sigma-Aldrich (Oakville, ON).

Table 1. Kinetic Data for PFMP Degradation via Photolysis and Hydrolysis ($N = 2$) at Two Different pH Values (For Complete Photolysis Data, Refer to the SI)

mechanism	conditions	rate constant k (s^{-1})	lifetime τ (hours)
photolysis	45° N June 21	3.5×10^{-6a}	79.4
photolysis	45° N December 21	5.9×10^{-7a}	471
photolysis	45° N March 21/Sept 21	2.1×10^{-6a}	132
hydrolysis	pH 5.6	$1.9 \times 10^{-4} \pm 1 \times 10^{-5b}$	1.5 ± 0.1
hydrolysis	pH 8.5	$3.1 \times 10^{-4} \pm 3 \times 10^{-5b}$	0.9 ± 0.1

[a] Averaged 24 h rate constant. [b] Pseudo-first-order rate constant.

■ RESULTS AND DISCUSSION

Photolysis Kinetics. Photolysis lifetimes of PFMP have been determined experimentally in two studies, yielding lifetimes of approximately 1−2 weeks[10] and 1 week.[11] Using the flux conditions and quantum yield (0.043) previously described,[11] and the UV spectrum measured in this study (see SI), photolysis rates for PFMP were estimated. The photolysis rates, presented in Table 1, agree to within a factor of 2 with those reported in previous studies as well as previous measurements of the UV spectrum.[10,11] The 24-h averaged rate constants for photolysis of PFMP for different latitudes are given in the SI. Annual averaged photolytic rate constants (J) ranged from 3.1×10^{-6} to 8.2×10^{-7} s^{-1} corresponding to lifetimes of 4−14 days depending on latitude and time of year.

Photolytic Production of PFCAs under Low NO_x Conditions. Offline samples were taken to determine if photolytic degradation of PFMP could yield PFCAs. The formation of PFCAs in the chamber is only expected under low-NO_x conditions in the presence of HO_2 radicals. Material was not added specifically for the purpose of forming HO_2 radicals, but it is likely that HO_2 radicals are present in small quantities in all chamber experiments because of hydrocarbon residue on the walls of the chamber (the chamber has been used at Ford for many years to study hydrocarbon oxidation mechanisms). Large initial concentrations of PFMP (520 mTorr) were used in the smog chamber to facilitate detection of small yields of PFCAs.

Photolysis of PFMP can generate two different perfluoroacyl radicals:

$$CF_3CF_2C(O)CF(CF_3)_2 + h\nu \rightarrow CF_3CF_2\cdot + \cdot C(O)CF(CF_3)_2 \quad (1)$$

$$CF_3CF_2C(O)CF(CF_3)_2 + h\nu \rightarrow CF_3CF_2C\cdot(O) + \cdot CF(CF_3)_2 \quad (2)$$

Perfluoroacyl radicals either decompose via elimination of CO or add O_2 to give perfluoroacyl peroxy radicals. In low-NO_x environments, perfluoroacyl peroxy radicals can react with HO_2 to give PFCAs:[12]

$$CF_3(CF_2)_xC\cdot(O) + O_2 \rightarrow CF_3(CF_2)_xC(O)OO\cdot \quad (3)$$

$$CF_3(CF_2)_xC(O)OO\cdot + HO_2 \rightarrow CF_3(CF_2)_xC(O)OH + O_3 \quad (4)$$

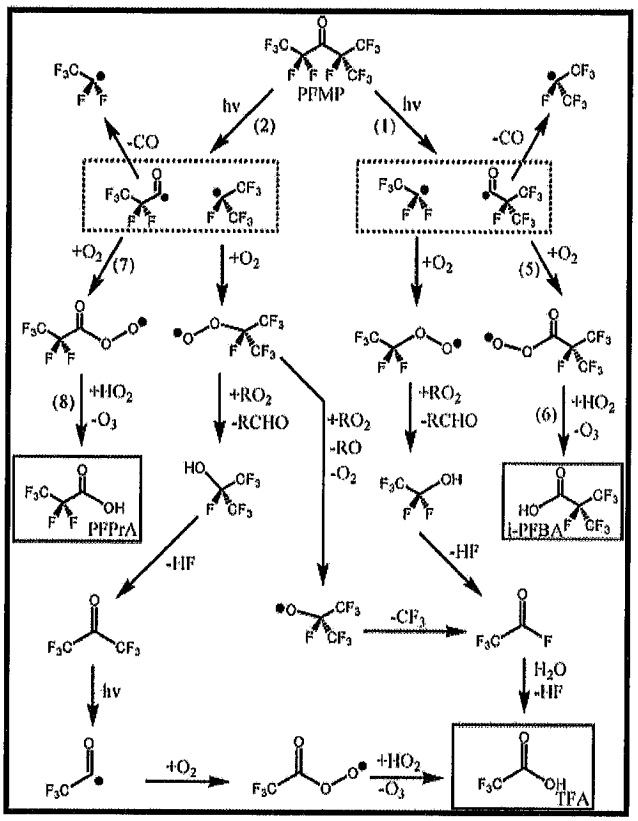

Figure 1. Proposed mechanistic pathways leading to the formation of PFCAs after photolysis of PFMP in the absence of NO_x. Reaction numbers from the text are given in parentheses. Compounds in black boxes represent stable degradation products observed experimentally. Compounds in red boxes represent stable degradation products that were predicted but not observed.

The perfluoroacyl radicals derived from the photolysis of PFMP can react to give *i*-PFBA or PFPrA as follows:

$$(CF_3)_2CFC\cdot(O) + O_2 \rightarrow (CF_3)_2CFC(O)OO\cdot \quad (5)$$

$$(CF_3)_2CFC(O)OO\cdot + HO_2 \rightarrow (CF_3)_2CFC(O)OH\ (i\text{-PFBA}) + O_3 \quad (6)$$

$$CF_3CF_2C\cdot(O) + O_2 \rightarrow CF_3CF_2C(O)OO\cdot \quad (7)$$

$$CF_3CF_2C(O)OO\cdot + HO_2 \rightarrow CF_3CF_2C(O)OH\ (PFPrA) + O_3 \quad (8)$$

PFPrA was observed in offline samples taken after 45 min of irradiation, at a concentration of 0.061 mTorr. *i*-PFBA was not detected in any of the samples.

The high concentrations of PFMP used in the experiments saturated the FTIR signal and a direct determination of the amount of PFMP photolyzed was not possible. The amount of PFMP lost via photolysis was estimated from the photolysis half-life (determined to be 26 h by the observed formation of $CF_3C(O)F$ as discussed previously[10]) in the chamber conditions. We estimate that 10.4 mTorr of PFMP was photolyzed after 45 min and hence the yield of PFPrA is 0.6%. The low PFPrA yield observed in this experiment probably reflects the low level of

HO_2 radicals available in the system. Sulbaek Andersen et al.[19] reported that the yield of PFPrA from $CF_3CF_2C\cdot(O)$ via reactions 7 and 8 was 24 ± 4%. Similarly, the yield of *n*-PFBA in reactions analogous to 5 and 6 was shown to be 10 ± 2%.[12] We expect the yield of *i*-PFBA following formation of $(CF_3)_2CFC\cdot(O)$ radicals in an excess of HO_2 radicals to be similar to that reported for *n*-PFBA. The low yield of PFPrA observed in the present experiments suggests either that the yield of $CF_3CF_2C\cdot(O)$ radicals in the photolysis of PFMP is low, or that the concentration of HO_2 radicals in the channel is low and conversion of $CF_3CF_2C\cdot(O)$ radicals into PFPrA is inefficient. The absence of any discernible formation of *i*-PFBA suggests the latter explanation is more probable. Figure 1 illustrates some mechanistic pathways leading to PFCAs following photolysis of PFMP in the absence of NO_x. Note, as indicated in Figure 1, decomposition via elimination of CO is a significant fate of $CF_3CF_2C\cdot(O)$ radicals.[13]

The presence of PFPrA and the absence of *i*-PFBA suggests reaction 2 is favored over reaction 1. This observation was surprising given the perfluoroisopropyl radical is less stable than the perfluoroethyl radical. In the perfluoroethyl radical, two fluorine atoms are able to donate electron density from their lone pair orbitals into the singly occupied p orbital on the radical center, resulting in stabilization. Because the experimental results suggest this is happening, it is proposed that the stabilities of the corresponding perfluoroacyl radicals must allow this observed regioselectivity to occur.

Hydrolysis Kinetics. The hydrolysis reaction of PFMP can proceed by the well-known Haloform reaction mechanism in which a ketone with a suitable alkyl leaving group reacts with water to form a carboxylate and an alkane.

In a typical Haloform reaction, a methyl ketone is tri-iodinated followed by treatment with base to produce a carboxylic acid and iodoform which precipitates as a yellow solid. This reaction is the classic qualitative test for a methyl ketone. The following steps mechanistically describe the Haloform reaction:

$$RC(O)CX_3 + OH^- \rightarrow RC(O^-)(OH)CX_3 \qquad (9)$$

$$RC(O^-)(OH)CX_3 \rightarrow RC(O)(OH) + CX_3^- \qquad (10)$$

$$RC(O)(OH) + CX_3^- \rightarrow RC(O)(O^-) + CHX_3 \qquad (11)$$

where X = Cl/Br/I.

The final step in the Haloform reaction is a rapid and exothermic proton transfer from the carboxylic acid to the carbanion which makes the whole process irreversible. The overall mechanism of the reaction is $B_{AC}2$ which consists of separate addition and elimination steps via a tetrahedral intermediate. The rate determining step is reaction 9. The final two products expected from PFMP hydrolysis are PFPrA and HFC-227ea. The mechanism for hydrolysis of PFMP is shown in Figure 2.

The hydrolysis of PFMP and the detection of both products has been reported by Saloutina et al.[20] however this study was performed at pH values much higher than those relevant for the environment. The objective of the present study was to investigate whether PFMP could undergo hydrolysis at pH values more typical of those found in the environment. The two pH values chosen were 5.6 and 8.5 because pH 5.6 is typical of atmospheric water.[21] A pH of 8.5 was also chosen to represent the upper environmental limit where hydrolysis would likely be the fastest since the Haloform reaction is base catalyzed.

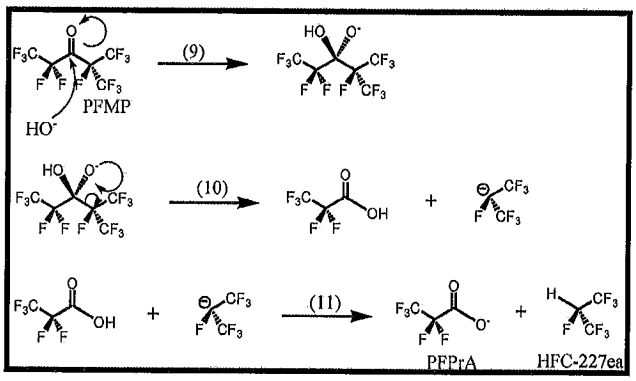

Figure 2. Hydrolysis mechanism of PFMP to produce PFPrA and HFC-227ea under mildly basic conditions. Reaction numbers in the text are given in parentheses.

To measure the kinetics of PFMP degradation, an analytical method to quantify PFMP is required. Liquid chromatography is not suitable to analyze PFMP because authentic standards would rapidly degrade in any protic solvent. It was confirmed in a separate study (data not shown) that PFMP reacts rapidly with methanol to produce HFC-227ea and the methyl ester of PFPrA. PFMP is certainly volatile enough to be analyzed by gas chromatography−mass spectrometry. However aqueous samples would need to be extracted into a suitable GC solvent prior to injection. PFMP was found to have very low solubilities in almost every solvent tested. In addition, such a procedure would require a separate extraction for every time point, greatly increasing the amount of material needed. We decided that ^{19}F NMR would offer the best capability for measuring the kinetics of PFMP in situ. The hydrolysis reaction was performed in an NMR tube and scans of the reaction mixture were taken at various time intervals for subsequent analysis. ^{19}F NMR offers acceptable signal-to-noise ratios and since neither water nor the buffers used contain fluorine atoms, a purely deuterated solvent does not need to be used. For NMR data to be considered quantitative to 99+% accuracy, it is necessary that the relaxation delay between scans be five times that of the longest spin−lattice relaxation time (T_1) in the compound of interest. Because T_1 values can depend on the solvent used, a standard of PFPrA in the aqueous buffer of interest was used as a surrogate for the T_1 of PFMP. It was found that the longest observed T_1 (PFPrA) = 4.0 s, thus making a suitable relaxation delay for PFMP to be 20 s.

The current Varian NMR processing software, VnmrJ, is capable of analyzing kinetic data using a nonlinear fitting algorithm, provided the fit is exponential. Because the concentration of both OH^- and water are constant in each experiment, pseudo-first-order conditions with respect to PFMP were achieved and an exponential decrease in [PFMP] is expected due to hydrolysis. After fitting the data points, the software provides the 1/e lifetime of the compound (τ), which is simply the reciprocal of the pseudo-first-order rate constant, k_{obs}.

The ^{19}F NMR spectrum of PFMP consists of four peaks: each a multiplet due to the long-range J coupling observed for fluorine atoms. The spectra of PFPrA and HFC-227ea combined resemble that of PFMP but the chemical shifts are distinct and the coupling patterns are very different. Thus, it is straightforward to distinguish PFMP from its degradation products. For examples

of ^{19}F NMR spectra of both PFMP and its photolysis products, please see the SI.

In summary, we observed the 1/e lifetime of PFMP hydrolysis to vary depending on the pH of the buffer used. The reaction was faster in more alkaline solutions as shown in Table 1. This is entirely reasonable given the base-catalyzed nature of the reaction. Both PFPrA and HFC-227ea were positively identified as the sole products of the hydrolysis reaction. PFPrA was confirmed by comparison to an authentic standard. HFC-227ea was confirmed by comparison to a literature spectrum.[22]

Saloutina et al.[20] did not report any kinetics in their study on the hydrolysis of PFMP, however it is not surprising they observed high yields in PFPrA and HFC-227ea given the strongly basic conditions of their reaction solutions. A further study by the same group[23] elaborated on the specificity of the C−C bond cleavage step to exclusively produce the more stable carbanion leaving group. In the case of perfluorinated compounds, the more substituted anion is more stable because of increased hyperconjugation from the anion lone pair to the vicinal antibonding C−F orbitals. Sykes et al.[24] confirmed the regioselectivity of the Haloform reaction for a number of polyfluorinated ketones. Hence, there is precedent for the Haloform reaction to occur regioselectively in fluorinated ketones to produce the less substituted carboxylate and the more substituted hydrofluoroalkane.

Hydration of PFMP. Aldehydes and ketones can react with water to produce a geminal diol by the following reaction scheme.

$$RC(O)R' + H_2O \rightarrow RC(OH)(OH)R' \qquad (12)$$

The reaction is catalyzed by both acids and bases and is usually a reversible equilibrium reaction. For most aldehydes and ketones, the equilibrium constant, K_{hyd}, usually strongly favors the carbonyl compound due to the high strength of the C=O bond. Exceptionally, formaldehyde (HC(O)H) exists in aqueous solution purely as the gem-diol (HC(OH)(OH)H) due to its high K_{hyd} value ($\log K_{hyd} = 3.36$).[25] The vast majority of ketones are quite unreactive to hydration (acetone has $\log K_{hyd} = -2.85$[25]) and the geminal diol form is usually neglected in reaction schemes. Other exceptions can be halogenated ketones; trichloroacetaldehyde has a $\log K_{hyd} = 4.45$ and hexafluoroacetone-(HFA) has $\log K_{hyd} = 6.08$.[25] Effectively, there is quantitative conversion of the carbonyl to the hydrate in aqueous solution and the reverse reaction back to the carbonyl does not occur appreciably at room temperature. For example, HFA is provided commercially as the geminal diol derivative.

It might be reasonable to assume that the electron withdrawing groups of HFA impart a strong partial positive charge at the fluorinated carbonyl carbon, resulting in enhanced electrophilicity and hence, a greater degree of hydration. However, Linderman et al.[26] used Hartree−Fock computational methods and found most of the positive electric potential in HFA is found on the CF_3 carbons and not the carbonyl carbon. Instead, they propose the lower energy level of the LUMO of fluorinated ketones compared to their hydrogenated analogs is the major cause of the enhanced reactivity toward water. Because PFMP is perfluorinated like HFA, it would be a reasonable assumption that PFMP could rapidly and irreversibly form a geminal diol in the environment. The PFMP hydrate would not absorb actinic radiation due to the absence of the C=O chromophore. In addition, formation of the diol would increase water solubility and decrease vapor pressure, resulting in a greater rate of wet deposition and enhancing the potential role of hydrolysis. Thus, it is important to determine whether PFMP could form a stable hydrate in the same manner as HFA.

The hydration reaction of PFMP was investigated in our laboratory and no evidence of such a hydrated species was observed (data not shown). This was puzzling as other fluorinated ketones are known to hydrate readily.[25] To provide further insight, computational methods were used to estimate K_{hyd} for PFMP and compare it to other fluorinated carbonyls using the methods of Gomez-Bombarelli et al.[18] The effects of including an aqueous PCM solvent model were also studied although Guthrie et al.[27] previously noted difficulties of applying the PCM model to halogenated compounds. For full details on the computational work, please see the SI.

Depending on the method used to calculate K_{hyd} (see SI), different values for PFMP were obtained ($-2.09 < \log K_{hyd} < -0.43$) but the range suggests hydrate formation is not significant for PFMP. Given the perfluorinated nature of PFMP and that even partially fluorinated ketones such as trifluoroacetone ($\log K_{hyd} = 1.54$)[25] have large K_{hyd} values we were surprised by the low values of K_{hyd} calculated for PFMP. The computational methods used in the present study (B3LYP/6-311++G(d,p)) were able to compute K_{hyd} values for several fluorinated ketones (fluoroacetone, trifluoroacetone, and hexafluoroacetone) with fairly good accuracy, providing confidence in the method used. A single point molecular orbital calculation on geometry-optimized PFMP in the gas phase (B3LYP/6-311++G(d,p)) gave the energy level of the LUMO (−84.1 kcal/mol) as almost identical to the LUMO of HFA (−81.4 kcal/mol), especially when compared to the computed LUMO of acetone (−19.3 kcal/mol). This supports the results of Linderman et al.[26] who proposed these energy differences as the reason for the enhanced reactivity of HFA to hydration. In the case of PFMP, steric hindrance could be the reason for its decreased hydration equilibrium constant compared to HFA. We conclude that geminal diol formation is not a significant environmental fate for PFMP.

■ ENVIRONMENTAL IMPLICATIONS

We have investigated the potential for photolysis, hydrolysis, and hydration to contribute to the environmental fate of PFMP. As discussed in the previous section, hydration is not a significant fate for PFMP. While the rate constant for hydrolysis is much greater than that for photolysis, the levels of liquid water in the atmosphere are usually very low. A typical cloud only contains approximately 3×10^{-7} cm^3 liquid water per mL of total volume[28] and we conclude that even at night, the amount of PFPrA and HFC-227ea produced would not be significant and that photolysis dominates hydrolysis as the atmospheric fate of PFMP. Cahill and Mackay[29] came to the same conclusion in their modeling study. Interestingly, Cahill and Mackay predicted a hydrolysis rate constant at pH 5.6 of 2.2 s^{-1} which is approximately 10^4 times larger than the hydrolysis rate constant we measured. Hence, our work suggests hydrolysis is an even less important fate for PFMP compared to photolysis than the ratio Cahill and Mackay[29] predicted; the ratio of rates of photolysis to hydrolysis is approximately 980,000,000:1. For full details on this calculation, please see the SI. Photolysis will always dominate over hydrolysis. It is clear the very low fraction of liquid water in the atmosphere contributes heavily to this ratio and more than offsets the higher hydrolysis rate constant. This ratio is so great that even at night time during a heavy rain event it is unlikely hydrolysis will occur to any significant extent.

