



Project Summary

Atmospheric Chemistry and Physical Fate of HCFCs and HFCs and Their Degradation Products

E.O. Edney

Laboratory experiments were conducted to determine the fate of the proposed CFC substitutes HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b, HFC-125, HFC-134a, and HFC-152a. The laboratory program consisted of (1) photochemical oxidation experiments to identify stable oxidation products and measure their yields; (2) deposition studies to measure the extent oxidation products are absorbed into aqueous media; and (3) experiments to determine the fate of hydrolysis products during evaporation of aqueous media. An elementary multimedia model was used as a tool for discussing the implications of the laboratory findings.

The product studies showed that acid halides, including COF_2 , COFCl , CF_3CFO , HFCO , and CF_3CClO , are major oxidation products of HCFCs and HFCs. The deposition studies were compatible with significant uptake of the acid halides to aqueous media, followed by hydrolysis reactions leading to the formation of HF , HCl , and CF_3COOH . Model results, obtained using laboratory derived lower limits estimates for aqueous deposition velocities and assuming a well mixed atmosphere, suggest the uptakes rates to cloudwater and oceans are sufficiently fast such that significant buildup of gas phase products is unlikely. However, for a global emission rate of 10^6 tonnes yr^{-1} , precipitation concentrations as high as 20 pmol ml^{-1} of the apparently long lived species CF_3COO^- are possible. The laboratory studies suggest that product accumulations in

aqueous media could be affected by losses during evaporation. Direct loss by evaporation of halogenated acids and/or production of volatile compounds after further reactions of the dissolved acids could return halogenated compounds to the atmosphere.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

There is little doubt that chlorofluorocarbons (CFCs) released into the environment contribute significantly to destruction of the stratospheric O_3 layer. Any thinning of the layer is apt to increase adverse effects associated with exposure to UV-B. The first international agreement aimed at reducing CFC emissions, The Montreal Protocol on Substances that Deplete the Ozone Layer, was agreed to in 1987. However, by the time the treaty was to be implemented, O_3 depletion in the Antarctica by Cl and Br compounds was of sufficient concern to amend the treaty to accelerate the phase-out time tables. Under the 1990 London Amendments, CFCs, halons, and carbon tetrachloride are scheduled to be completely phased out by the year 2000, with methyl chloroform phased out five years later. The 1990 Clean Air Act Amendments (CAAA) also established similar phase-out schedules



for O_3 depleting compounds, with the exception of more rapid phase-out time tables for hydrochlorofluorocarbons (HCFCs) and methyl chloroform. However, recent O_3 depletion measurements have led the U.S. to consider phasing out O_3 depleting compounds at an even more rapid rate. At present, discussions are underway to implement options in the 1990 CAAAs to phase out CFCs by the end of 1995.

As it became clear that CFCs and halons would be phased out, industry initiated programs aimed at finding substitute compounds. The focus of replacement strategies was largely on developing H atom bearing compounds that react in the troposphere. The compounds that have received the most attention are the HCFCs and the hydrofluorocarbons (HFCs). Although the removal of HCFCs and HFCs by reaction with OH will decrease their tropospheric concentrations and reduce the possibility of the compounds reaching the stratosphere, they do not eliminate the possibility their release could affect stratospheric O_3 depletion, global climate change, human health, damage to the ecosystem, and tropospheric air and water quality. Rather it shifts such questions to the impact of the oxidation products. To establish the information necessary to determine the life cycles of the proposed substitutes, a multimedia research program was initiated. The program consisted of photochemical oxidation experiments, product deposition studies, evaporation experiments, and multimedia modeling studies.

Procedure

Laboratory Experiments

Laboratory experiments were conducted to identify and determine the yields of the major stable gas phase products of the following CFC substitutes: HCFC-22, HCFC-123, HCFC-124, HFC-125, HFC-134a, HCFC-141b, HCFC-142b, and HFC-152a. The laboratory experiments were conducted by irradiating ppm levels of the compounds in the presence of Cl_2 in dry air and identifying the products by long path Fourier transform spectroscopy. Cl atoms, formed by photolysis of Cl_2 , mimic the action of OH removing H atoms from the compounds being studied. The major products detected and their room temperature yields in 700 Torr of air (ϵ) were: COF_2 , $\epsilon = 1.11 \pm 0.06$, (HCFC-22); CF_3CClO , $\epsilon = 1.01$, (HCFC-123); CF_3CFO , $\epsilon = 1.00 \pm 0.04$, (HCFC-124); COF_2 , $\epsilon = 1.09 \pm 0.05$, (HFC-125); CF_3CFO , $\epsilon = 0.16 \pm 0.03$, HFCO, $\epsilon = 0.83 \pm 0.22$, COF_2 , $\epsilon = 0.23 \pm 0.02$, (HFC-134a); $COFCl$, $\epsilon = 0.94$, (HCFC-141b); COF_2 , $\epsilon = 0.98 \pm 0.03$,

(HCFC-142b); and COF_2 , $\epsilon = 1.00 \pm 0.05$, (HFC-152a).