Photolysis is the dominant mechanism by which PFMP is removed from the atmosphere. It has been established previously[10,11] that photolysis of PFMP in the presence and absence of NO_x will lead to the formation of $CF_3C(O)F$ in a molar yield of approximately 100%. The atmospheric fate of $CF_3C(O)F$ is hydrolysis to give trifluoroacetic acid (TFA). TFA is a ubiquitous naturally occurring component of the hydrosphere and the additional burden associated with PFMP photolysis is not significant. In the present work, we also show that small amounts of PFPrA are also formed as a result of PFMP photolysis. To provide a crude upper limit estimate for the amount of PFPrA that might be expected in precipitation as a result of atmospheric degradation of PFMP we applied the following logic (see SI for details). The production of PFMP by 3 M is 100−1000 t $year^{-1}$ and began in approximately 2003.[30] Given PFMP is used entirely in fire-protection systems that are released by an alarm, it can be considered stored emission potential with releases averaging 1−3% $year^{-1}$.[30] Combining the upper limit of production (1000 t $year^{-1}$) with a 3% emission factor provides an upper limit of 30 t of PFMP released into the atmosphere each year. Reactions subsequent to the formation of $CF_3CF_2C(O)$ radicals in air in the presence of excess HO_2 give PFPrA in a molar yield of 24%.[12] Using a simple model (see SI), and assuming the photolysis of PFMP proceeds exclusively via reaction 2, we derive an upper limit of 0.6 ng L^{-1} for the average concentration of PFPrA in precipitation resulting from PFMP oxidation. Perfluoropropionic acid has been detected in rainwater at several sites in North America at concentrations on the order of 1−10 ng L^{-1} and these levels have yet to be explained.[3] The photolysis of PFMP contributes to, but does not appear to be the major source of, PFPrA observed in precipitation.

■ ASSOCIATED CONTENT

Supporting Information. All computational experiment methodologies, photolysis rate constants from the TUV model, full modeling calculations on the environment fate of PFMP, ^{19}F NMR spectra, and the UV−vis spectrum of PFMP. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank Prof. Mark Taylor and Dr. Mima Staikova for assistance in the computational modelling. Funding to D.A.J. was provided through an Ontario Graduate Scholarship. Funding to C.J.Y. was provided by an NSERC Canada Graduate Scholarship.

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Atmos. Chem. Phys., 10, 5903–5910, 2010
www.atmos-chem-phys.net/10/5903/2010/
doi:10.5194/acp-10-5903-2010
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Atmospheric Chemistry and Physics

Accelerating growth of HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) in the atmosphere

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Received: 16 March 2010 – Published in Atmos. Chem. Phys. Discuss.: 24 March 2010
Revised: 16 June 2010 – Accepted: 30 June 2010 – Published: 2 July 2010

Abstract. We report the first measurements of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), a substitute for ozone depleting compounds, in air samples originating from remote regions of the atmosphere and present evidence for its accelerating growth. Observed mixing ratios ranged from below 0.01 ppt in deep firn air to 0.59 ppt in the current northern mid-latitudinal upper troposphere. Firn air samples collected in Greenland were used to reconstruct a history of atmospheric abundance. Year-on-year increases were deduced, with acceleration in the growth rate from 0.029 ppt per year in 2000 to 0.056 ppt per year in 2007. Upper tropospheric air samples provide evidence for a continuing growth until late 2009. Furthermore we calculated a stratospheric lifetime of 370 years from measurements of air samples collected on board high altitude aircraft and balloons. Emission estimates were determined from the reconstructed atmospheric trend and suggest that current "bottom-up" estimates of global emissions for 2005 are too high by a factor of three.

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1 Introduction

Hydrofluorocarbons (HFCs) are second-generation replacements for compounds responsible for the anthropogenic stratospheric ozone depletion. As they do not contain any chlorine, bromine or iodine their Ozone Depletion Potentials are virtually zero. Due to the phase-out of chlorofluorocarbons (CFCs) and also their first-generation replacements (i.e. hydrochlorofluorocarbons, HCFCs, e.g. Clerbaux and Cunnold (2007)) HFCs have become increasingly important. In return atmospheric growth has been reported in the recent past for many HFCs (e.g. Montzka et al., 1996; Oram et al., 1998; Vollmer et al., 2006; Greally et al., 2007; Stemmler et al., 2007; O'Doherty et al., 2009). HFC-227ea (i.e. CF_3CHFCF_3 or 1,1,1,2,3,3,3-heptafluoropropane) has been proposed for various applications such as a propellant in pharmaceutical or foam-forming aerosols (Deger, 1992; Yquel, 1995; Jager et al., 2005), as a refrigerant (Emmen et al., 2000; Park et al., 2001), in fire extinguishers (Hynes et al., 1998) and also for plasma-etching (Karecki et al., 1998). Jager et al. (2005) even state, that CFCs are already being replaced by approximately 90% HFC-134a and 10% HFC-227ea in metered dose inhalers (MDIs).

Additional desirable properties of CFC replacements are relatively low atmospheric lifetimes and low Global Warming Potentials (GWPs). Here, HFC-227ea shows some disadvantages as both its estimated lifetime as well as its reported GWP are relatively high (34.2 years and 3220 on a 100-year time horizon, Forster et al., 2007) and comparable to those of CFC-11. Despite these perhaps not optimal properties HFC-227ea is being used, and emissions (EDGAR, 2009) reported. Missing so far has been the actual detection of HFC-227ea in the remote atmosphere, a determination of its rate of growth and "top-down" emission estimates.

2 Experimental methods

Air samples were collected from a range of platforms and at various locations:

1. On board a Lufthansa aircraft at cruising altitudes of 8 to 13 km between Frankfurt (Main), Germany and Cape Town, South Africa on 27 and 28 October 2009 (www.caribic-atmospheric.com).

2. In the mid- and high-latitudinal upper troposphere and stratosphere (10 to 20 km) on board the Geophysica high altitude aircraft during two flights from and returning to Oberpfaffenhofen, Germany on 30 October and 4 November 2009 (48–54° N, 7–12° E) and one flight from and returning to Kiruna, Sweden on 22 January 2010 (68–77° N, 20–24° E).

3. In the tropical upper troposphere and stratosphere with a balloon-borne whole-air-sampler launched in June 2008 near Teresina, Brazil (5°04′ S, 42°52′ W) by the French Space Agency CNES (Centre National d'Etudes Spatiales).

4. From deep firn air in Greenland at 77.445° N, 51.066° W and 2484 m a.s.l. in July 2008 (the North Greenland Eemian Ice Drilling project; NEEM). Four of the 17 measured samples were contaminated with HFC-227ea which is attributed to a different type of close-off valve used on those particular sample canisters. These samples were excluded from further analysis.

Please refer to Brenninkmeijer et al. (2007), Kaiser et al. (2006), Laube et al. (2008) as well as to http://neem.nbi.ku.dk/ for further details on sample collection.

All samples were analysed using gas chromatography with mass spectrometric detection (GC-MS). After drying using an on-line drying tube with $Mg(ClO_4)_2$, condensable trace gases were pre-concentrated from about 300 ml of air at −78 °C in a 1/16″ sample loop filled with an adsorbent (Hayesep D, 80/100 mesh) which was heated to 100 °C immediately after injection. Separation was carried out with an Agilent 6890 gas chromatograph using an Agilent GS-GasPro column (length 30 m, ID 0.32 mm) coupled to a high sensitivity tri-sector (EBE) mass spectrometer (Micromass/Waters AutoSpec). This instrument has a proven detection limit < 1 attomole and was operated in EI-SIR (Electron Impact-Selected Ion Recording) mode using a mass resolution of 1000. The GC column temperature was ramped from −10 °C to 200 °C at 10 °C per minute. CF_3CHFCF_3 eluted after about 13.6 min and was measured by means of the fragment ions $C_3HF_6^+$ (*m/z* 151.00) and $C_2HF_4^+$ (*m/z* 101.00). No chromatographic interferences were found for these ions at the given retention time window. In addition, due to the relatively high mass resolution (as compared to common single quadrupole mass spectrometers) a possible interference from an unknown co-eluent is very unlikely.

In order to confirm the identity of the compound and to assign mixing ratios to the air samples we prepared static dilutions of CF_3CHFCF_3 in Oxygen-free Nitrogen (OFN) obtained from BOC Gases, UK. For this purpose we constructed a dedicated drum dilution system based on an existing system described in Fraser et al. (1999). To evaluate this system CF_2Cl_2 was added as an internal reference and diluted similarly. The resulting mixing ratios (which are dry air mole fractions) agreed with the internationally recognized calibration scale of NOAA (2001 scale) within 1.3%. Summing up all uncertainties that could affect the calibration values gives about 14%. However, taking into account the good agreement with the NOAA scale for CF_2Cl_2 as well as the small variability between calibrations for HFC-227ea (< 4%) we estimate our scale uncertainty to be not larger than 5%. The air standard used to assign mixing ratios to the samples was found to contain 0.354 ppt HFC-227ea and the respective average 1 σ measurement precision was 1.4%. More details on configuration and evaluation of the calibration system can be found in the supplemental information.

To ascertain the potential presence of contaminants, one of the dilutions was measured while running the MS in scan mode across the range *m/z* 47 to 200. The chromatogram confirmed the purity of both compounds as no significant amounts of other halocarbons were observed. The obtained spectrum can be found in Table 1 and was compared to the one reported by Reizian-Fouley et al. (1997). All major peaks were present except one at *m/z* 117 which we did not observe. However, no ion is assigned to this peak in Reizian-Fouley et al. (1997) and there is no possible primary fragment of 1,1,1,2,3,3,3-heptafluoropropane with such a mass to charge ratio. Therefore we suggest that its occurrence is very likely to have been an instrumental artefact. The observed relative abundances are of limited comparability due to the different experimental setups. We generally observed much higher relative abundances for ions with lower mass to charge ratios which could be caused by different mass discrimination effects of the mass spectrometers or the use of a non-fluorinated internal reference compound (i.e. n-hexadecane) in our study.

Finally, 1,1,2,2,3,3,3-heptafluoropropane as a potential isomeric impurity is unlikely as the chromatographic system

Table 1. Mass spectral data for HFC-227ea obtained from a 143 ppt dilution in nitrogen as measured on a GC-MS system in scan mode which gives only low mass resolution (see text for details). The spectrum was background-corrected, but some minor residual peaks resulting from the internal mass axis calibration gas (i.e. n-hexadecane) remain. The major peaks are the same as in the mass spectrum reported by Reizian-Fouley et al. (1997) except for an additional peak reported at *m/z* 117 which is a very untypical mass fragment for HFC-227ea and was not observed in this study.

m/z	Normalised abundance	Suggested fragment
69	999	CF_3^+
51	272	CHF_2^+
82	128	$C_2HF_3^+$
50	25	CF_2^+
151	24	$C_3HF_6^+$
55	21	residual n-$C_{16}H_{34}$
63	14	$C_2HF_2^+$
70	11	$^{13}CF_3^+$
54	9	res. n-$C_{16}H_{34}$
56	8	res. n-$C_{16}H_{34}$
53	8	res. n-$C_{16}H_{34}$
101	6	$C_2HF_4^+$
100	6	$C_2F_4^+$

should be able to separate the compounds (boiling point difference of about 2 K between isomers). However, as an additional check we calculated the ratio of the two ions measured in SIR mode (*m/z* 151.00 and 101.00). It was found to be comparable for all samples and dilutions.

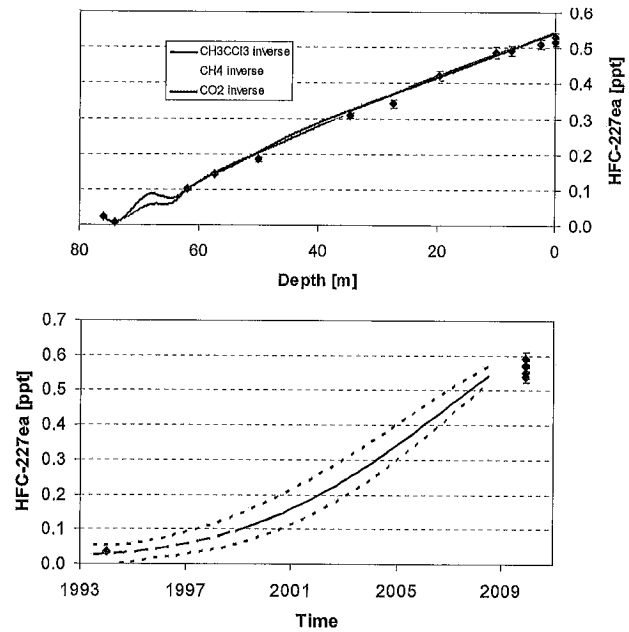

Fig. 1. Mixing ratios of HFC-227ea as a function of depth as measured in air samples collected from deep firn in Greenland in 2008 (upper part) alongside with three modelled diffusivity profiles as described in Sect. 3.1. The lower part shows the northern hemispheric temporal trend inferred from these mixing ratios via inverse modelling. The short-dashed lines represent the maximum of the two σ root mean square deviations while the continuous line shows the mean of the three corresponding best estimate trends. The lack of data between 62 and 74 m leads to high uncertainties in the trend before 1999 which is why it is displayed as a long-dashed line. The additional red points are all from northern mid-latitude samples. They originate from upper tropospheric aircraft samples (2009), and an archived air sample collected at Niwot Ridge near Boulder, USA (1994).

3 Results and discussion

3.1 Firn air measurements and results

The Greenland firn air samples showed good measurement precisions for HFC-227ea and revealed that mixing ratios were monotonically decreasing with increasing depth (Fig. 1). As the age of the air also increases with depth this indicates a recent growth in the atmosphere. Moreover, the very low mixing ratios are observed around 74 m indicate a recent onset of emissions and thus an entirely anthropogenic origin of the compound.

The relationship between past atmospheric time trends and concentration profiles in firn can be established using models of trace gas transport in firn (e.g. Schwander et al., 1993; Butler et al., 1999; Sturrock et al., 2002 and references therein). Please note, that all of the trends derived from measurements of air entrapped in firn are dependent on the assumption that the respective compound is chemically (no destruction) and physically (no adsorption or dissolution) unaffected in the firn over the time periods represented by the measured trends. Here we use direct and inverse models that are developments of those described by Rommelaere et al. (1997), Fabre et al. (2000) and Martinerie et al. (2009). The following is a brief description whereas a fuller description will be given in a forthcoming publication from the NEEM project community. The firn diffusivity is first evaluated using three reference gases: CO_2, CH_4 and CH_3CCl_3, for which measurements were made by NOAA-ESRL, CSIRO Marine and Atmospheric Research, IUP Heidelberg and UEA and atmospheric time trends estimates have been determined. For the latter we used publicly available atmospheric data from NOAA-ESRL (http://www.esrl.noaa.gov/gmd), AGAGE (http://cdiac.ornl.gov/ndps/alegage.html, Prinn et al., 2000), the GAW database (WMO Global Atmospheric Watch, World Data Centre for Greenhouse Gases, http://gaw.kishou.go.jp/wdcgg/) and firn and ice records from McFarling-Meure et al. (2006) for CO_2 and CH_4 as well as emission-based atmospheric modelling

(Martinerie et al., 2009) for CH_3CCl_3. For HFC-227ea we further needed to know its diffusion coefficient in air. We used the Chen and Othmer (1962) calculation to derive an estimate for this, not the more commonly used method of Fuller et al. (1966), due to the reportedly greater robustness of the former (Massman, 1998). For HFC-227ea a diffusion coefficient relative to that of CO_2 of 0.465 was obtained. A very similar ratio of 0.471 was calculated using the Fuller et al. (1966) parameterisation.

Both a Monte-Carlo approach (Bräunlich et al., 2001) and a linear inverse approach (Rommelaere et al., 1997) were used to infer the atmospheric time trend for the HFC-227ea mixing ratios. Consistent results (within the respective model uncertainties) were obtained with the two methods. The time trend obtained with the inverse model (Rommelaere et al., 1997) is shown in Fig. 1 alongside with the actual measurements as a function of depth. It is most likely, that the emissions started in the early 1990s or late 1980s. Please note, that below 0.1 ppt the scenario essentially relies on the last two data points. The data gap in this region of the firn creates high uncertainties and does not allow further constraints on the emission start date or the trend prior to 1999. However, good agreement of the early trend (1993/1994) was observed with a northern hemispheric air sample (Colorado mountains, USA) remotely collected in 1994 (see Fig. 1) although this sample can not be directly compared with the firn air data (different locations). The more recent part of the scenario is better constrained and shows a sustained growth of HFC-227ea since 1999 until mid 2008. The average growth rate accelerated continuously from 0.029 ppt yr^{-1} in 2000 to 0.053 ppt yr^{-1} in 2005 and 0.056 ppt yr^{-1} in 2007. The firn air itself was collected in July 2008, therefore an averaged growth rate cannot be provided for 2008, but mixing ratios continued to increase. Please also note that these growth rates represent only best estimates and contain considerable uncertainties within the envelopes shown in Fig. 1. Additional data from samples collected on board aircraft flying in the Northern Hemispheric upper troposphere in late 2009 clearly indicate a further growth since during this period (see Fig. 1).

3.2 Emission estimates

We derived the emissions required to produce the temporal trend in the atmospheric concentrations inferred from the firn air data using a 2-D atmospheric chemistry-transport model. The model contains 24 equal area latitudinal bands and 12 vertical levels, each of 2 km. Thus the latitude band applicable to the NEEM firn site is the most northerly (66.4°–90.0°) and since the altitude of the site is about 2.5 km, the concentrations for the second level (2–4 km) were used. The emissions were assigned predominantly to the northern mid-latitudes with only 2% released in the Southern Hemisphere (distribution as in EDGAR, 2009). Using CFC-11, CFC-12 and CH_3CCl_3 Reeves et al. (2005) showed that the model's

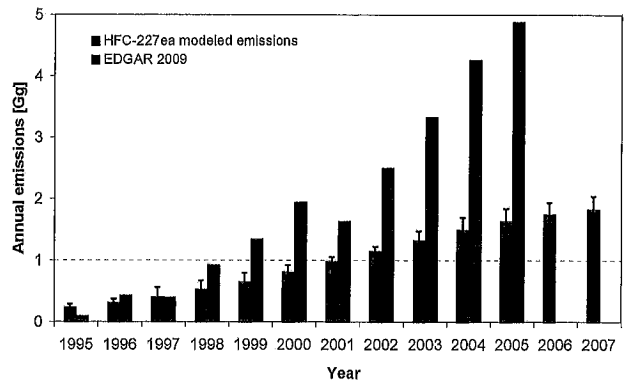

Fig. 2. Emission estimates as derived from trends of HFC-227ea in firn air in comparison with those reported by the EDGAR emission database (EDGAR, 2009). The primary sink for HFC-227ea is reaction with the OH radical in the troposphere. Therefore error bars were calculated as the root of mean of the squares of the summed uncertainty in the OH concentration and in the respective reaction rate coefficient as well as firn air related uncertainties (corresponding to the minimum and maximum scenarios in Fig. 1).

transport scheme (Hough, 1989) typically reproduces the observed concentrations in the Arctic to within 10%, when constrained to observed southern hemispheric concentrations.

The major known atmospheric sink of HFC-227ea is the reaction with the OH radical (Zellner et al., 1994). The model's OH field was adjusted to give a partial lifetime for CH_3CCl_3, with respect to reaction with OH (τ_{OH}), in agreement with Clerbaux and Cunnold (2007) (6.1 years) when using a reaction rate coefficient of (1.2×10^{-12}) $\exp[-1440/T]$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2008). The model then gives a value of 46.5 years for τ_{OH} for HFC-227ea when using a reaction rate coefficient of (5.3×10^{-13}) $\exp[-1770/T]$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2008). The diffusive transport out of the top of the model is then adjusted to account for stratospheric loss equivalent to a partial lifetime (τ_{strat}) of 450 years which is within the range calculated in Sect. 3.3. Overall the model gives a total lifetime of 42.1 years for HFC-227ea. This is higher than the 34.2 years reported in Clerbaux and Cunnold (2007) but the difference is mostly due to recent changes in the reaction rate of HFC-227ea with OH as reported in Atkinson et al. (2008).

Using the model the temporal trend in the global emissions was adjusted to match the trend of HFC-227ea from the firn model (Fig. 2). This has been done for the best, maximum and minimum mixing ratios derived from the firn air. The error bars shown in Fig. 2 are the root mean squares of the uncertainties from these minimum and maximum scenarios plus uncertainties in the OH loss of +59% and −40%. The latter were derived from an uncertainty of 14% in the OH concentrations (Prinn et al, 2001) and an uncertainty range of −37% to +57% in the reaction rate coefficient at 298 K (Atkinson et al., 2008). Given the relatively long lifetime

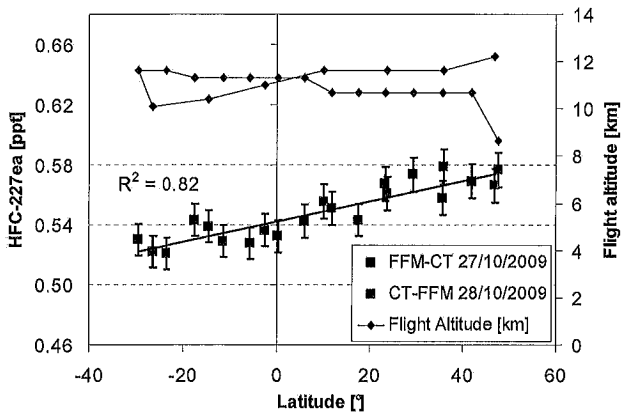

Fig. 3. Upper tropospheric mixing ratios of HFC-227ea as a function of latitude in air samples collected on board a Lufthansa aircraft during two flights from Frankfurt (Main), Germany (FFM) to Cape Town, South Africa (CT) and back. Two samples were collected at potential vorticity values indicating air from the tropopause region, but due to the long stratospheric lifetime of HFC-227ea this has little influence on the correlation.

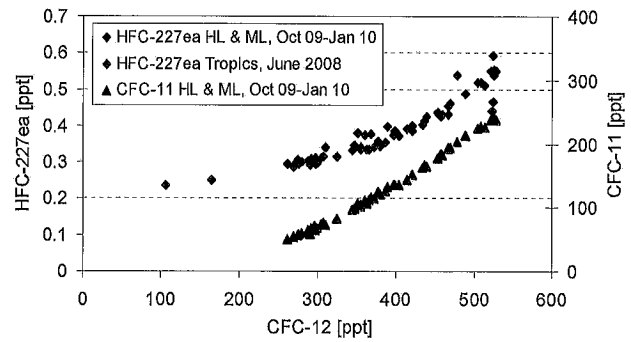

Fig. 4. Stratospheric correlation of HFC-227ea (black) and CFC-11 (green) with CFC-12 as derived from measurements on air samples collected on board the Geophysica high altitude aircraft in high and mid-latitudes (HL and ML). The red points belong to four samples collected with a balloon-borne whole-air sampler in the tropical upper troposphere and stratosphere (only CFC-12 vs. HFC-227ea displayed). The 1 σ measurement uncertainties are less than the size of the symbols in all cases.

of HFC-227ea compared to the period of rapidly increasing emissions, the uncertainty in this loss rate has a negligible impact on the derived emissions.

Also shown in Fig. 2 are the emissions from "bottom-up" estimates based on industrial production and use (EDGAR, 2009). The annual estimates for the years 1999 to 2001 from EDGAR are around twice those derived from the firn data and the respective discrepancy increases with time from 2001 on reaching a factor of 3.0 in 2005. The firn and emission model uncertainties as well as the above mentioned uncertainties connected to OH cannot bridge this gap. We suspect that the discrepancy is likely to be caused by an overestimation of the bottom-up emissions. However, the currently available data are of insufficient temporal and spatial coverage to verify this suspicion.

3.3 Upper tropospheric data and stratospheric lifetime

Mixing ratios from upper tropospheric air samples collected in October 2009 (CARIBIC) are given in Fig. 3. The transect from 48° N (Frankfurt) to 30° S (Cape Town) was nearly true north-south (between 6 and 19° E) and reveals a compact linear trend of HFC-227ea with latitude. This systematic behaviour with little scatter indicates that the observed air masses had not been in contact with sources recently and were representative for the upper troposphere at the given time and location. Backward trajectories (publicly available at http://www.knmi.nl/samenw/campaign_support/CARIBIC) indicate that, with the exception of the ITCZ region, air masses had been predominantly advected over the Atlantic Ocean from the west. The observed north-south gradient implies that the source regions are in the Northern Hemisphere. To maintain such a gradient also implies that HFC-227ea mixing ratios were still increasing in 2009. Assuming, that the observed mixing ratios are representative of the global upper troposphere, we calculate that the interhemispheric ratio (NH/SH) must be at least 1.1.

The stratospheric data are shown in Fig. 4 as a function of the concomitant CF_2Cl_2 (CFC-12) mixing ratios. Long-lived organic compounds are known to form such compact correlations in this atmospheric region (Plumb and Ko, 1992). As an example the correlation of CFC-12 with $CFCl_3$ (CFC-11) is also displayed in Fig. 4. The slope of these correlations at the tropopause can be used to calculate a stratospheric lifetime (Volk et al., 1997). However, vertical stratospheric transport times are very slow (on the order of years). Thus, a correction must be made to account for the change in the entry mixing ratios over time. Here we use a method based on the mean age of air (i.e. the mean stratospheric transit time of a given air parcel) as derived from mixing ratios of SF_6 and its global tropospheric trends from NOAA-ESRL which were obtained from http://www.esrl.noaa.gov/gmd/ (updated from Geller et al., 1997). Please refer to Engel et al. (2002) for further details on the mean age calculation. As global tropospheric trends are only available until early 2009 yet, we complemented it via an extension to the values observed at the tropopause in late 2009. Subsequently the above determined tropospheric trend of HFC-227ea was shifted by 6 months to account for transport into the tropics and then propagated into the stratosphere assuming no chemical degradation en route. The difference between this and the actual measured mixing ratios in the stratosphere is the inorganic fraction released at a given altitude. This inorganic fraction relative to the amount that initially entered the stratosphere is then the Fractional Release Factor (FRF). Thus, FRFs represent the detrended relative inorganic fraction released from a given long-lived compound at a given location and time in

the stratosphere. The exact method for their calculation is described in Laube et al. (2010). If such a set of FRFs for two compounds are multiplied by their globally representative mixing ratios it yields their detrended correlation for a given date. After this correction it is possible to calculate the stratospheric lifetime τ_{strat} via the known lifetime of a reference compound τ_{ref} using Eq. (1) (adapted from Volk et al., 1997).

$$\tau_{\mathrm{strat}} = \tau_{\mathrm{strat,ref}} \frac{\bar{\sigma}}{\bar{\sigma}_{\mathrm{ref}}} \Bigg/ \left[\frac{d\chi}{d\chi_{\mathrm{ref}}} \bigg| \chi_{\mathrm{ref}}^{\mathrm{trop}} \right] \tag{1}$$

The reference compounds used here were CFC-11 and CFC-12 and their global average atmospheric mixing ratios $\bar{\sigma}$ (which take into account the loss in the stratosphere) were inferred by adjusting the values derived by Volk et al. (1997) to the mixing ratios observed at the tropopause in late 2009 (using monthly averaged NOAA-ESRL global tropospheric trends from Montzka et al., 1999 for detrending, as updated and publicly available from http://www.esrl.noaa.gov/gmd/).The slope of the detrended correlation already indicates that HFC-227ea is significantly longer-lived than CFC-12. Therefore we performed calculations with values of $\bar{\sigma}$ between 95 and 100% of the mixing ratio observed at the tropopause (95% is the value for CFC-12). The final unknown quantity ($d\chi/d\chi_{\mathrm{ref}} \big| \chi_{\mathrm{ref}}^{\mathrm{trop}}$) is the slope of the mixing ratio correlation at the tropopause. This was calculated from a least-square quadratic polynomial fit through the data.

Assuming a stratospheric lifetime of 45 years for CFC-11 (taken from Clerbaux and Cunnold, 2007) results in a stratospheric lifetime of 380 years for HFC-227ea for $\bar{\sigma} = 100\%$ (negligible stratospheric loss) and 360 years for $\bar{\sigma} = 95\%$ (same loss as CFC-12). As the exact value is likely to be between these values we infer 370 years as the best estimate. Calculations using the correlation with CFC-12 (100 year lifetime), different lifetimes of the CFCs (41 and 79 years, from Volk et al., 1997) as well as the above stated different values for $\bar{\sigma}$ give a range of 330 to 490 years. To assess the uncertainties of the correlation slope we performed similar calculations after subtraction and addition of the $1\,\sigma$ measurement uncertainty from the ten data points next to the tropopause. This test revealed the limitations of this method for very long-lived compounds with correlation slopes close to zero. The corresponding lifetime range was 270 to 840 years. Due to the rather long tropospheric lifetime of HFC-227ea (37.8 years, Naik et al., 2000) uncertainties related to its tropospheric decomposition should have only a minor impact on this range. Thus, our experimentally derived stratospheric lifetime (best estimate of 370 years) agrees with the model-derived 633 years of Naik et al. (2000) within the respective uncertainties. However, it should be noted, that there are further uncertainties related to the approximated global tropospheric trend which can not be accounted for so far.

4 Conclusions

We report the first observations of HFC-227ea, a replacement for ozone depleting CFCs and halons, in remote regions of the atmosphere (i.e. in firn air and high-altitude samples). A dilution system has been built and evaluated for quantification of this and other compounds. A mass spectrum has been obtained and all high abundant ions of a spectrum reported in the literature were found to be present except one. A reconstruction of the atmospheric history of HFC-227ea from firn air reveals that emissions were very low in the early 1990s. In combination with further measurements in the upper troposphere we find strong evidence for its growth until the end of our available observations in 2009. Emission estimates inferred from this trend do not agree with estimates from the EDGAR database (EDGAR, 2009) and even show a discrepancy that is increasing with time. We can not resolve these disagreements with the observations and the related uncertainties presented here. Further studies, which should include observations from global ground-based networks, are needed to improve the understanding of the emission processes and patterns and the global distribution of HFC-227ea. Finally, compact correlations with other long-lived gases in the stratosphere have been used to derive a stratospheric lifetime of 370 years (range: 270 to 840 years) which agrees with the 633 years reported by Naik et al. (2000) within the uncertainties. It is the first time that this measurement-based approach has been used to evaluate a modelled stratospheric HFC lifetime.

Acknowledgements. We would like to thank the UK Natural Environment Research Council (Research Fellowship NE/F015585/1 & Research Award NE/F021194/1), the European Union (SCOUT-O3 project GOCE-CT-2003-505390), the European Space Agency and CNRS-INSIS (PEPS-automatique project MODELINEVE) for funding. NEEM is directed and organized by the Center of Ice and Climate at the Niels Bohr Institute and US NSF, Office of Polar Programs. It is supported by funding agencies and institutions in Belgium (FNRS-CFB and FWO), Canada (GSC), China (CAS), Denmark (FIST), France (IPEV, CNRS/INSU, CEA and ANR), Germany (AWI), Iceland (RannIs), Japan (NIPR), Korea (KOPRI), The Netherlands (NWO/ALW), Sweden (VR), Switzerland (SNF), UK (NERC) and the USA (US NSF, Office of Polar Programs). The Geophysica flights from Oberpfaffenhofen were funded by ESA under the PremieEx project and by Forschungszentrum Jülich. The Geophysica flights from Kiruna were funded by the EC as part of the FP7 project RECONCILE (Grant number: RECONCILE-226365-FP7-ENV-2008-1). In addition we are grateful for contributions from Thijs F. Duindam, all CARIBIC partners, the Geophysica team and the CNES balloon team (sample collection and campaign organisation) as well as from the NOAA-ESRL GMD, AGAGE and WMO GAW teams and from CSIRO Marine and Atmospheric Research, Australia, the Institute of Arctic and Alpine Research (INSTAAR) at the University of Colorado at Boulder, USA and the IUP Heidelberg, Germany (provision of publicly available and also unpublished data).

Edited by: R. MacKenzie

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/10/5903/2010/ acp-10-5903-2010-supplement.pdf.

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Atmospheric Chemistry of $C_2F_5C(O)CF(CF_3)_2$: Photolysis and Reaction with Cl Atoms, OH Radicals, and Ozone

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Received: September 10, 2002; In Final Form: December 13, 2002

Smog-chamber Fourier-transform infrared (FTIR) techniques were used to study the kinetics and photochemistry of $C_2F_5C(O)CF(CF_3)_2$ in 50−700 Torr of air at 296 K. Upper limits for the rate constants of reactions of Cl atoms, OH radicals, and ozone with $C_2F_5C(O)CF(CF_3)_2$ were established: $k_{Cl} < 1.7 \times 10^{-19}$, $k_{OH} < 5 \times 10^{-16}$, and $k_{O_3} < 4 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1}. The ultraviolet absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ has a maximum at 305 nm where $\sigma_e = 6.8 \times 10^{-20}$ cm^2 molecule^{-1}. $C_2F_5C(O)CF(CF_3)_2$ is removed from the atmosphere by photolysis, which occurs on a time scale of approximately 1−2 weeks. As a result of its short atmospheric lifetime, the global warming potential of $C_2F_5C(O)CF(CF_3)_2$ is negligible.

1. Introduction

CF_2ClBr (Halon-1211) and CF_3Br (Halon-1301) are effective and widely used fire-suppression agents. Unfortunately, the release of Halons into the atmosphere leads to stratospheric ozone depletion.[1,2] International agreements, outlined in the Montreal Protocol, 1987 and subsequent amendments, are now in place to phase out the use of such compounds. Alternative fire-suppression agents are needed. Perfluoro-(4-methylpentan-3-one), $C_2F_5C(O)CF(CF_3)_2$, is under consideration as an environmentally friendly fire-suppression agent. This material has a boiling point of 48 °C and a vapor pressure of 304 Torr at 25 °C and will be released into the atmosphere during use. Prior to its large-scale industrial use, an assessment of the atmospheric chemistry, and hence the environmental impact, of this compound is needed. We report herein the results of the first investigation of the atmospheric chemistry of $C_2F_5C(O)CF(CF_3)_2$. The ultraviolet (UV) absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ and kinetics of its reaction of OH radicals were measured at MIT. The kinetics of the reactions of Cl atoms and ozone with $C_2F_5C(O)CF(CF_3)_2$ and the rate and mechanism of UV photolysis were measured in a smog chamber at Ford. The results are reported herein and discussed with respect to the atmospheric chemistry of $C_2F_5C(O)CF(CF_3)_2$.

2. Experimental Section

The experimental systems used are described in detail elsewhere.[3,4] All samples of $C_2F_5C(O)CF(CF_3)_2$ used in this work were supplied by the 3M Company at a purity of >99.99% (by $^1H/^{19}F$ NMR). Samples of $C_2F_5C(O)CF(CF_3)_2$ were degassed at liquid-nitrogen temperature and used without further purification. Uncertainties reported in this paper are two standard deviations unless stated otherwise.

2.1. Fourier-Transform Infrared (FTIR) Photolysis System at MIT. An upper limit to the rate constant for the OH + $C_2F_5C(O)CF(CF_3)_2$ reaction was established by monitoring the rate of $C_2F_5C(O)CF(CF_3)_2$ loss relative to CH_4 and CH_3Cl in the presence of OH radicals at 296 K. OH radicals were generated by photolysis of ozone at 254 nm in the presence of water vapor.

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (2)$$

The long-path absorption cell, made of Pyrex glass, had a volume of 7.6 L and a base length of 60 cm, which was adjusted to give a total of 24 passes, and an optical path length of 14.4 m. Concentrations of the reactants and products were monitored using a FTIR spectrometer (Nicolet 20SX). The mercury photolysis lamp (Ace Hanovia 450-W medium-pressure mercury lamp) was enveloped in a Vycor tube that transmits 254-nm radiation but absorbs the 185-nm Hg line and was placed inside the absorption cell. Control experiments performed in the absence of O_3 established that photolysis of $C_2F_5C(O)CF(CF_3)_2$ occurs in the chamber at a rate of $\sim 2 \times 10^{-4}$ s^{-1}. Appropriate corrections were applied to the data acquired in the relative rate study of $k(OH+C_2F_5C(O)CF(CF_3)_2)$ to account for such photolytic loss of $C_2F_5C(O)CF(CF_3)_2$.

The organic reactants were mixed with helium in a 3-L glass reservoir to yield mole fractions of ~1%. Ozone was prepared by first trapping the effluent from an ozonizer in cold silica gel and then desorbing the sample into a 12-L glass reservoir and subsequently mixing it with helium. Experiments were performed at room temperature in ~200 Torr of helium as a buffer gas in the presence of 3−5 Torr of ozone and 2−3 Torr of water vapor.

2.2. UV Spectrometer System at MIT. The UV absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ was recorded using a Cary 219 double-beam spectrophotometer by placing gaseous samples of the compound in a 14.5 cm long quartz cell at 296 K. Average

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10.1021/jp0220332 CCC: $25.00 © 2003 American Chemical Society
Published on Web 03/22/2003

absorption cross sections in the 200−400 nm wavelength range were obtained by measuring absorbances at four different pressures in the 1−5 Torr range.

2.3. FTIR Smog-Chamber System at Ford Motor Company. Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[4] The reactor was surrounded by 22 fluorescent lamps, which were used to photochemically initiate the experiments. In the present experiments, eight of the lamps were GE FS40 "sunlamps" with a phosphor coating, which has a maximum emission at approximately 310 nm, while the other 14 lamps were GE F15T8-BL "blacklamps", which have a maximum emission at approximately 360 nm. Cl atoms were generated by the photolysis of molecular chlorine in air diluent at 700 Torr total pressure at 296 ± 2 K.

$$Cl_2 + h\nu \rightarrow 2Cl \quad (3)$$

The loss of $C_2F_5C(O)CF(CF_3)_2$ and $^{13}CH_3{}^{13}CHO$ and the formation of products (COF_2, $CF_3C(O)F$, and ^{13}CO) were monitored by FTIR spectroscopy using an infrared path length of 27.4 m, and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms.

Three sets of experiments were performed at Ford. First, the rate of $C_2F_5C(O)CF(CF_3)_2$ photolysis was measured relative to $^{13}CH_3{}^{13}CHO$ using the UV output of either 8 sunlamps or 14 blacklamps. Second, relative rate techniques were used to investigate the reactivity of Cl atoms with $C_2F_5C(O)CF(CF_3)_2$. Third, the reactivity of ozone with $C_2F_5C(O)CF(CF_3)_2$ was investigated. All experiments were performed at 296 K.

3. Results and Discussion

3.1. Relative Rate Study of $k(OH+C_2F_5C(O)CF(CF_3)_2)$. The kinetics of reaction 4 were measured relative to reactions 5 and 6 using the experimental system at MIT.

$$OH + C_2F_5C(O)CF(CF_3)_2 \rightarrow \text{products} \quad (4)$$

$$OH + CH_4 \rightarrow \text{products} \quad (5)$$

$$OH + CH_3Cl \rightarrow \text{products} \quad (6)$$

Following the generation of OH radicals in the system, CH_4 and CH_3Cl were observed to decay, but there was no discernible loss (<2%) of $C_2F_5C(O)CF(CF_3)_2$ (over and above that ascribed to photolysis, see section 2.1). Using $k_5 = (6.3 \pm 0.6) \times 10^{-15}$ and $k_6 = (3.6 \pm 0.7) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1},[5] we derive upper limits of $k_4 < 5 \times 10^{-16}$ and $< 2 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. We cite a final value of $k_4 < 5 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. Perfluoroalkanes (CF_4, C_2F_6, etc.) do not react with OH radicals,[6] the results from the present work suggest that $C_2F_5C(O)CF(CF_3)_2$ is similarly unreactive toward OH radicals. There has been some recent discussion in the literature that a significant fraction of the reaction of OH radicals with ketones proceeds via addition to the C=O group followed by displacement of one of the alkyl groups.[7−9] We observe no evidence of such a channel for reaction 4.

3.2. UV Absorption Cross Sections of $C_2F_5C(O)CF(CF_3)_2$ and CH_3CHO. Figure 1 and Table 1 give the UV absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ measured at MIT. The complete spectrum is available in digital form upon request to ltmolina@mit.edu or mmolina@mit.edu. The absorption spectrum has a maximum at 305 nm where $\sigma_{max} = 6.8 \times 10^{-20}$ cm^2 $molecule^{-1}$. For comparison, the absorption spectrum of CH_3CHO[10] is also shown in Figure 1. As seen from Figure 1, $C_2F_5C(O)CF(CF_3)_2$ has an absorption spectrum that is shifted approximately 20 nm to the red and is somewhat more intense than that of CH_3CHO.

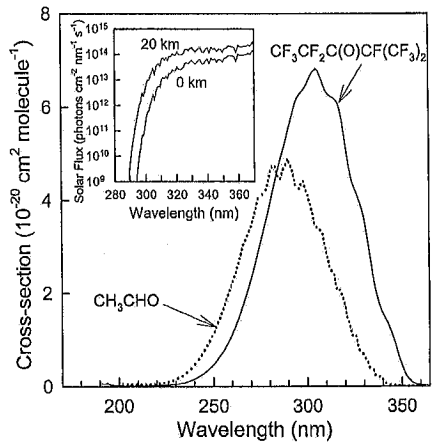

Figure 1. UV absorption cross sections of $C_2F_5C(O)CF(CF_3)_2$ (solid line) and CH_3CHO (dotted line) over the wavelength range 190−365 nm at 296 K. The insert shows the solar flux at sea level (0 km) and at 20 km altitude in the atmosphere.

TABLE 1: Measured UV Absorption Cross Section Data for $CF_3CF_2C(O)CF(CF_3)_2$

wavelength[a]	cross section[b]	wavelength[a]	cross section[b]
230	0.05	300	6.48
235	0.09	305	6.81
240	0.16	310	6.36
245	0.29	315	6.16
250	0.47	320	5.30
255	0.75	325	4.27
260	1.13	330	3.65
265	1.65	335	2.36
270	2.30	340	1.57
275	3.07	345	1.12
280	3.87	350	0.47
285	4.72	355	0.11
290	5.47	360	0.03
295	6.19	300	6.48

[a] In nanometers. [b] In 10^{-20} cm^2 $molecule^{-1}$.

3.3. Photolysis of $C_2F_5C(O)CF(CF_3)_2$: Rate and Mechanism. The rate and mechanism of the photolysis of $C_2F_5C(O)CF(CF_3)_2$ were studied in the smog chamber at Ford. Control experiments were performed in which $C_2F_5C(O)CF(CF_3)_2$/air mixtures were allowed to stand in the chamber in the dark to check for heterogeneous loss of $C_2F_5C(O)CF(CF_3)_2$. There was neither any discernible (<2%) loss of $C_2F_5C(O)CF(CF_3)_2$ nor any discernible formation of products (<0.02% molar yield of COF_2) when $C_2F_5C(O)CF(CF_3)_2$/air mixtures were allowed to stand in the dark for 16 h. Upon irradiation of $C_2F_5C(O)CF(CF_3)_2$/air mixtures with the output from UV fluorescent lamps (see section 2.3 for details), loss of $C_2F_5C(O)CF(CF_3)_2$ and formation of products were observable in the IR spectra.

Figure 2 shows typical IR spectra in the wavenumber region 1850−2000 cm^{-1} obtained before (panel A) and after (panel B) a 90 min UV irradiation of a mixture of 1.54 Torr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of synthetic air at 296 K. Panel C shows the residual spectrum of panel A from panel B, which corresponds to the photoproducts produced from a mixture of $C_2F_5C(O)CF(CF_3)_2$ in air by UV radiation. Comparison of panel C with reference spectra of $CF_3C(O)F$ and COF_2 in panels D and E, respectively, shows that these species are products. $CF_3O_3CF_3$ and CF_3OH were also identified as products by virtue of their characteristic IR features at 897[11] and 3664 cm^{-1}, respectively.[12] When photolysis mixtures were left in the dark

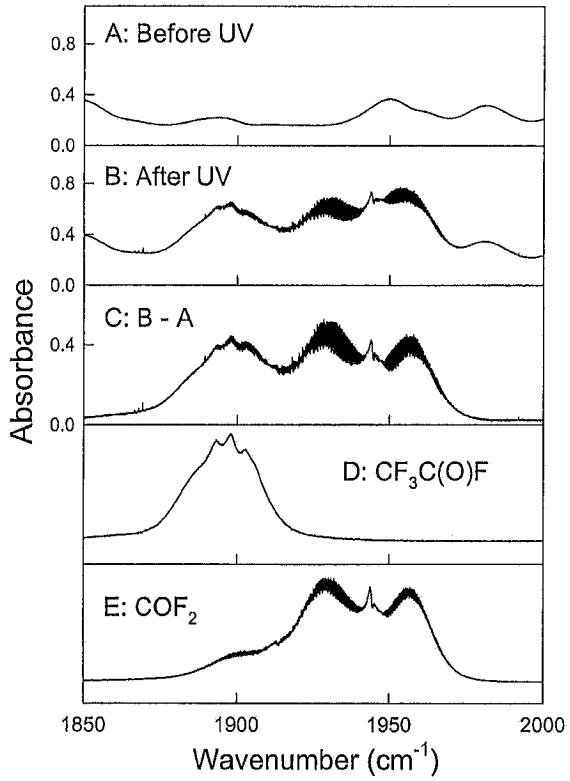

Figure 2. IR spectra acquired (A) before and (B) after a 90 min UV irradiation of a mixture containing 1.54 Torr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent at 296 K. Panel C shows the result of subtracting panel A from panel B. Reference spectra of $CF_3C(O)F$ and COF_2 are given in panels D and E.

for 90 min, there was no observable change in $CF_3C(O)F$ or $CF_3O_3CF_3$ concentrations while, consistent with previous observations,[12] there was a 20% loss of CF_3OH (first-order loss rate $k_{loss} = 4 \times 10^{-5}\ s^{-1}$) and a corresponding increase in the amount of COF_2 in the chamber. In the present work, the half-life of CF_3OH with respect to decomposition into COF_2 was 4−5 h (consistent with the range of 1−5 h reported previously).[12]

$$CF_3OH \rightarrow COF_2 + HF \quad (7)$$

Figure 3 shows the observed formation of COF_2 and $CF_3C(O)F$ during the UV irradiation (blacklamps) of a mixture of 154 mTorr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent. As seen from Figure 3, for short irradiation times, the yields of COF_2 and $CF_3C(O)F$ were indistinguishable, while at longer irradiation times, the yield of COF_2 exceeds that of $CF_3C(O)F$. It is also evident from Figure 3 that the formation of $CF_3C(O)F$ scales linearly with irradiation time consistent with its formation as a primary product following photolysis of $C_2F_5C(O)CF(CF_3)_2$. After 7 h of irradiation, the loss of $C_2F_5C(O)CF(CF_3)_2$ was determined to be 2.5% ± 1.0%, that is, 3.9 ± 1.5 mTorr, indistinguishable from the $CF_3C(O)F$ yield.

The simplest explanation of the experimental observations is that photolysis of $C_2F_5C(O)CF(CF_3)_2$ occurs via cleavage of one of the C−C bonds associated with the carbonyl group to yield a perfluoroalkyl radical and a perfluoroacetyl radical. By analogy to similar alkyl radicals, these radicals will add O_2 to give the corresponding peroxy radicals and undergo self- and cross-reactions to give alkoxy radicals. For example, if photolysis occurs via rupture of the $C_2F_5-C(O)CF(CF_3)_2$ bond then, by analogy to the substantial database concerning the

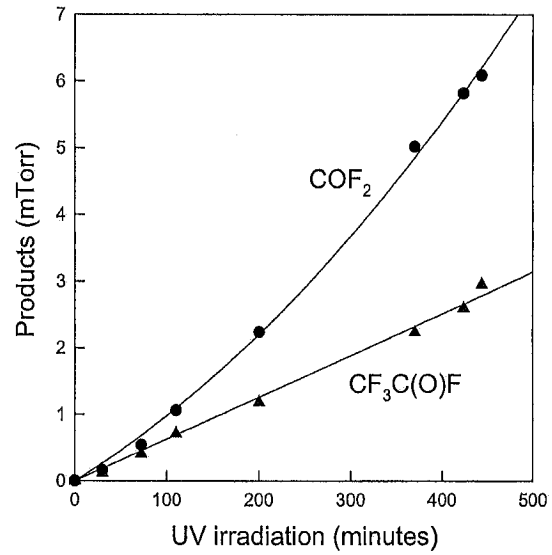

Figure 3. Formation of (●) COF_2 and (▲) $CF_3C(O)F$ as a function of irradiation time (using blacklamps) of a mixture of 154 mTorr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent at 296 K. The lines through the $CF_3C(O)F$ and COF_2 data are first- and second-order regressions.

atmospheric oxidation mechanisms of hydrofluorocarbons,[13] the chemistry is expected to be

$$C_2F_5C(O)CF(CF_3)_2 + h\nu \rightarrow C_2F_5 + C(O)CF(CF_3)_2 \quad (8)$$

$$C_2F_5 + O_2 + M \rightarrow C_2F_5O_2 + M \quad (9)$$

$$C(O)CF(CF_3)_2 + O_2 + M \rightarrow OOC(O)CF(CF_3)_2 + M \quad (10)$$

$$C_2F_5O_2 + RO_2 \rightarrow C_2F_5O + RO + O_2 \quad (11)$$

$$OOC(O)CF(CF_3)_2 + RO_2 \rightarrow OC(O)CF(CF_3)_2 + RO + O_2 \quad (12)$$

$$C_2F_5O + M \rightarrow CF_3 + COF_2 + M \quad (13)$$

$$OC(O)CF(CF_3)_2 + M \rightarrow CO_2 + CF(CF_3)_2 + M \quad (14)$$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \quad (15)$$

$$CF(CF_3)_2 + O_2 + M \rightarrow OOCF(CF_3)_2 + M \quad (16)$$

$$OOCF(CF_3)_2 + RO_2 \rightarrow OCF(CF_3)_2 + RO + O_2 \quad (17)$$

$$CF_3O + CF_3O_2 + M \rightarrow CF_3O_3CF_3 + M \quad (18)$$

$$OCF(CF_3)_2 + M \rightarrow CF_3C(O)F + CF_3 + M \quad (19)$$

If photolysis occurs via rupture of the $C_2F_5C(O)-CF(CF_3)_2$ bond, then reactions 20−23 will be followed by reactions 9, 11, 13, and 15−19:

$$C_2F_5C(O)CF(CF_3)_2 + h\nu \rightarrow C_2F_5C(O) + CF(CF_3)_2 \quad (20)$$

$$C_2F_5C(O) + O_2 + M \rightarrow C_2F_5C(O)O_2 + M \quad (21)$$

$$C_2F_5C(O)O_2 + RO_2 \rightarrow C_2F_5C(O)O + RO + O_2 \quad (22)$$

$$C_2F_5C(O)O + M \rightarrow C_2F_5 + CO_2 + M \quad (23)$$

In the above scheme, there is only one loss mechanism for CF_3O radicals, namely, association with CF_3O_2 to give the trioxide,

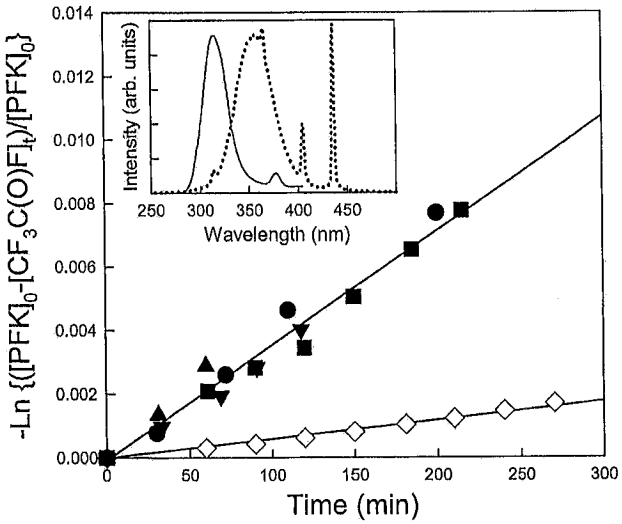

Figure 4. Decay of $C_2F_5C(O)CF(CF_3)_2$ inferred from the formation of $CF_3C(O)F$ as a function of irradiation time of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent at 296 K using either 8 sunlamps (filled symbols) or 14 blacklamps (open symbols). Initial concentrations of $C_2F_5C(O)CF(CF_3)_2$ were (○) 154 mTorr, (□) 481 mTorr, (◇) 745 mTorr, (▽) 1.54 Torr, and (△) 1.83 Torr. The insert shows the spectral distribution (arbitrary units) of the sunlamps (solid curve) and blacklamps (dotted curve).

$CF_3O_3CF_3$. In smog-chamber experiments, there is another loss mechanism for CF_3O radicals, reaction with hydrogen-containing compounds present in the chamber (e.g., HCHO desorbing from the chamber walls, impurities in the air diluent, or both) to give CF_3OH, [13] which was an observed product in the present work.

The loss of $C_2F_5C(O)CF(CF_3)_2$ was small (2.5% loss after 7 h of irradiation) and difficult to monitor directly. To provide greater precision in the measurement of the photolysis of $C_2F_5C(O)CF(CF_3)_2$, its loss was monitored indirectly by measuring the formation of $CF_3C(O)F$. Upon the basis of the mechanism outlined above, it seems reasonable to assume that the photolysis of $C_2F_5C(O)CF(CF_3)_2$ gives $CF_3C(O)F$ in a molar yield of unity. Accordingly, Figure 4 shows the loss of $C_2F_5C(O)CF(CF_3)_2$ as inferred from the formation of $CF_3C(O)F$ as a function of irradiation time for several different $C_2F_5C(O)CF(CF_3)_2$/air mixtures using either sunlamps (filled symbols) or blacklamps (open symbols). Within the admittedly significant data scatter evident from inspection of the data represented by filled symbols in Figure 4, there is no evidence for any systematic dependence of the first-order loss rate with variation of the initial $C_2F_5C(O)CF(CF_3)_2$ concentration over the range 0.154−1.83 Torr. The line through the filled data in Figure 4 is a linear least-squares fit to the composite data set, which gives a photolysis rate of $J(C_2F_5C(O)CF(CF_3)_2) = (6 \pm 2) \times 10^{-7}\ s^{-1}$ for eight sunlamps. Similarly, a least-squares fit to the data obtained using blacklamps gives $J(C_2F_5C(O)CF(CF_3)_2) = (1.0 \pm 0.1) \times 10^{-7}\ s^{-1}$ for 14 blacklamps.

The insert in Figure 4 shows the spectral distribution of the output from the sunlamps (solid curve) and blacklamps (dotted curve) taken from the manufacturers specifications. The data in the insert provide an indication of the spectral region over which the lamps emit and not the absolute intensity of the lights. The maximum of both output curves has been scaled to the same value for display purposes. Finally, it should be noted that absorption by the Pyrex walls (Pyrex cuts off at ~300 nm) will modify the spectrum of UV light within the chamber. It is evident from Figure 4 that the sunlamps, although less numerous than the blacklamps, are much more effective in photolyzing $C_2F_5C(O)CF(CF_3)_2$. This behavior presumably reflects the better spectral overlap of emission from the sunlamps with the spectrum of $C_2F_5C(O)CF(CF_3)_2$ (compare insert in Figure 4 with spectrum in Figure 1).

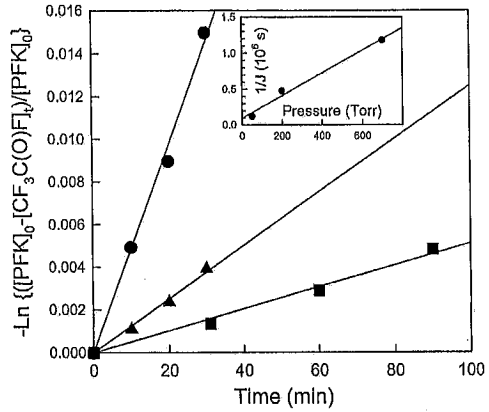

Figure 5. Decay of $C_2F_5C(O)CF(CF_3)_2$ during UV irradiation (sunlamps) of mixtures of 1.5 Torr of $C_2F_5C(O)CF(CF_3)_2$ in (■) 700, (▲) 200, or (●) 50 Torr of air diluent at 296 K. Lines are linear least-squares fits. The insert is a plot of the reciprocal of the photolysis rate versus the pressure of air diluent.

Figure 5 shows the loss of $C_2F_5C(O)CF(CF_3)_2$ following the irradiation (sunlamps) of mixtures containing 1.5 Torr of $C_2F_5C(O)CF(CF_3)_2$ in either 700 (squares), 200 (triangles), or 50 (circles) Torr of air diluent. It is clear from Figure 5 that as the total pressure of air is decreased, the rate of photolysis increases. This observation suggests that the photolytically excited state of $C_2F_5C(O)CF(CF_3)_2$ has a lifetime that is sufficiently long that collisions with diluent gas can cause significant quenching. This can be represented as follows:

$$C_2F_5C(O)CF(CF_3)_2 + h\nu \rightarrow [C_2F_5C(O)CF(CF_3)_2]^* \quad (24)$$

$$[C_2F_5C(O)CF(CF_3)_2]^* \rightarrow \text{photolysis products} \quad (25)$$

$$[C_2F_5C(O)CF(CF_3)_2]^* + M \rightarrow C_2F_5C(O)CF(CF_3)_2 + M^* \quad (26)$$

Assuming that processes 25 and 26 are the only loss mechanisms for $[C_2F_5C(O)CF(CF_3)_2]^*$, it can be shown that $1/J = 1/k_{24} + [k_{26}/(k_{24}k_{25})][M]$, where J is the observed photolysis rate, k_{25} and k_{26} are the rate constants for processes 25 and 26, and [M] is the pressure of the diluent gas. Least-squares analysis of the data in Figure 5 leads to values of $J = 8.5 \times 10^{-7}$, 2.1×10^{-6}, and $8.3 \times 10^{-6}\ s^{-1}$ in the presence of 700, 200, and 50 Torr of air. The insert in Figure 5 shows a plot of $1/J$ versus the pressure of diluent gas; the linearity of this plot is consistent with the simple Stern−Volmer-type analysis given above. It was not the intention in the present work to map out the details of quenching of the excited state of $C_2F_5C(O)CF(CF_3)_2$ by air diluent, and hence, the data in Figure 5 are rather sparse. Nevertheless, it is evident from Figure 5 that quenching of the excited state is significant and in one atmosphere of air leads to substantial reduction in the photolysis rate from that observed in the presence of little, or no, diluent.

To provide a means of translating the measured photolysis rate of $C_2F_5C(O)CF(CF_3)_2$ in the chamber to an estimate of its photolysis rate in the atmosphere, a series of experiments were conducted to measure the rate of photolysis of CH_3CHO in the chamber. The UV spectrum, photolysis quantum yield, and

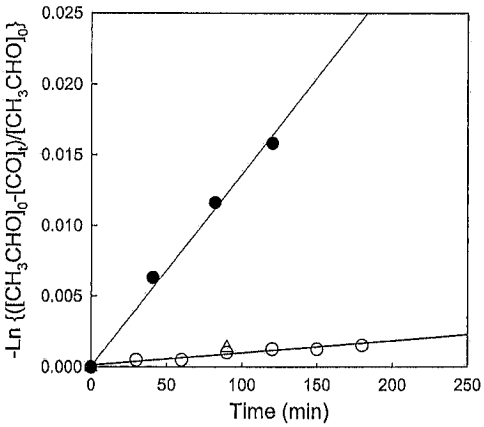

Figure 6. Loss of $^{13}CH_3{}^{13}CHO$ as a function of irradiation time using either sunlamps (filled symbols) or blacklamps (open symbols) of mixtures of $^{13}CH_3{}^{13}CHO$ in 700 Torr of air diluent at 296 K. Initial concentrations of $^{13}CH_3{}^{13}CHO$ were (●) 12 mTorr, (△) 30 mTorr, or (○) 40 mTorr.

photolysis lifetime of CH_3CHO in the atmosphere are well understood.[10,14] If the rate of $C_2F_5C(O)CF(CF_3)_2$ photolysis is measured relative to that of CH_3CHO, the known photolysis rate of CH_3CHO can be used as a scaling factor to provide an estimate of the atmospheric photolysis rate of $C_2F_5C(O)CF(CF_3)_2$. For the portion of the solar spectrum present in the troposphere, photolysis of CH_3CHO gives CH_3 and HCO radicals. Reaction of HCO radicals with O_2 gives CO.

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \quad (27)$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad (28)$$

As with $C_2F_5C(O)CF(CF_3)_2$, the photolysis of CH_3CHO was slow and difficult to measure directly in the chamber. For increased precision, the loss of CH_3CHO was measured indirectly by monitoring the formation of CO. To avoid potential complications caused by other sources of CO in the system, istopically labeled $^{13}CH_3{}^{13}CHO$ was used and the formation of ^{13}CO was monitored. Figure 6 shows the loss of $^{13}CH_3{}^{13}CHO$, inferred from the observed formation of ^{13}CO when mixtures containing $^{13}CH_3{}^{13}CHO$ in 700 Torr of air were irradiated using the sunlamps or blacklamps. Linear least-squares regressions to the data in Figure 6 give photolysis rates of 2.3×10^{-6} s^{-1} (sunlamps) and 1.5×10^{-7} s^{-1} (blacklamps). Comparing these values to the results obtained for $C_2F_5C(O)CF(CF_3)_2$ (6×10^{-7} s^{-1} for sunlamps and 1.0×10^{-7} s^{-1} for blacklamps), we can see that photolysis of CH_3CHO is 4 and 1.5 times more rapid than photolysis of $C_2F_5C(O)CF(CF_3)_2$ using sunlamps and blacklamps, respectively. The qualitative difference in the effectiveness of the two different types of fluorescent lamps is consistent with the relative overlap of their spectral output (see insert in Figure 4) with the spectra of $C_2F_5C(O)CF(CF_3)_2$ and CH_3CHO (see Figure 1).

From Figure 1, it is clear that the absorption cross sections of $C_2F_5C(O)CF(CF_3)_2$ are greater than those of CH_3CHO at all wavelengths transmitted by the Pyrex walls of the chamber. From the absorption cross section data alone, it would be reasonable to predict that $C_2F_5C(O)CF(CF_3)_2$ would photolyze more rapidly than CH_3CHO. Interestingly, the opposite is observed, namely, that $C_2F_5C(O)CF(CF_3)_2$ photolyzes more slowly than CH_3CHO. This observation indicates that the photolysis quantum yield for $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air at 296 K is significantly less than unity. This conclusion is consistent with the observation that the photolysis rate in 50 Torr of air diluent is approximately a factor of 10 greater than that in 700 Torr of air (see insert in Figure 5). A similar effect has been observed in studies of CH_3CHO in which the photolysis quantum yield decreases from 0.96 to 0.40 (for 300 nm radiation) and 0.74 to 0.15 (for 313 nm radiation) as the total pressure of air diluent is increased from 50 to 700 Torr of air.[10,15]

The solar flux at sea level and 20 km altitude in the atmosphere is given in the insert in Figure 1. The solar flux drops dramatically at wavelengths below 300 nm. For purposes of discussing the atmospheric photolysis of $C_2F_5C(O)CF(CF_3)_2$ and CH_3CHO, we need only consider the wavelength range 295−350 nm. The UV fluorescent lamps used in the present study provide a broad coverage of this spectral region. The sunlamps provide output rich in the blue part of this region, while light from the blacklamps is rich in the red part of the range. The atmospheric photolysis rate of CH_3CHO at 0.5 km altitude is 7×10^{-6} s^{-1} for a solar zenith angle of 0° and 5×10^{-6} s^{-1} for a solar zenith angle of 40°,[10] and CH_3CHO has an atmospheric lifetime with respect to photolysis of approximately 3−4 days. Upon the basis of the relative photolysis rates in the chamber, it seems reasonable to conclude that the lifetime of $C_2F_5C(O)CF(CF_3)_2$ with respect to photolysis will be 1.5−4 times that of CH_3CHO, that is, approximately 1−2 weeks. At this point, the approximate nature of the estimated photolysis lifetime should be stressed. A more precise determination would require a study of the photolysis quantum yield as a function of wavelength, diluent pressure, and temperature. Such a study is beyond the scope of the present study and is unlikely to change the important conclusion of the present work, namely, that photolysis is an effective process by which $C_2F_5C(O)CF(CF_3)_2$ is removed from the atmosphere.

3.4. Kinetics of Reaction of $C_2F_5C(O)CF(CF_3)_2$ with Cl Atoms and O_3. The reaction of $C_2F_5C(O)CF(CF_3)_2$ with Cl atoms was studied by relative rate experiments at Ford, in which CF_3OCF_2H was used as a reference compound for the Cl reaction:

$$Cl + C_2F_5C(O)CF(CF_3)_2 \rightarrow \text{products} \quad (29)$$

$$Cl + CF_3OCF_2H \rightarrow \text{products} \quad (30)$$

Reaction mixtures consisted of 1.8 mTorr of $C_2F_5C(O)CF(CF_3)_2$, 2.08 Torr of Cl_2, and 2.4 mTorr of CF_3OCF_2H in 700 Torr of N_2 diluent. UV radiation for 140 min typically led to no discernible loss (<1%) of $C_2F_5C(O)CF(CF_3)_2$, while the consumption of CF_3OCF_2H was 8−80%. Using the literature value of $k_{30} = (2.3 \pm 0.3) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1},[16] we derive an upper limit of $k_{29} < 1.7 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 296 K.

To investigate the reaction of O_3 with $C_2F_5C(O)CF(CF_3)_2$, a mixture containing 3 mTorr of $C_2F_5C(O)CF(CF_3)_2$ and 74 mTorr of O_3 in 700 Torr of air was introduced into the chamber. The mixture was allowed to stand in the dark in the chamber for 360 min. There was no discernible loss of $C_2F_5C(O)CF(CF_3)_2$ (<2%) during this period, while there was a small (9%) decrease in the ozone in the chamber, which we attribute to decomposition on the chamber walls. From this experiment, we derive an upper limit for the rate constant of reaction of O_3 with $C_2F_5C(O)CF(CF_3)_2$ of $k_{O_3} < 4 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1} at 296 K.

4. Conclusions

The results presented here comprise the first study of the atmospheric degradation mechanism of $C_2F_5C(O)CF(CF_3)_2$. There was no discernible reaction of $C_2F_5C(O)CF(CF_3)_2$ with

OH radicals, Cl atoms, or O_3. It seems likely that homogeneous gas-phase reactions do not play any role in the atmospheric loss of $C_2F_5C(O)CF(CF_3)_2$. The ultraviolet absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ is similar in shape and magnitude to that of CH_3CHO but is red-shifted by approximately 20 nm. The atmospheric lifetime of $C_2F_5C(O)CF(CF_3)_2$ with respect to photolysis is estimated to be 1−2 weeks. Photolysis of $C_2F_5C(O)CF(CF_3)_2$ in air gives $CF_3C(O)F$ and COF_2. $CF_3C(O)F$ will be incorporated into rain/cloud/seawater where it will undergo hydrolysis to give trifluoroacetic acid.[13] Similarly, COF_2 will undergo hydrolysis to give CO_2 and HF. At the concentrations expected in the environment, none of these degradation products is considered harmful. With an atmospheric lifetime of 1−2 weeks (or less if processes other than photolysis contribute), $C_2F_5C(O)CF(CF_3)_2$ will have a global-warming potential that, for all practical purposes, is negligible.

Acknowledgment. N.T. thanks the Japan Society for Promotion of Science for a fellowship for young scientists.

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Photolysis Study of Perfluoro-2-methyl-3-pentanone under Natural Sunlight Conditions

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The UV–vis and infrared absorption cross sections of perfluoro-2-methyl-3-pentanone ($CF_3CF_2C(O)CF(CF_3)_2$, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone), has been obtained, and a photolysis study was carried out under natural sunlight conditions in the European simulation chamber, Valencia, Spain (EUPHORE). The photolysis loss rate, J_{photol}, equaled $(6.4 \pm 0.3) \times 10^{-6}$ s^{-1} in the period of 10–14 GMT, July 14, 2003 in Valencia (0.5 W, 39.5 N) and corresponded to an effective quantum yield of photolysis of 0.043 ± 0.011 over the wavelength range of 290–400 nm; the error limits correspond to 2σ from the statistical analyses. The atmospheric lifetime of $CF_3CF_2C(O)CF(CF_3)_2$ is estimated to be around 1 week, and the global warming potential of the compound is negligible.

Introduction

The identification of suitable industrial alternatives to Halons is challenging due to the complex combination of performance, safety, and environmental properties required. Perfluoro-2-methyl-3-pentanone ($CF_3CF_2C(O)CF(CF_3)_2$, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone, heptafluoroisopropyl pentafluoroethyl ketone, perfluoro(ethyl isopropyl ketone), perfluoro-(4-methylpentan-3-one), NOVEC 1230 3M), hereafter abbreviated PFMP, is a new fire protection fluid intended for applications such as critical electronics housed in occupied spaces. PFMP has also been suggested as a solvent for certain lubricants, a surface-cleaning agent, a blowing agent, and a surface shield component in Mg or Mg-alloy casting.

As part of ongoing work in our laboratory concerning the atmospheric chemistry of fluorinated industrial replacement compounds we have recorded the UV–vis and infrared spectra of PFMP and report here our findings on the photolysis of PFMP under natural sunlight conditions in the large outdoor simulation chamber, EUPHORE, in Valencia, Spain. The UV–vis spectrum and results from a photolysis study employing fluorescent "sunlamps" and "blacklamps" have previously been reported by Taniguchi et al. (*1*) who also investigated the possible reactions of PFMP with OH radicals, Cl atoms, and O_3. They concluded that PFMP will be removed from the atmosphere by photolysis on a time scale of 1–2 weeks.

Experimental Section

UV–Vis Spectrum. Absorption cross sections in the UV–vis region were measured at 298 ± 2 K using an Agilent 8453E photodiode array spectrophotometer having a spectral resolution of 2 nm. The spectra were recorded in the wavelength range from 190 to 1100 nm at sampling intervals of 1 nm. The integration time was set to 0.5 s. The pressure of the pure PFMP vapor was in the range of 9–30 hPa and was measured using an MKS baratron-type 122A pressure transducer with a stated accuracy of ±0.15%. A gas cell of 8.0 ± 0.1 cm path length with quartz windows was used.

Infrared Spectrum. Infrared spectra of the pure gases at 298 ± 2 K were recorded in the region of 4000–400 cm^{-1} using a Bruker IFS 113v FTIR spectrometer employing a nominal resolution of 1.0 cm^{-1} and Blackman–Harris 3-term apodization of the interferograms. A Ge/KBr beam splitter was used to cover the spectral region. To ensure optical linearity, a DTGS detector was used. Eight single-channel spectra, each recorded with 32 scans, were averaged to yield one background or sample spectrum. A gas cell of 2.34 ± 0.02 cm equipped with windows of KBr was employed. The partial pressures of the gases in the cells were from 1 to 16 hPa and were measured using the MKS baratron pressure transducer as described before. The absorption cross sections were obtained from the absorbance spectra assuming that the gas was ideal and applying a baseline correction. The baseline correction was performed by subtracting a polynomial function, obtained by fitting the regions of the spectrum where no absorptions were expected.

The absorption cross section of a compound X at a specific wavenumber $\tilde{\nu}$ is given by $\sigma(\tilde{\nu}) = \{A_e\}/\{n_X\}l$, where $A_e(\tilde{\nu}) = -\ln\tau(\tilde{\nu})$ is the naperian absorbance, τ is the transmittance, n_l is the number density of X, and l is the path length where the absorption takes place. The integrated absorption cross section, S, is given as the integral of $\sigma(\tilde{\nu})$ over the absorption band or, as here, over regions of overlapping bands:

$$S = \int_{\text{band}} \sigma(\tilde{\nu})\, d\tilde{\nu} \qquad (1)$$

Experiments Performed at EUPHORE. A detailed description of the EUPHORE facility and the existing analytical instruments has been previously reported in the literature (*2–6*). The present photolysis experiments were carried out in a hemispherical outdoors simulation chamber of volume about 195 m^3 made of FEP foil with a thickness of 0.127 mm. The FEP foil has a transmission of more than 75% of the solar radiation in the wavelength range between 290 and 550 nm. The chamber was equipped with a Nicolet Magna 550 FTIR spectrometer coupled with a white-type multireflection mirror system for in situ analysis. The optical path length was 553.5 m. FTIR spectra were recorded every 10 min by adding 570 interferograms with a resolution of 1.0 cm^{-1}.

The photolysis of PFMP was studied in purified, dry air (dewpoint less than −20 °C) at T = 301–309 K (see Becker (*2*) for a description of the drying and purification system). The large volume of the chamber minimizes the effects of wall reactions, thus resembling the free troposphere as closely as possible. Unlike the typical laboratory smog chamber, purified air is constantly added to compensate for loss through connections and loss due to continuous sampling by ozone and NO_x monitors, and this has to be corrected for as dilution of the sample in the data analysis. The mixing

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10.1021/es048088u CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/13/2005

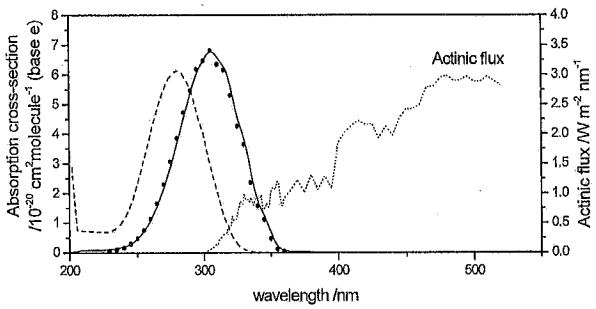

FIGURE 1. UV absorption cross sections of PFMP, 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone (full curve), and 2-pentanone (dashed curve). (●) Data from Taniguchi et al. (*1*). Dotted curve: actinic flux in the chamber at 15:20 (solar time).

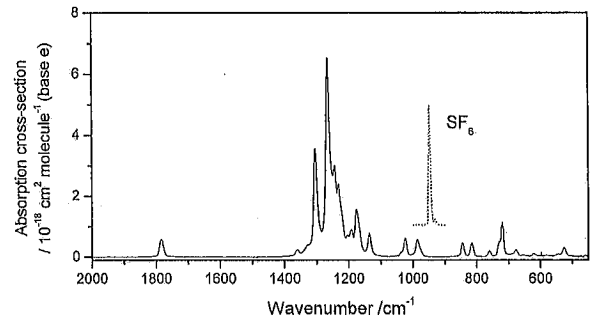

FIGURE 2. Infrared absorption cross section of PFMP (1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone) overlaid by the $\nu_3(F_{1u})$ band of SF_6.

ratio of PFMP in the chamber was initially ca. 1 ppm, and it may be reduced by photolysis (*2*) and dilution (*3*) as homogeneous gas-phase reactions do not play any role in the atmospheric loss (*1*).

$$\text{PFMP} + h\nu \rightarrow \text{Products} \qquad J_{obs} \qquad (2)$$

$$\text{PFMP} \rightarrow \text{Loss by sampling} \qquad k_{dilution} \qquad (3)$$

Approximately 20 ppb of SF_6 was added to the reaction chamber to determine the overall dilution rate coefficient, $k_{dilution}$:

$$SF_6 \rightarrow \text{Loss by sampling} \qquad k_{dilution} \qquad (4)$$

$$\ln\{[SF_6]_0/[SF_6]_t\} = k_{dilution}t \qquad (5)$$

where $[SF_6]_0$ and $[SF_6]_t$ are the initial SF_6 concentration and that after a time t, respectively.

Thus, the apparent photolysis rate coefficient of PFMP, J_{obs}, can be obtained from the expression:

$$\ln\{[\text{PFMP}]_0\}/\{[\text{PFMP}]_t\} = (k_{dilution} + J_{obs})t \qquad (6)$$

The effective quantum yield for the photolysis of the compound under study can be calculated according to the following expression:

$$\Phi_{eff} = J_{obs}/J_{max} \qquad (7)$$

where the maximum photolysis rate coefficient, J_{max}, is given by:

$$J_{max} = \int \sigma(\lambda)F(\lambda)\, d\lambda \qquad (8)$$

Here $\sigma(\lambda)$ is the absorption cross section (base e) of the compound in units of cm^2 $molecule^{-1}$ and $F(\lambda)$ is the solar actinic flux (photons cm^{-2} s^{-1}). The actinic flux was measured by a Bentham DM300 spectroradiometer as recently described by Wenger et al. (*6*), and the integration was carried out over the wavelength range of 290−400 nm.

Results and Discussion

UV−Vis Absorption Cross Section. The UV−vis absorption cross section of PFMP at 298 ± 2 K was determined by a least-squares fit of the data from three independent measurements in pure gas at different pressures. The obtained UV−vis absorption cross section (base e) is shown in Figure 1 (the absorption cross section is available in JCAMP format as Supporting Information). The absorption band corresponds to the weak $\pi^* \leftarrow n$ transition of the carbonyl group. When systematic errors in pressure measurements, temperature, optical path length, and instrumental drift are added to the 2σ error from the least-squares fit (0.6%), it is estimated that the absolute error limit of the integrated cross section is approximately 2%. For comparison, Figure 1 includes the recently published data by Taniguchi et al. (*1*) and the UV spectrum of 2-pentanone (*7*), $CH_3C(O)CH_2CH_2CH_3$, which is the only other ketone studied under similar conditions in the EUPHORE reactor (*8*). It is apparent that (i) the agreement between the two UV−vis data sets for PFMP is better than 5% in the region around the absorption maximum, (ii) the fluorinated ketone, PFMP, absorbs between 240 and 350 nm with a maximum around 305 nm and with an integrated absorption cross section apparently slightly larger than that of 2-pentanone (*7*), and (iii) the intensity maximum is red-shifted ca. 26 nm obviously caused by the electronegative substitutents in the α,α′-positions in analogy with the situation in fluorinated propanones (*9*).

Infrared Absorption Cross Section. The integrated cross section of the absorption bands were determined by plotting the integrated absorbance against the product of the number density and the path length. None of the regression lines had a y-intercept significantly different from zero. A least-squares method that forced the regression line through zero was therefore used to determine the absorption intensities. Quantified systematic errors are pressure measurements (0.15%), path length (0.90%), and temperature (0.67%). The IR absorption cross section (base e) of PFMP is shown in Figure 2 (the IR absorption cross section is available in JCAMP format as Supporting Information). The integrated absorption cross section over the 1880−480 wavenumber region is (40.5 ± 0.8) × 10^{-17} cm $molecule^{-1}$; the estimated uncertainty in the total absorption cross section of PFMP includes the additional 2σ error from the least-squares fit (0.7%) to the above-mentioned systematic errors.

We use the absorption cross section of HCFC-22, which has been critically evaluated by Ballard et al. (*10*), as a benchmark. Our measurements of HCFC-22 are constantly within 5% of the absorption intensities reported by Ballard and co-workers. In recent studies of a series fluorinated compounds (*11*−*13*), we demonstrated excellent agreement with previous results for the infrared cross sections. We therefore believe that our measurements of PFMP are not affected by any large systematic errors.

Effective Quantum Yield of Photolysis. A photolysis experiment with PFMP was carried out at the EUPHORE simulation chamber in Valencia, Spain (0.5 W, 39.5 N) during the month of July 2003. The removal of SF_6 and PFMP from the chamber was monitored by FTIR. The concentration of SF_6 was determined from the integrated intensity of the ν_3-(F_{1u}) band around 947.5 cm^{-1}, which does not overlap the PFMP absorption bands (see Figure 2). The relative concentrations of PFMP were determined by a spectral subtraction procedure involving the initial PFMP spectrum and a reference spectrum of water and limited to the carbonyl-

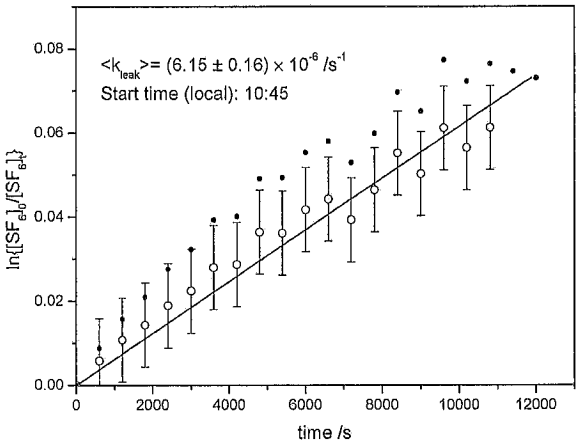

FIGURE 3. Plot of ln{[SF_6]$_0$/[SF_6]$_t$} vs time, showing the mass loss from the reactor (Teflon) to the surrounding: (●) uncorrected data; (○) data corrected for changes in (*P*, *T*) during the experiment.

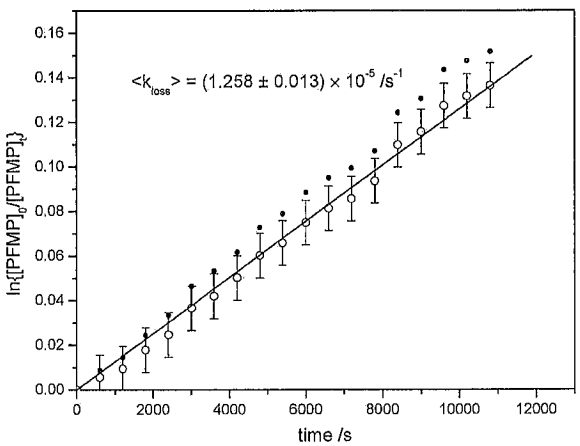

FIGURE 4. Plot of ln{[PFMP]$_0$/[PFMP]$_t$} vs time, showing the total loss from the reactor (Teflon) during photolysis: (●) uncorrected data; (○) data corrected for changes in (*P*, *T*) during the experiment.

stretching band (1820−1760 cm^{-1}); the carbonyl-stretching bands of the photolysis products CF_2O and CF_3CFO both fall at higher wavenumbers and do not overlap this band (*1*). The pressure and the temperature inside the chamber were not constant during the experiment. The observed reductions in SF_6 and PFMP concentrations were therefore corrected according to the changes in pressure and temperature using the ideal gas law—the corrections being less than 1.5%. From a least-squares analysis of the decay in SF_6 concentration (Figure 3), the dilution rate coefficient during the photolysis experiment was found to be $(6.15 \pm 0.16) \times 10^{-6}$ s^{-1} (2σ). Figure 4 presents the simultaneous decay of the PFMP concentration given as a plot of ln{[PFMP]$_0$/[PFMP]$_t$} versus the photolysis time, from which the total removal rate coefficient of PFMP was determined to be $(1.258 \pm 0.013) \times 10^{-5}$ s^{-1} (2σ)—in 3 h around 13% of PFMP was removed from the reactor. The data obtained (Figures 2 and 3) indicate that the total reduction in PFMP concentration during midday conditions in July was about twice the reduction in concentration of the inert tracer, SF_6. As there are no other known loss processes, the effective photolysis rate is found by correcting for dilution giving a value for J_{obs} of $(6.4 \pm 0.3) \times 10^{-6}$ s^{-1} (2σ) at July 14 in Valencia 2003. This corresponds to a lifetime of 44 h under conditions of atmospheric pressure with $\langle J_{NO_2} \rangle = 7.85 \times 10^{-3}$ s^{-1}. A conservative estimate of the atmospheric lifetime of PFMP with respect to photolysis is around 1 week. For comparison, Taniguchi et al. (*1*) estimated

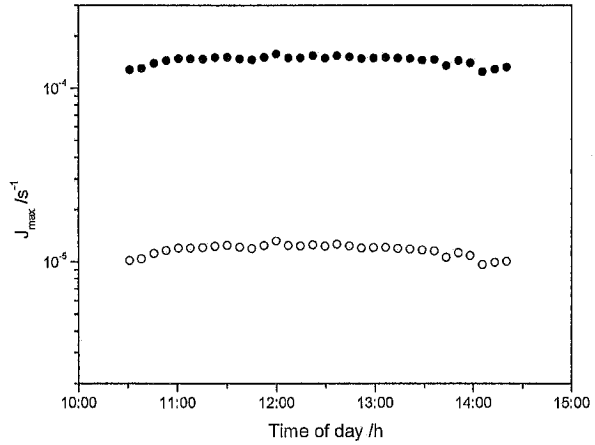

FIGURE 5. Plot of the calculated maximal photolysis rates, J_{max}, of PFMP (1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone, CF_3CF_2−C(O)−$CF(CF_3)_2$) (●) and 2-pentanone, CH_3−C(O)−CH_2CH_2-CH_3 (○) vs time of day (GMT solar) assuming a uniform quantum efficiency. The UV−vis data for 2-pentanone are taken from ref *7*.

the atmospheric photolysis lifetime of PFMP to be between 1 and 2 weeks from laboratory studies employing sunlamps. Although the integrated absorption cross section of PFMP is large, the short atmospheric lifetime makes the global warming potential of the compound negligible.

The maximum photolysis rate coefficient, J_{max} (see eq 8), during the experiment is shown in Figure 5, which also includes J_{max} for 2-pentanone for comparison—the only related ketone studied under similar conditions (*8*). J_{max} for PFMP varies between 1.24 and 1.57×10^{-4} s^{-1} with a time average during the experiment of 1.49×10^{-4} s^{-1}. The observed photolysis rate therefore corresponds to an effective quantum efficiency of photolysis under tropospheric sunlight conditions of $\Phi_{eff} = 0.043 \pm 0.011$ (2σ), which compares to 0.07 ± 0.1 for 2-pentanone (*8*). As shown by Taniguchi et al. (*1*) nonradiative (collision assisted) relaxation processes are extremely effective following the initial $S_0 \rightarrow S_1$ excitation. However, an effective fluorescence via the $S_1 \rightarrow S_0$ transition similar to the situation in CF_3CHO (*11*) cannot be ruled out.

Acknowledgments

This work is part of the project "Impact of Fluorinated Alcohols and Ethers on the Environment" (IAFAEE) and has received support from the CEC Environment and Climate program through Contract ENVK2-1999-00099. Fundación CEAM is supported by Generalidad Valenciana and Fundación Bancaixa.

Supporting Information Available

UV−vis and infrared absorption cross sections of 1,1,1,2,2,-4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone in JCAMP format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review December 3, 2004. Revised manuscript received August 15, 2005. Accepted September 13, 2005.

ES048088U

The large contribution of projected HFC emissions to future climate forcing

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Edited by Mark H. Thiemens, University of California at San Diego, La Jolla, CA, and approved May 14, 2009 (received for review March 13, 2009)

The consumption and emissions of hydrofluorocarbons (HFCs) are projected to increase substantially in the coming decades in response to regulation of ozone depleting gases under the Montreal Protocol. The projected increases result primarily from sustained growth in demand for refrigeration, air-conditioning (AC) and insulating foam products in developing countries assuming no new regulation of HFC consumption or emissions. New HFC scenarios are presented based on current hydrochlorofluorocarbon (HCFC) consumption in leading applications, patterns of replacements of HCFCs by HFCs in developed countries, and gross domestic product (GDP) growth. Global HFC emissions significantly exceed previous estimates after 2025 with developing country emissions as much as 800% greater than in developed countries in 2050. Global HFC emissions in 2050 are equivalent to 9–19% (CO_2-eq. basis) of projected global CO_2 emissions in business-as-usual scenarios and contribute a radiative forcing equivalent to that from 6–13 years of CO_2 emissions near 2050. This percentage increases to 28–45% compared with projected CO_2 emissions in a 450-ppm CO_2 stabilization scenario. In a hypothetical scenario based on a global cap followed by 4% annual reductions in consumption, HFC radiative forcing is shown to peak and begin to decline before 2050.

HCFC consumption | radiative forcing | scenarios

Global production and use of chlorofluorocarbons (CFCs) and halons have decreased significantly as a result of the phaseout schedules of the 1987 Montreal Protocol and its subsequent amendments and adjustments (1). The use of HCFCs and HFCs have increased as replacements for CFCs and halons in developed (non-A5) and developing (A5) countries that are parties to the Protocol (1, 2). HCFCs are low-ozone-depletion-potential substitutes for high-ozone-depleting-potential substances, particularly CFCs and halons, and were classified under the Protocol as "transitional substitutes" during the time it took to commercialize new ozone-safe alternatives and replacements. Ultimately, HCFCs will be phased out globally under the Montreal Protocol leaving much of the application demand for refrigeration, AC, heating and thermal-insulating foam production to be met by HFCs (2). The demand for HCFCs and/or HFCs in many applications is expected to increase in both developed and developing countries, but especially in Asia, in the absence of regulations. HFCs do not deplete the ozone layer but, along with CFCs and HCFCs, are greenhouse gases that contribute to the radiative forcing (RF) of climate (2, 3). Thus, the transition away from ozone depleting substances (ODSs) has implications for future climate.

The technical, economic and environmental trade-offs of replacing CFCs and HCFCs with HFCs and hydrocarbons have been analyzed for refrigerators, chillers, and AC (4–6). Hydrocarbons, ammonia and CO_2, which generally have lower Global Warming Potentials (GWPs) than HFCs, have been found suitable for systems with small refrigerant charges where a refrigerant leak would not pose an unacceptable flammability or toxicity risk and for industrial systems with large refrigerant charges expertly managed for fire and toxicity risk. HFCs are the preferred refrigerant in consumer products requiring a large charge, where hydrocarbon flammability is problematic (6). The use of HFCs is expected to be minor in many other applications because other low-GWP compounds and not-in-kind (i.e., non-halocarbon based) technologies are available. Overall, not-in-kind technologies are not expected to initially satisfy as large a fraction of future demand as was the case during the CFC phaseout (7).

Multiple scenarios of global HFC emissions are available from SRES (8) and IPCC/TEAP (2). These scenarios are now of limited use because of limited range of years (IPCC/TEAP) or outdated assumptions concerning the transition from HCFCs to HFCs (SRES). The SRES GWP-weighted emissions for refrigeration and AC are ≈20% below what we infer here from observed atmospheric mixing ratios for 2007 (*SI Text*). The 2007 HFC emissions for these applications from IPCC/TEAP (2) are somewhat higher, but this scenario ends in 2015. Others (9–11) have reported HFC scenarios similar to the SRES assumptions and do not consider a more detailed market development as discussed here.

We report new baseline scenarios for the consumption and emissions of HFCs to 2050 based only on existing policies. As in the SRES scenarios, the growth in demand for these compounds is based on GDP and population (8, 12). However, the new scenarios incorporate more recent information such as (*i*) rapid observed growth in demand, substantiated by atmospheric observations, for products and equipment using HCFCs and HFCs in developing countries (see *SI Text*); (*ii*) reported increases in consumption of HCFCs in developing countries; (*iii*) replacement patterns of HCFCs by HFCs as reported in developed countries; (*iv*) accelerated phaseout schedules of HCFCs in developed and developing countries, and; (*v*) increases in reported use of HFC-134a in mobile AC in developed and developing countries. The analysis results in significantly larger emissions in 2050 than could be expected based on previous projections.

Montreal Protocol regulation of HCFCs and other ODSs already has protected both ozone and climate (13, 14). HFCs are in the "basket of gases" regulated under the 1997 Kyoto Protocol (15), a global treaty to reduce developed-country emissions of greenhouse gases. We use the new emission scenarios and GWPs of HFCs to calculate their CO_2-equivalent emissions and RF contributions to global climate forcing. The results are compared with "business-as-usual" SRES CO_2 emissions and those required to stabilize CO_2 concentrations at 450 and 550 parts per

Author contributions: G.J.M.V., D.W.F., J.S.D., M.M., and S.O.A. designed research; G.J.M.V. performed research; G.J.M.V. analyzed data; and G.J.M.V., D.W.F., J.S.D., M.M., and S.O.A. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Freely available online through the PNAS open access option.

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This article contains supporting information online at www.pnas.org/cgi/content/full/0902817106/DCSupplemental.

Table 1. Replacement pattern of HCFC consumption by HFC consumption adopted for developing countries

Compound	Consumption	R-404A	R-410A	HFC-134a	HFC-245fa	Not-in-kind
HCFC-22	66.5%	35%	55%			10%
HCFC-141b	30.0%				50%	50%
HCFC-142b	3.5%			50%		50%
Total HFC consumption		23%	37%	2%	15%	23%

The replacement pattern is the same as found for developed countries based on a DuPont analysis*. Consumption values represent developed country usage. R-404A is a blend of HFC-143a (52%), HFC-125 (44%), and HFC-134a (4%). R-410A is a blend of HFC-32 (50%) and HFC-125 (50%). HFC-245fa is as surrogate for both it and HFC-365mfc, an alternative compound, for insulating foam production. Not-in-kind refers here to nonfluorocarbon applications or alternative technologies.

million (ppm) (16, 17). We also consider a range of hypothetical mitigation options, some of which reflect current policy proposals, to demonstrate how projected consumption and, hence, RF in 2050 could be reduced. Finally, the need to consider the potential for changes in overall energy efficiency in HFC and HCFC applications is discussed.

New HFC Baseline Scenarios

The growth rates for population and GDP in developed and developing countries for the new HFC baseline scenarios were adopted from the 4 SRES storylines (A1, A2, B1, and B2). The scenarios include HFC-134a, HFC-152a, HFC-245fa, and HFC-365mfc and the blends R-404A and R-410A (see Table 1, Table S1, and *SI Text*).* The use and emissions of other HFCs (e.g., HFC-227ea, HFC-236fa, and HFC-43–10mee) are currently small and are not included in the scenarios. Emissions and atmospheric mixing ratios of HFCs are calculated for the baseline scenarios based on the principles that for each HFC (*i*) annual global demand, production, and consumption are equal, (*ii*) annual consumption is added to individual compound banks for each applications, (*iii*) constant emission factors prescribe the fractions annually released from the respective banks, and (*iv*) demand is not constrained by new regulations. The release rates from banks, which depend on the application, cause time delays of years to decades between consumption and emissions (see *SI Text*).

The new baseline scenarios use HCFC consumption data (1) from 1989 to 2007 as the starting point for the demand for HCFCs in developing countries. Consumption in developing countries increased from 1989 to 2007 by ≈20% per year, only in part due to CFC consumption decreases over this period (Fig. 1*A*). The total consumption of CFCs + HCFCs (in kilotons per year) in developing countries increased by ≈8% per year from 1998 to 2007, larger than the mean annual increase in GDP from 1990 to 2010 of 4–6% per year in Asia, Africa and Latin America in the SRES scenarios. These increases in consumption are confirmed by long-term growth and recent acceleration of growth in observed atmospheric mixing ratios of HCFCs (18, 19). Recent changes in northern-latitude observations are consistent with less developed country use and more developing country use of HCFCs (18). In the new scenarios, HCFC consumption in developing countries from 2003 to 2007 is extrapolated linearly through 2012, after which the Montreal Protocol sets limits on HCFC consumption.

The demand for HCFCs in developing countries is assumed to grow by 3.8–6.3% per year, proportional to SRES GDP, from 2013 to 2050 (8, 12). The difference between the HCFC demand and the Montreal Protocol limits is satisfied in the scenarios with HFCs and not-in-kind replacements (Fig. 1) according to the replacement pattern found in developed countries (Table 1). HCFC consumption is divided among HCFC-22 (66.5%), HCFC-141b (30%), HCFC-142b (3.5%), based on the average distribution found by UNEP in developing countries between 2002 and 2006 (20). The resulting HFC consumption is limited, per application, to the per capita consumption of HFCs projected for the USA in 2020, the year in which the developed-country HCFC phaseout is virtually complete. Increases in the fraction of not-in-kind replacements for HCFC applications beyond the value in Table 1 (23%) would reduce projected HFC emissions.

The new baseline scenarios include the accelerated HCFC phaseout agreed to by the Montreal Protocol Parties in September 2007 (21). Under the agreement, HCFC consumption in developing countries will be frozen in 2013 at the average production levels in 2009–2010. More importantly, the Parties agreed to cut production and consumption in developing countries by 10% in 2015, 35% by 2020 and 67.5% by 2025 with the phaseout virtually complete in 2030. Before the 2007 agreement, developing countries could maintain 2015 consumption levels until 2040. The HCFC cumulative emissions reduction attributable to the accelerated phaseout is estimated to be 12–15 $GtCO_2$-eq (22).

Developed countries have agreed to reduce HCFC consumption by 75% in 2010 and 90% in 2015 with the phaseout virtually complete in 2020. The HCFC phaseout is already mostly completed in Europe and Japan and well on its way in the USA. The consumption of HFCs in developed countries in the baseline scenarios (Fig. 1) starts with the reported HFC sales in the European Union (EU) (23) and in Japan (see *SI Text*) in 2007 and projected demand for HFCs in the USA for 2007 to 2020 (24). The HFC demand in Europe is increased annually by 2% per year and in Japan by 2.7% per year from 2008 to 2020 to account for the final conversion of HCFCs to HFCs and population growth (see *SI Text*). Annual HFC demand increases in the USA by an average of 7.4% per year from 2008 to 2020 (24). From 2020 to 2050 the consumption grows proportional to the population following SRES (growth range of 0.1–0.4% per year). The annual total consumption in developed countries is defined as the sum in the USA, Europe, and Japan increased by 17% to account for the HFC demand in other developed countries.

Projections for HFC-134a are calculated separately from the other HFCs. The baseline scenarios take into account rapidly growing consumption of HFC-134a for mobile AC. Globally >80% of 4-wheel passenger cars and commercial vehicles are equipped with AC systems that use HFC-134a (2, 25). In developed countries ≈50% of the annual consumption of HFC-134a is for the manufacture and service of mobile AC. The baseline scenario takes into account that in Europe the use of HFC-134a for mobile AC in new cars will be phased out between 2011 and 2017 (26). HFC-134a must be replaced by refrigerants with a GWP (100-year) <150. The consumption of HFC-134a for mobile AC in developing countries is estimated based on of the number of vehicles in 2006, the average lifetime of the vehicles (15 years), the emission of HFC-134a per vehicle over its lifetime (1,400 g), and a conservative 80% market penetration of mobile AC systems in new vehicles (25). The consumption of HFC-134a

*McFarland M (2008) Potential climate benefits of a global cap and reduction agreement for HFCs. Presentation at 20th meeting of the Parties to the Montreal Protocol, Doha, Qatar.

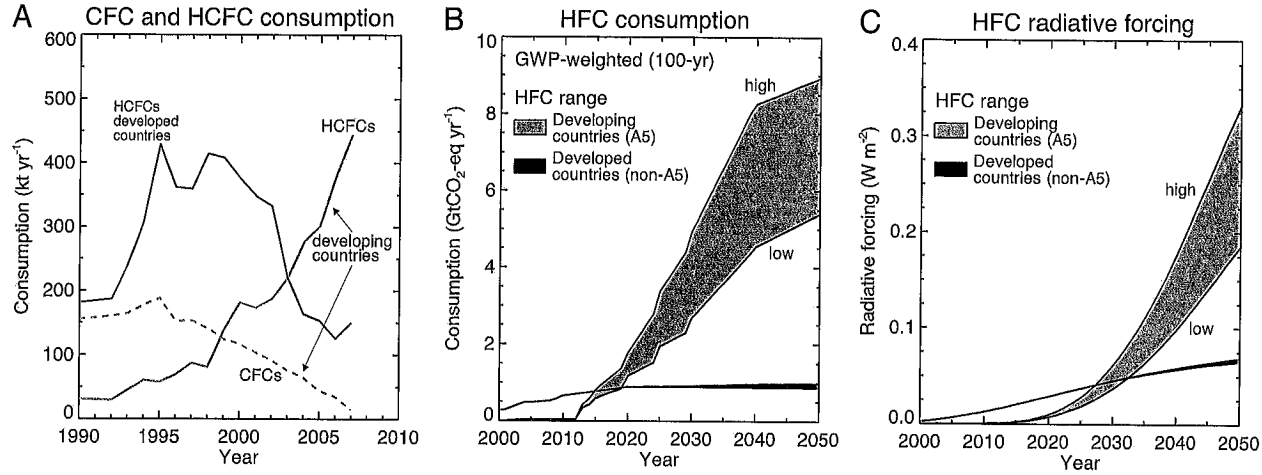

Fig. 1. CFC and HCFC consumption (*A*), HFC consumption (*B*), and HFC RF (*C*) for 2000–2050 in developing (A5) and developed (non-A5) countries. The CFC and HCFC mass consumption values in *A* are derived from reported data (1). The shaded regions for GWP-weighted consumption in *B* and RF in *C* are bounded by high and low limits as defined by the upper and lower ranges of the baseline scenarios in both developed and developing countries. The consumption values expressed in equivalent $GtCO_2$ per year in *B* are sums over the consumption of individual HFC compounds each multiplied by their respective GWP (100-year time horizon) (3).

for this application grows in the scenarios with the same rate as for other applications.

The baseline scenarios do not include HFC-23 because its use as a substitute for ODSs is negligible. Estimated future demand for HFC-23, which is an unintentional byproduct in the production of HCFC-22, is small compared with other leading HFCs, especially past 2015 (2, 27). Nevertheless, continued emissions of HFC-23 have significant potential to contribute to climate forcing because of its large GWP [14,800 (100-year)].

GWP-Weighted Consumption and Emissions

The new HFC baseline scenarios are shown in Figs. 1 and 2 as consumption, emissions, and RF values between 2000 and 2050. Consumption and emissions are scaled to CO_2-equivalent values, using 100-year GWPs (3) (Table S2). The high and low limits of the HFC ranges shown in the figures follow from the differences in GDP and population growth in the underlying SRES scenarios. The high end of the range for developing countries follows A1 and the low end follows A2, both determined primarily by GDP. For developed countries the range, driven primarily by population, follows A2 on the high end and B2 on the low end. Per-capita HFC demand (i.e., market penetration) is expected to saturate in developed country markets in the next decade and in developing countries *ca.* 2040 at the high end of the scenario range. Total HFC GWP-weighted consumption grows strongly from 2012, primarily in developing countries, reaching 6.4–9.9

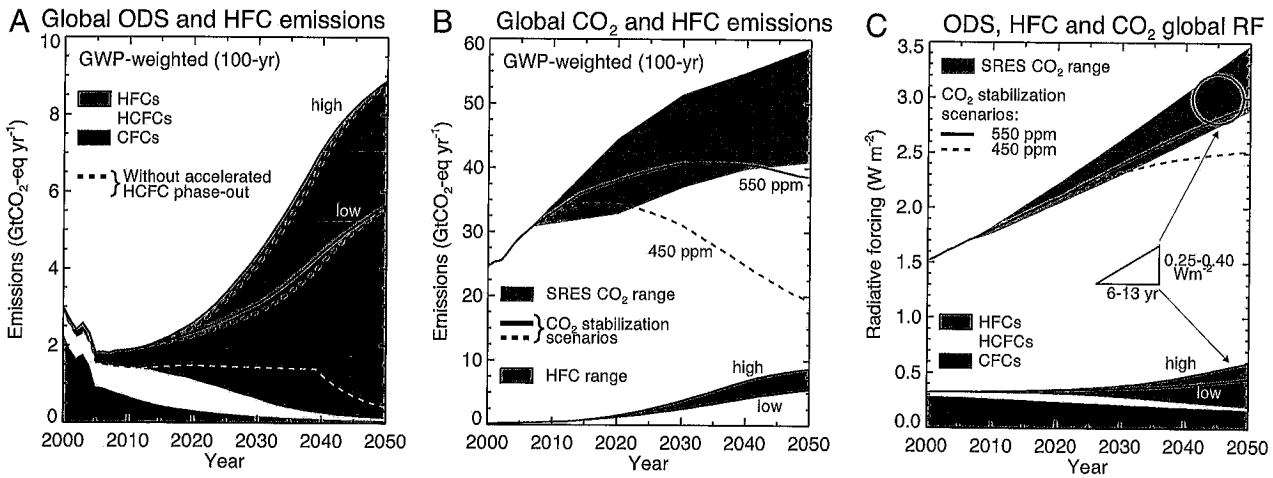

Fig. 2. Global ozone-depleting substances (ODSs) and HFC emissions (*A*), global CO_2 and HFC emissions (*B*), and ODS, HFC, and CO_2 global RF (*C*) for the period 2000–2050. Global emissions are the total from developing and developed countries. The CFC data include all principal ODSs in the Montreal Protocol except HCFCs. The emissions of individual gases are multiplied by their respective GWPs (direct, 100-year time horizon) to obtain aggregate emissions expressed in *A* and *B* as equivalent $GtCO_2$ per year (3). The color-shaded regions show emissions and RFs as indicated in the panel legends. The high and low labels identify the upper and lower limits, respectively, in the global baseline scenarios. The dashed lines in *A* show the HCFC and HFC scenario values calculated without the emission changes caused by the 2007 accelerated HCFC phaseout. Shown for reference in *B* and *C* are emissions and RF for the range of SRES CO_2 scenarios and the 450- and 550-ppm CO_2 stabilization scenarios (16, 17). The CO_2 data from 2000 to 2007 are based on reported emissions and observed concentrations. The triangle in *C* shows the range of HFC RF in 2050 from the baseline scenarios compared with the range in years needed to obtain the same RF change from CO_2 emissions in the SRES scenarios near 2050.

Table 2. Consumption, emissions and RF, and a comparison of RF with CO_2 RF increases for HFC baseline and mitigation scenarios

Scenario	Consumption in 2013–2050 ($GtCO_2$-eq)*	Emissions in 2013–2050 ($GtCO_2$-eq)*	RF in 2050 ($W\ m^{-2}$)	Years of CO_2 RF increase equal to HFC RF change 2050§	
				IPCC/SRES CO_2 Scenerios	IPCC 550-ppm CO_2 stabilization scenario
Totals for baseline scenario range	146–231	110–170	0.25–0.40	6–13	11–18
		Mitigation scenarios			
Reductions from Lieberman-Warner proposal for USA	13–14	10–11	0.024–0.026	0.6–1.0	1.1–1.2
Reductions from global ban mobile AC, EU style regulation†	7–10	6–8	0.017–0.025	0.4–0.8	0.8–1.1
Reduction from global mitigation					
Freeze from 2014/2024‡	69–118	45–77	0.12–0.20	3–7	5–9
Freeze & −2% $year^{-1}$ from 2014/2024‡	91–148	59–97	0.15–0.25	3–9	7–11
Freeze & −4% $year^{-1}$ from 2014/2024‡	106–171	70–113	0.18–0.30	4–10	8–13

*The values are multiplied by their GWPs (100-year time horizon) to obtain equivalent $GtCO_2\ year^{-1}$. Range corresponds to high and low limits in the range of baseline scenarios (see text).

†Limits for European cars on the use of HFCs with a GWP >150 in mobile AC is included in the baseline scenario with an estimated reduction in total consumption of 1.7 $GtCO_2$-eq from 2013–2050.

‡Freeze starts in 2014 in developed and in 2024 in developing countries, both at the previous year's level. Reduction of 2%/year and 4%/year are relative to the freeze level.

§Calculated as (years) x (annual growth rate of CO_2 RF in 2050) = (HFC RF of RF reduction in 2050) for each scenario.

$GtCO_2$-eq per year in 2050 (Fig. 1*B*). The consumption in developing countries becomes larger than that in the developed countries before 2020 and exceeds that in developed countries by up to 800% by 2050, a reflection of larger populations and higher GWP growth in these countries. With emissions closely following consumption, but lagging by a few years, total GWP-weighted HFC emissions are 5.5–8.8 $GtCO_2$-eq per year by 2050 (Fig. 2*A* and *B*). Total direct-GWP-weighted emissions of CFCs + HCFCs decrease between 2000 and 2050, whereas HFC emissions monotonically increase, exceeding those of CFCs + HCFCs after *ca.* 2020 (Fig. 2*A*). Global HFC consumption (mass basis) in 2050 in the baseline scenario is 2.3–3.5 times the 1989 peak value of global CFC + HCFC consumption.

The total GWP-weighted HFC emissions for the new baseline scenarios are significantly larger than those of SRES by 2020 (Fig. S1*a*). In 2050, the comparable SRES emissions are in the range of 1.3–2.3 $GtCO_2$-eq per year (13, 27), a factor of 4 lower. Lower SRES values are expected based on historical events and current market information as noted in the Introduction. More specifically, the greater emissions in the new baseline scenarios are largely the result of higher starting points (2008) for HFC consumption in combination with the use of HFCs with higher GWPs (*SI Text*). The new scenarios assume consumption of the refrigerant blends R-410A and R-404A in some applications instead of HFC-134a in most applications as was assumed in SRES. HFC-125 and HFC-143a are the primary components of R-410A and R-404A. These blends have higher GWPs than HFC-134a (see *SI Text*), thereby increasing the weighted emissions. The larger use of R-410A and R-404A in developing countries is assumed to follow the pattern in developed countries (6) as supported by emissions of the component HFCs derived from atmospheric concentrations observed through 2007. The GWP-weighted emissions in 2007 of HFC-125 and HFC-143a derived from atmospheric measurements are ≈0.068 and 0.064 $GtCO_2$-eq per year, respectively; these values are 2–3 times larger than SRES values of 0.028 and 0.027 $GtCO_2$-eq per year, respectively (see *SI Text*). These higher values raise the starting point for the 2050 projections above SRES values and, hence, all future values. The GWP-weighted emissions of HFC-134a derived from observed atmospheric concentrations are ≈0.18 $GtCO_2$-eq per year, slightly lower than the 0.20 $GtCO_2$-eq per year in SRES.

In adopting the accelerated phaseout of HCFCs in 2007, the Montreal Protocol Parties agreed to promote the use of HCFC alternatives that minimized the impact on climate (21). The significant influence of the acceleration on HCFC emissions in the next few decades is shown in Fig. 2*A*. In contrast, the influence of the accelerated phaseout on the projected emissions of CFCs + HCFCs + HFCs is small, with direct-GWP-weighted increases between 2020 and 2050 bounded by 0.4 $GtCO_2$-eq per year for both the high and low range limits. The small overall impact results because the accelerated HCFC phaseout, whereas it increases the replacement rate of HCFCs with HFCs, does not mandate the use of replacement compounds with overall lower GWPs. The replacement pattern in Table 1 causes the average GWP of HFCs consumed after the phaseout to be larger than the average of the replaced HCFCs (Table S2).

The new scenario results are put into context by comparing to projected global CO_2 emissions. In 2050 in the 4 SRES scenarios (i.e., no adoption of a CO_2 stabilization target), CO_2 concentrations will be >500 ppm and rising, and emissions will be 40–60 $GtCO_2$ per year (27). Projected HFC emissions are 9–19% of these CO_2 values. Instead, if the scenarios are chosen to be those of long-term CO_2 stabilization at atmospheric mixing ratios of 450 and 550 ppm (16, 17), the projected HFC emissions in 2050 are 28–45% and 14–23%, respectively, of CO_2 emissions (Fig. 2*B*). These percentages would increase beyond 2050, without HFC regulation or even with constant HFC emissions, because CO_2 emissions continue to decrease monotonically in these stabilization scenarios.

These climate-forcing comparisons, using GWPs with a 100-year time horizon yield an HFC consumption of 6.4–9.9 $GtCO_2$-eq per year in 2050 (Fig. 1*B*). If, instead, a 20-year time horizon is used, the consumption increases to 12.6–20.0 $GtCO_2$-eq per year. With a 500-year time horizon, the consumption decreases to 2.1–3.2 $GtCO_2$-eq per year. The climate forcing significance of a given time series of HFC emissions is highly sensitive to the time-horizon assumed because the HFC lifetimes (Table S2) are short compared with the CO_2 lifetime (≈100–1000s years).

Radiative Forcing

Calculated RFs provide a direct measure of the climate influence of greenhouse-gas accumulation in the atmosphere. RF

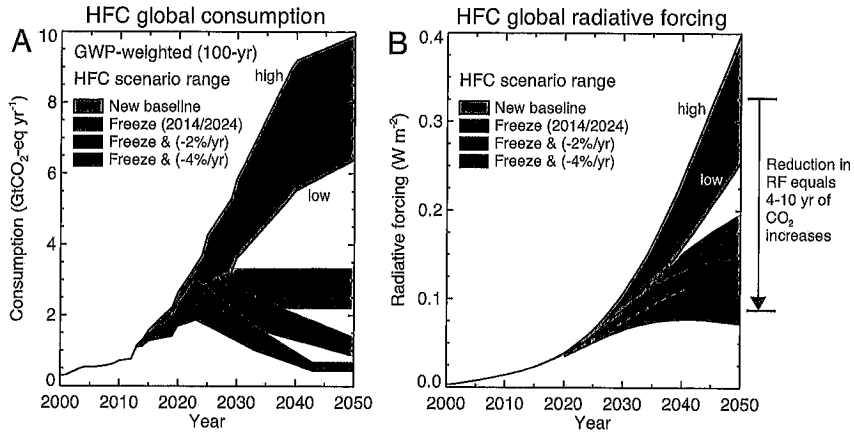

Fig. 3. Global HFC consumption (*A*) and RF (*B*) for the new baseline scenarios and chosen mitigation scenarios for the period 2000–2050. The baseline scenarios (red) represent global HFC values (i.e., the sum of developing and developed country values in Fig. 1). The consumption values in *A* are multiplied by their GWPs (100-year time horizon) to obtain equivalent $GtCO_2$ per year (3). Three mitigation scenarios are shown: a freeze in consumption in 2014 for developed countries and in 2024 for developing countries at the previous year's level (green); and 2% per year (blue) and 4% per year (purple) annual decreases relative to the freeze level. The reduction of consumption in the mitigation scenarios has a maximum of 80%.

values are derived from atmospheric concentrations of contributing gases and their radiative efficiencies and do not depend on their GWPs. The projected RF from global HFCs monotonically increases throughout the baseline scenarios (Fig. 1*C* and Fig. S1*b*). The RF contribution from developing countries surpasses that of developed countries around 2030 (Fig. 1*C*), ≈10 years later than found in the comparison of GWP-weighted emissions (Fig. 1*B*). In 2050, the RF of global HFCs is in the range of 0.25–0.40 $W \cdot m^{-2}$, which is more than a factor of 3 larger than SRES HFC values (Fig. S1*b*). In a comparison with the SRES CO_2 scenarios in 2050, the HFC RF fraction is 7–12% of the CO_2 values. The HFC RF in 2050 is equal to 6–13 years of RF growth from CO_2 in the 2050 time frame (Table 2). In the comparison with the 450- and 550-ppm CO_2 stabilization scenarios the HFC fraction increases to 10–16% and 9–14%, respectively (Fig. 2*C*).

HFC Mitigation Scenarios

The potentially large contribution of HFC emissions to future climate forcing in the coming decades has attracted the attention of policymakers seeking climate protection. A recent regulatory development that influenced the new HFC scenarios is the EU F-gas directive on mobile AC (26) as discussed above. Other regulatory actions that might affect future emissions include: USA cap-and-reduction proposals on HFCs, the intention of the European Commission to reduce HFC emissions through a climate treaty (28), and proposals of individual states in the USA. In addition, the Montreal Protocol Parties have expressed concern over the potential future climate contribution of HFCs (29).

Five modifications to the new baseline scenarios illustrate the impact of potential future regulatory actions. The first is the cap and reduction of HFC consumption in the USA proposed in the Lieberman–Warner (LW) Climate Security Act (30). In LW, HFC CO_2-eq consumption in the USA is reduced in steps between 2012 and 2040 to achieve a 70% reduction relative to a predefined 2012 level. The second is a global phaseout between 2011 and 2017 of mobile-AC refrigerants with a 100-year GWP >150, as is in place in the EU. The third is a freeze in HFC consumption in developed countries in 2014 and in developing countries in 2024, each at the previous year's level. Adopting a later freeze date for developing countries follows the practice of the Montreal Protocol. The fourth and fifth scenarios start with the 2014/2024 freeze followed by annual decreases in consumption of 2% per year and 4% per year, respectively, with a maximum reduction of 80%. The GWP-weighted emissions and RF results for these scenarios are shown in Fig. 3 and Table 2.

The LW scenario reduces cumulative GWP-weighted HFC consumption by 13–14 $GtCO_2$-eq over the 2013–2050 period and yields a small reduction in RF of ≈0.025 $W \cdot m^{-2}$ in 2050. The global ban on high-GWP HFCs in mobile AC reduces consumption by 7–10 $GtCO_2$-eq over the 2013–2050 period and RF by 0.017–0.025 $W \cdot m^{-2}$ in 2050. The ranges result from the variation in GDP and population growth in the baseline scenarios. Both of these mitigation scenarios yield an RF reduction that is equal to ≈0.4–1 year of CO_2 RF growth in the 2050 time frame. The global-freeze scenario yields reductions in cumulative consumption of 69–118 $GtCO_2$-eq over the 2013–2050 period and in RF of 0.12–0.20 $W \cdot m^{-2}$ in 2050. The freeze followed by 4% per year annual decreases in consumption yields reductions of 106–171 $GtCO_2$-eq over the 2013–2050 period and 0.18–0.30 $W \cdot m^{-2}$ by 2050. The latter reduction corresponds to 4–10 years of CO_2 RF growth in the 2050 time frame using the SRES scenarios or 8–13 years of CO_2 RF growth, using the 550-ppm CO_2 stabilization scenario. With the 4% per year annual decreases, HFC RF reaches a peak *ca.* 2040 and is decreasing before 2050 (Fig. 3*C*). Thus, in the scenarios considered here, a global freeze followed by modest annual reductions in both developed and developing countries is more effective in limiting the RF contribution from HFCs than is a single regional cap and reduction of HFCs.

The example mitigation scenarios presented here limit consumption of HFCs, not emissions. Mitigation options limiting consumption, as used in the Montreal Protocol, and those limiting emissions (containment), as in the Kyoto Protocol, have different implications. These different policy strategies for HFCs in refrigeration and AC have been explored for Germany (31). The comparison showed that containment strategies are generally more effective in reducing emissions in the short term, whereas strategies based on consumption limits (as in a phaseout or phasedown) have the potential for greater reductions in the long term. With limits on emissions, the banks of HFCs generally increase implying increased importance of bank management, recovery, and destruction. Limits on consumption are expected to stimulate containment in the short term and development and deployment of new technologies in the longer term. Furthermore, limits on consumption are easier to enforce with only a few producers worldwide compared with limits on emissions with

hundreds of millions of pieces of equipment and, hence, sources of emissions.

Importance of Energy Efficiency

In the analysis of the new scenarios, only the direct contribution to climate forcing due to HFC emissions was considered. Indirect climate forcings associated with HFC or other halocarbon usage derive from the energy used or saved during the application or product lifetime and energy used to manufacture the product, including the HFC it uses. For example, insulating foam products in buildings and appliances reduce energy consumption and refrigeration, and AC systems consume energy over their lifetimes. Analyses of the total potential climate impact of specific refrigeration and AC systems, for example, can be estimated by life cycle climate performance models that account for all direct and indirect contributions (2, 25, 32). Thus, an evaluation of the total climate forcing resulting from the global transition from HCFCs to HFCs and possible HFC mitigation scenarios requires consideration of both direct and indirect impacts over all associated halocarbon and not-in-kind application lifecycles.

ACKNOWLEDGMENTS. We thank Stephen A. Montzka, Benjamin R. Miller, Stella Papasavva, Gian-Kasper Plattner, John Rugh, Madhava Sarma, and Zenta Senoo for providing data and/or for comments on the manuscript. The views presented in this article are the views of the authors and do not necessarily represent the views of the organizations where they are employed.

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EUROPEAN COMMISSION

PRESS RELEASE

Brussels, 7 November 2012

Climate action: Commission proposes significant reduction in emissions of climate-warming fluorinated gases

The European Commission took an important step today towards long-term climate objectives by presenting a proposal to significantly reduce emissions of fluorinated gases (F-gases). Emissions of F-gases, which have a warming effect up to 23,000 times more powerful than carbon dioxide, have risen by 60% since 1990, while all other greenhouse gases have been reduced. The proposed Regulation aims to reduce F-gas emissions by two-thirds of today's levels by 2030. It also bans the use of F-gases in some new equipment, such as household fridges, where viable more climate-friendly alternatives are readily available.

F-gases are commonly used in refrigeration and air conditioning, as well as in electrical equipment, insulation foams, aerosol sprays and fire extinguishers. They leak into the atmosphere from production plants, from appliances they are used in, and when such appliances are thrown away.

Connie Hedegaard, EU Commissioner for Climate Action, said: "*I am proud to present this new initiative just when we are celebrating the 25th anniversary of the Montreal Protocol. By limiting the amount of f-gases that can be sold in the EU, this new legislation will benefit the climate and create great business opportunities. Our existing legislation has successfully broken a growing trend in emissions and driven technological innovation. Now that more climate-friendly products can be made, we go one step further in reducing emissions from f-gases cost-effectively*"

Today's proposal introduces a phase-down measure that from 2015 limits the total amount of the most significant group of F-gases - Hydrofluorocarbons (HFCs) – that can be sold in the EU and reduces this in steps to one fifth of today's sales by 2030. This measure will build on the successful phasing out of ozone-depleting substances which was achieved in the EU 10 years ahead of the schedule agreed internationally.

The EU supports global action on HFCs under the Montreal Protocol. The proposed measure anticipates and facilitates agreement on a global phase-down of consumption and production of HFCs which is to be discussed at the 24th Meeting of the Parties to the Montreal Protocol later this month. Also it reinforces the call at the climate change conference under the United Nations Framework Convention on Climate Change in Doha later this month for urgent actions on HFCs from other countries to close the gap between the necessary emission reductions by 2020 and currently envisaged mitigation actions.

With the right legal framework in place, EU consumers and commercial users of equipment can drive the change and spur technological development in all sectors that use F-gases today. This will lead to increased market shares for those companies seizing the opportunity to develop climate-friendly products and equipment. Recent studies show that a number of alternatives exist that are technically sound, safe to use, cost-efficient and can lead to energy savings.

The proposal will replace the existing Regulation on fluorinated greenhouse gases which requires companies to take a range of measures to reduce leaks from equipment containing F-gases and to recover the gases at the end of the equipment's lifetime. The current Regulation also established requirements on training and certification for personnel involved in servicing equipment, labelling of F-gas equipment, reporting on production, imports and exports of F-gases as well as some bans in a few specific areas. All of these requirements are maintained and/or strengthened in the new proposal.

Next steps

The proposal will be submitted to the European Parliament and the Council for discussion and adoption under the ordinary legislative procedure.

Background

The European Commission's low-carbon roadmap lays out a cost-efficient way to achieve the necessary reduction in emissions required under a global effort to limit warming to 2 degrees Celsius above pre-industrial levels. In order to achieve this objective, all sectors and greenhouse gases must contribute.

The roadmap envisages a reduction of emissions of over 70% by 2030 for the industrial sector that includes F-gases. The new proposal has been designed to achieve these savings, representing a cost-efficient contribution from the F-gas sector to the overall economic effort needed to avoid more costly consequences of climate change in the future.

Further information

DG Climate Action, F-gas page:

http://ec.europa.eu/clima/policies/f-gas/index_en.htm

EEA monitoring report on F-gases:

http://www.eea.europa.eu/highlights/potent-greenhouse-gases

EEA greenhouse gas data viewer:

http://www.eea.europa.eu/highlights/pressroom/data-and-maps/data/data-viewers/greenhouse-gases-viewer

See also MEMO/12/840 (questions & answers)

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UNITED
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EP

UNEP/OzL.Pro.WG.1/32/6

Distr.: General
10 May 2012

Original: English

United Nations
Environment
Programme

Open-ended Working Group of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer
Thirty-second meeting
Bangkok, 23-27 July 2012
Item 11 of the provisional agenda*
Proposed amendments to the Montreal Protocol

Proposed amendment to the Montreal Protocol

Note by the Secretariat

Pursuant to paragraph 2 of Article 9 of the Vienna Convention for the Protection of the Ozone Layer, the Secretariat is circulating in the annex to the present note a joint proposal submitted by Canada, Mexico and the United States of America to amend the Montreal Protocol in respect of hydrofluorocarbon phase-down. The proposal is being circulated as received and has not been formally edited by the Secretariat.

* UNEP/OzL.Pro.WG.1/32/1

Text of HFC Phasedown Amendment Proposal

Article I: Amendment

A. Article 1, paragraph 4

In paragraph 4 of Article 1 of the Protocol, for the words:

"Annex C or Annex E"

there shall be substituted:

"Annex C, Annex E or Annex F"

B. Article 2, paragraph 5

In paragraph 5 of Article 2 of the Protocol, for the words:

"and Article 2H"

there shall be substituted:

"Articles 2H and 2J"

C. Article 2, paragraph 5 ter

The following paragraph shall be added after paragraph 5 bis of Article 2 of the Protocol:

"5 ter. Any Party not operating under paragraph 1 of Article 5 may, for one or more control periods, transfer to another such Party any portion of its calculated level of consumption set out in Article 2J, provided that the calculated level of consumption of controlled substances in Annex F of the Party transferring the portion of its calculated level of consumption did not exceed [1000] kilograms per capita in [2008] and that the total combined calculated levels of consumption of the Parties concerned do not exceed the consumption limits set out in Article 2J. Such transfer of consumption shall be notified to the Secretariat by each of the Parties concerned, stating the terms of such transfer and the period for which it is to apply."

D. Article 2, paragraphs 8(a) and 11

In paragraphs 8(a) and 11 of Article 2 of the Protocol, for the words:

"Articles 2A to 2I"

there shall be substituted:

"Articles 2A to 2J".

E. Article 2, paragraph 9

The "and" at the end of subparagraph 9(a)(i) of Article 2 of the Protocol shall be moved to the end of subparagraph 9(a)(ii).

The following subparagraph shall be inserted after subparagraph 9(a)(ii) of Article 2 of the Protocol:

"(iii) Adjustments to the global warming potentials specified in Annexes C and F should be made and, if so, what the adjustments should be;"

In paragraph 9(c) of Article 2 of the Protocol, the following language shall be inserted immediately after the words "In taking such decisions":

"under subparagraphs 9(a)(i) and (ii)":

For the final semi-colon of paragraph 9(c) of Article 2 of the Protocol there shall be substituted:

". In taking such decisions under subparagraph 9(a)(iii), the Parties shall reach agreement by consensus only; "

F. Article 2J

The following Article shall be inserted after Article 2I of the Protocol:

"Article 2J: Hydrofluorocarbons

1. Each Party shall ensure that for the twelve-month period commencing on 1 January [2016], and in each 12-month period thereafter, its calculated level of consumption of the controlled substances in Annex F does not exceed, annually, [ninety] per cent of the average of its calculated levels of consumption of Annex F controlled substances plus eighty five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008. Each Party producing one or more of these substances shall, for the same period, ensure that its calculated level of production of the substances does not exceed, annually, [ninety] per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of the average of its calculated level of production of Annex F controlled substances plus eighty five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008.

2. Each Party shall ensure that for the twelve-month period commencing on 1 January [2020], and in each 12-month period thereafter, its calculated level of consumption of the controlled substances in Annex F does not exceed, annually, [seventy] per cent of the average of its calculated levels of consumption of Annex F controlled substances plus eighty-five per cent of Annex C Group I controlled substances for the years 2005, 2006, 2007 and 2008. Each Party producing one or more of these substances shall, for the same period, ensure that its calculated level of production of the substances does not exceed, annually, [seventy] per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008.

3. Each Party shall ensure that for the twelve-month period commencing on 1 January [2025], and in each 12-month period thereafter, its calculated level of consumption of the controlled substances in Annex F does not exceed, annually, [fifty] per cent of the average of its calculated levels of consumption of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007, and 2008. Each Party producing one or more of these substances shall, for the same period, ensure that its calculated level of production of the substances does not exceed, annually, [fifty] per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007, and 2008.

4. Each Party shall ensure that for the twelve-month period commencing on 1 January [2029], and in each 12-month period thereafter, its calculated level of consumption of the controlled substances in Annex F does not exceed, annually, [thirty] per cent of the average of its calculated

levels of consumption of Annex F controlled substances plus eighty-five per cent of Annex C Group I controlled substances for the years 2005, 2006, 2007 and 2008. Each Party producing one or more of these substances shall, for the same period, ensure that its calculated level of production of the substances does not exceed, annually, [thirty] per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008.

5. Each Party shall ensure that for the twelve-month period commencing on 1 January [2033], and in each 12-month period thereafter, its calculated level of consumption of the controlled substances in Annex F does not exceed, annually, [fifteen] per cent of the average of its calculated levels of consumption of Annex F controlled substances plus eighty-five per cent of Annex C Group I controlled substances for the years 2005, 2006, 2007 and 2008. Each Party producing one or more of these substances shall, for the same period, ensure that its calculated level of production of the substances does not exceed, annually, [fifteen] per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007 and 2008.

6. Each party manufacturing Annex C Group I or Annex F substances shall ensure that for the 12-month period commencing on January 1, 2016, and in each 12-month period thereafter, its calculated level of emissions of Annex F, Group II substances generated as a byproduct in each production line that manufactures Annex C, Group I or Annex F substances does not exceed [0.1] per cent of the mass of Annex C, Group I or Annex F substances manufactured in that production line. The obligation under this paragraph does not apply to emissions from production lines that have an approved project under the Clean Development Mechanism to control emissions of Annex F Group II substances so long as those emissions are covered by and continue to generate emissions reduction credits under a Clean Development Mechanism project.

7. Each Party shall ensure that any destruction of Annex F, Group II substances generated by facilities that produce Annex C, Group I or Annex F substances shall occur only by technologies to be approved by the Parties."

G. Article 3

The preamble to Article 3 of the Protocol should be replaced with the following:

"1. Except as specified in paragraph 2, for the purposes of Articles 2, 2A to 2J and 5, each Party shall, for each group of substances in Annex A, Annex B, Annex C, Annex E or Annex F determine its calculated levels of:"

For the period at the end of subparagraph (c) of Article 3 of the Protocol there shall be substituted a semi-colon, and the "and" at the end of subparagraph (b) of Article 3 of the Protocol shall be moved to the end of subparagraph (c).

The following text should be added to the end of Article 3 of the Protocol:

"(d) Emissions of Annex F, Group II substances generated as a byproduct in each production line that manufactures Annex C, Group I or Annex F substances by including, among other things, amounts emitted from equipment leaks, process vents, and destruction devices, but excluding amounts destroyed, sold for use, or stored.

2. When calculating average levels of production, consumption, imports, exports and emissions of Annex F and Annex C Group I substances for purposes of Article 2J, paragraph 5ter of Article 2, and paragraph 1(d) of Article 3, each Party shall use the global warming potentials of these substances as specified in Annexes C and F."

H. Article 4, paragraph 1 sept

The following paragraph shall be inserted after paragraph 1 sex of Article 4 of the Protocol:

"1 sept. Within one year of the date of entry into force of this paragraph, each Party shall ban the import of the controlled substances in Annex F from any State not party to this Protocol."

I. Article 4, paragraph 2 sept

The following paragraph shall be inserted after paragraph 2 sex of Article 4 of the Protocol:

"2 sept. Within one year of the date of entry into force of this paragraph, each Party shall ban the export of the controlled substances in Annex F to any State not party to this Protocol."

J. Article 4, paragraphs 5, 6 and 7

In paragraphs 5, 6 and 7 of Article 4 of the Protocol, for the words:

"Annexes A, B, C and E".

there shall be substituted:

"Annexes A, B, C, E and F".

K. Article 4, paragraph 8

In paragraph 8 of Article 4 of the Protocol, for the words:

"Articles 2A to 2I"

there shall be substituted:

"Articles 2A to 2J".

L. Article 4B

The following paragraph shall be inserted after paragraph 2 of Article 4B of the Protocol:

"2 bis. Each Party shall, by 1 January 2016 or within three months of the date of entry into force of this paragraph for it, whichever is later, establish and implement a system for licensing the import and export of new, used, recycled and reclaimed controlled substances in Annex F. Any Party operating under paragraph 1 of Article 5 that decides it is not in a position to establish and implement such a system by 1 January 2016 may delay taking those actions until 1 January 2018."

M. Article 5, paragraph 4

In paragraph 4 of Article 5 of the Protocol, for the words:

"Articles 2A to 2I"

there shall be substituted:

"Articles 2A to 2J".

N. Article 5, paragraphs 5 and 6

In paragraphs 5 and 6 of Article 5 of the Protocol, for the words:

"Article 2I"

there shall be substituted:

"Articles 2I and 2J".

O. Article 5, paragraph 8 qua

The following paragraph shall be inserted after paragraph 8 ter of Article 5 of the Protocol:

"8 qua. Each Party operating under paragraph 1 of this Article shall:

(a) in order to meet its basic domestic needs, be entitled to delay its compliance with the control measures set out in paragraph 1 of Article 2J for two years, in paragraphs 2 and 3 of Article 2J for four years, in paragraph 4 of Article 2J for five years, and in paragraph 5 of Article 2J for ten years, subject to any adjustments made to the control measures in Article 2J in accordance with Article 2(9);

(b) for purposes of calculating its consumption baseline under Article 2J, use the average of its calculated levels of consumption of Annex C, Group I controlled substances in the years 2005, 2006, 2007, and 2008, instead of the average of its calculated levels of consumption of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007, and 2008;

(c) for purposes of calculating its production baseline under Article 2J, use the average of its calculated levels of production of Annex C, Group I controlled substances in the years 2005, 2006, 2007, and 2008, instead of the average of its calculated levels of production of Annex F controlled substances plus eighty-five per cent of Annex C, Group I controlled substances for the years 2005, 2006, 2007, and 2008; and

(d) ensure that its calculated level of consumption and production:

(i) for purposes of paragraph 1 of Article 2J does not exceed [one hundred] per cent, rather than [ninety] per cent, of the average of its calculated levels of consumption and production, respectively, of Annex C, Group I controlled substances in the years 2005, 2006, 2007, and 2008;

(ii) for purposes of paragraph 2 of Article 2J does not exceed [eighty] per cent, rather than [seventy] per cent, of the average of its calculated levels of consumption and production, respectively, of Annex C, Group I controlled substances in the years 2005, 2006, 2007, and 2008;

(iii) for purposes of paragraph 3 of Article 2J does not exceed [sixty] per cent, rather than [fifty] per cent, of the average of its calculated levels of consumption and production, respectively, of Annex C, Group I controlled substances in the years 2005, 2006, 2007, and 2008; and

(iv) for purposes of paragraph 4 of Article 2J does not exceed [forty] per cent, rather than [thirty] per cent, of the average of its calculated levels of consumption and production, respectively, of Annex C, Group I controlled substances in the years 2005, 2006, 2007, and 2008."

P. Article 6

In Article 6 of the Protocol, for the words:

"Articles 2A to 2I"

there shall be substituted:

"Articles 2A to 2J".

Q. Article 7, paragraphs 2, 3 and 3 ter

The following line shall be inserted after the line that reads "— in Annex E, for the year 1991," in paragraph 2 of Article 7 of the Protocol:

"— in Annex F, for the years 2005, 2006, 2007 and 2008,"

In paragraphs 2 and 3 of Article 7 of the Protocol, for the words:

"C and E"

there shall be substituted:

"C, E and F".

The following paragraph shall be added to Article 7 of the Protocol after paragraph 3 bis:

"3 ter. Each Party shall provide to the Secretariat statistical data of its annual emissions of Annex F, Group II controlled substances in accordance with Article 3(d) of the Protocol, as well as the amount of Annex F, Group II substances captured and destroyed by technologies to be approved by the Parties."

R. Article 10, paragraph 1

In Article 10, paragraph 1 of the Protocol, for the words:

"Articles 2A to 2E and Article 2I"

There shall be substituted:

"Articles 2A to 2E, Article 2I, and Article 2J".

The following shall be inserted at the end of Article 10, paragraph 1 of the Protocol:

"Where a Party operating under paragraph 1 of Article 5 chooses to avail itself of funding from any other financial mechanism that could result in meeting any part of its agreed incremental costs, that part shall not be met by the Financial Mechanism under Article 10 of this Protocol. If a Party has an approved project under the Clean Development Mechanism to control HFC-23 byproduct emissions for a facility or production line, then that facility or production line would not be eligible for support under the Financial Mechanism under Article 10 of this Protocol until the facility or production line is no longer covered by a Clean Development Mechanism project."

S. Annex C and Annex F

Annex C, Group I is amended to add the 100-year Global Warming Potential for the following substances:

Substance	100 year Global Warming Potential
HCFC-21	151
HCFC-22	1,810
HCFC-123	77
HCFC-124	609
HCFC-141b	725
HCFC-142b	2,310
HCFC-225ca	122
HCFC-225cb	595

A new Annex F shall be added to the Protocol, following Annex E. It shall read:

Annex F: Controlled Substances

Group Substance	100 year Global Warming Potential
Group I	
HFC-32	675
HFC-41	92
HFC-125	3,500
HFC-134	1,100
HFC-134a	1,430
HFC-143	353
HFC-143a	4,470
HFC-152	53
HFC-152a	124
HFC-161	12
HFC-227ea	3,220
HFC-236cb	1,340
HFC-236ea	1,370
HFC-236fa	9,810
HFC-245ca	693
HFC-245fa	1,030
HFC-365mfc	794
HFC-43-10mee	1,640
HFC-1234yf (HFO-1234yf)	4
HFC-1234ze(E) (HFO-1234ze(E))	6
Group II	
HFC-23	14,800

Article II: Relationship to the 1999 Amendment

No State or regional economic integration organization may deposit an instrument of ratification, acceptance or approval of or accession to this Amendment unless it has previously, or simultaneously, deposited such an instrument to the Amendment adopted at the Eleventh Meeting of the Parties in Beijing, 3 December 1999.

Article III: Relationship to the United Nations Framework Convention on Climate Change and Its Kyoto Protocol

This Amendment is not intended to have the effect of excepting hydrofluorocarbons from the scope of the commitments contained in Articles 4 and 12 of the United Nations Framework Convention on Climate Change and in Articles 2, 5, 7 and 10 of its Kyoto Protocol that apply to "greenhouse gases not controlled by the Montreal Protocol." Each party to this Amendment shall continue to apply the provisions of the

United Nations Framework Convention on Climate Change and its Kyoto Protocol identified above to HFCs as long as those provisions, respectively, remain in force with respect to such party.

Article IV: Entry into force

1. Except as noted in paragraph 2, below, this Amendment shall enter into force on 1 January 2014, provided that at least twenty instruments of ratification, acceptance or approval of the Amendment have been deposited by States or regional economic integration organizations that are Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer. In the event that this condition has not been fulfilled by that date, the Amendment shall enter into force on the ninetieth day following the date on which it has been fulfilled.

2. The changes in Sections H and I of Article I of this Amendment shall enter into force on 1 January 2014, provided that at least seventy instruments of ratification, acceptance or approval of the Amendment have been deposited by States or regional economic integration organizations that are Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer. In the event that this condition has not been fulfilled by that date, the Amendment shall enter into force on the ninetieth day following the date on which it has been fulfilled.

3. For purposes of paragraphs 1 and 2, any such instrument deposited by a regional economic integration organization shall not be counted as additional to those deposited by member States of such organization.

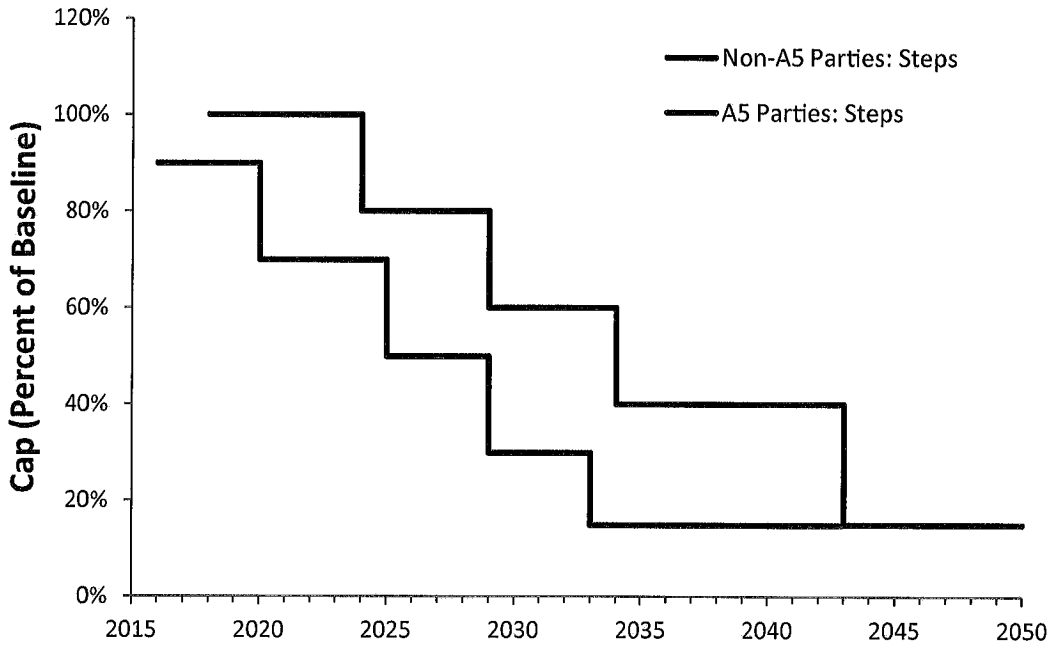
4. After the entry into force of this Amendment, as provided under paragraphs 1 and 2, it shall enter into force for any other Party to the Protocol on the ninetieth day following the date of deposit of its instrument of ratification, acceptance or approval.

Summary Points: North American HFC Submission to the Montreal Protocol

Key elements of the North American proposal:

- Lists 21 HFCs as a new Annex F, including two substances sometimes referred to as HFOs.
- Recognizes that there may not be alternatives for all HFC applications and therefore utilizes a gradual phasedown mechanism with a plateau, as opposed to a phaseout.
- Establishes provisions for developed country (non-Article 5) and developing country (Article 5) phasedown of production and consumption (see figure below).
  - The baseline for Article 5 countries is calculated based on HCFC consumption and production respectively averaged over years 2005-2008, recognizing there are HFC data limitations in some countries.
  - For non-Article 5 countries, the baseline is determined from a combination of HFC plus 85% of HCFC consumption and production respectively averaged over years 2005-2008.
  - Uses weighting by Global Warming Potential for HCFCs and HFCs as compared to typical Montreal Protocol practice of Ozone Depleting Potential.

HFC Reduction Steps for Article 5 and Non-Article 5 Countries (% of baseline)



- Includes provisions to limit HFC-23 byproduct emissions resulting from the production of HCFC-22 in each production line beginning in 2016. The provisions are intended for production lines that do not have an approved project under the Clean Development Mechanism to control emissions of HFC-23.
- Requires licensing of HFC imports and exports, and bans imports and exports to non-Parties.
- Requires reporting on production and consumption of HFCs, and HFC-23 byproduct emissions.

- Makes eligible for funding under the Montreal Protocol's Multilateral Fund the phasedown of HFC production and consumption as well as the reduction of HFC-23 byproduct emissions.

Potential Steps for Non-A5 Parties		Potential Steps for A5 Parties	
2016	90%	2018	100%
2020	70%	2024	80%
2025	50%	2029	60%
2029	30%	2034	40%
2033	15%	2043	15%

Cumulative Environmental Benefits:

- Cumulative benefits of the HFC phasedown estimated by the U.S. Government amount to reductions of 2,200 million metric tons of carbon dioxide equivalent (MMT CO_2eq) through 2020, and about 85,000 MMTCO_2eq through 2050.
- Cumulative benefits from HFC-23 byproduct emissions controls as estimated by the U.S. Government amount to an additional 11,300 MMTCO_2eq through 2050.

Cumulative HFC Reductions (MMTCO_2eq) 2016-2050	
Non-Article 5	42,100
Article 5	42,900
World	85,000
Byproduct Controls (HFC-23)	11,300
World Total	96,300

Relationship to HCFC phaseout:

- This amendment is designed to be compatible with the HCFC phaseout.
- The proposal recognizes that HFCs are alternatives in many existing HCFC applications, so baseline levels are set to accommodate some level of transition from HCFCs to HFCs.
- The suite of known alternative chemicals, new technologies, and improved process/handling practices can significantly reduce HFC consumption while simultaneously supporting the HCFC phaseout.

Relationship with the United Nations Framework Convention on Climate Change (UNFCCC):

- The proposal is intended to support overall global efforts aimed at climate system protection.
- The proposal constitutes an amendment to the Montreal Protocol and could be complemented by a related decision by the UNFCCC confirming the Montreal Protocol approach.
- The proposal leaves unchanged the provisions of the UNFCCC/Kyoto Protocol that govern HFC emissions. Parties could follow Montreal Protocol obligations to meet certain UNFCCC obligations.