The critical step in determining the oxidation products was the decomposition of the halogenated alkoxy radical generated after H atom abstraction from the HCFC or HFC. Alkoxy radical decomposition modes included C-C bond cleavage, Cl elimination, and H atom abstraction by reaction with O_2 . The decomposition pathway for HCFC-123, HCFC-124, and HCFC-22 halogenated alkoxy radicals was Cl elimination. In the case of HFC-125, C-C bond cleavage was the major decomposition route, whereas for HFC-134a, both C-C bond cleavage and reaction with O_2 contributed. Secondary Cl reactions in the HCFC-141b, HCFC-142b, and HFC-152a experiments prevented unambiguous determinations of the decomposition modes of the associated halogenated alkoxy radicals. The data were compatible with both C-C bond scission and Cl reactions with halogenated aldehydes producing COF_2 from HCFC-142b, and HFC-152a and $COFCl$ from HCFC-141b.

The detected oxidation products were in general resistant to further gas phase oxidation. In order to determine whether uptake to aqueous media could serve as a sink for oxidation products of HCFCs and HFCs, product deposition studies were carried out. The experimental program included single component exposure experiments where ppm levels of the oxidation product were exposed to quiescent aqueous solutions. The chemical composition of the aqueous solution was monitored as a function of exposure time using ion chromatography. Single component experiments consisted of exposing CF_3CClO , CF_3CFO , and COF_2 to deionized water and to acidic and alkaline solutions. The second phase of the program consisted of first irradiating HCFC/ Cl_2 and HFC/ Cl_2 mixtures in clean air and then exposing the irradiated mixture to deionized water. Irradiation/deposition experiments were conducted using HCFC-22, HFC-41, HCFC-123, HCFC-124, HFC-125, HFC-134a, HCFC-141b, HCFC-142b, and HFC-152a. The exposed aqueous solutions were analyzed for $HCOO^-$, F^- , and CF_3COO^- and the anionic concentrations were then used to calculate the effective deposition velocities to bulk aqueous solutions.

The deposition results showed that under laboratory conditions the products were taken up into the aqueous solutions at measurable rates. The uptake rates were consistent with the formation of halogenated acids by hydrolysis. The effective deposition velocities in $cm\ sec^{-1}$, for $T = 295 \pm 3\ ^\circ K$, were: 0.100 (COF_2); 0.051 ($COFCl$); 0.068 (CF_3CFO); 0.049

(CF_3CClO); and 0.052 (HFCO). Although the deposition measurements were consonant with removal of HCFC and HFC oxidation products by aqueous media, the data were not sufficient for extrapolating to ambient conditions. However, by assuming the total resistance to deposition was due to aqueous processes, a lower limit of $0.05\ cm\ sec^{-1}$ was obtained for the reciprocal of the aqueous resistance. For an aqueous diffusion coefficient of $1 \times 10^{-5}\ cm^2\ sec^{-1}$ and $T = 295\ ^\circ K$, the lower limit was consistent with $H/k_h = 0.65\ M\ atm^{-1}\ sec^{1/2}$, where H is the Henry's law constant and k_h is the first order hydrolysis constant.

For aqueous media such as rivers, streams, and oceans, deposition of an acid halide is likely to be a permanent sink because of the solubility of the hydrolysis products in these large aquatic bodies. However, for other tropospheric aqueous media, including cloudwater, dew and precipitation, evaporation can play a major role in determining the fate of the hydrolysis products. Whether uptake to these media constitutes a permanent atmospheric sink depends on the fate of hydrolysis products during evaporation.

Evaporation effects were investigated by conducting two laboratory experiments where aqueous films containing NH_4NO_3 , H_2O_2 , and either sodium fluoride (NaF) or sodium trifluoroacetate ($NaCF_3COO$) were exposed for five hours to irradiated smog mixtures of o-xylene/ NO_x / SO_2 . The exposure experiments were carried out by exposing on stainless steel panels films of aqueous solutions containing equal concentrations of NH_4NO_3 and either NaF or $NaCF_3COO$, but different H_2O_2 levels. At the end of the exposure, the films were collected and an aliquot was analyzed. The exposed films consisted of solutions containing dissolved oxidants, acids, and salts in the presence of either F^- or CF_3COO^- , with the films differentiated by and large by the H_2SO_4 levels. The unused portions of the aqueous films were then returned to the panels and allowed to evaporate overnight at room temperature, after which they were rinsed with DI water. This rinse was then chemically analyzed to determine the composition of material left after evaporation and by inference what material was re-emitted into the atmosphere.

The laboratory data agreed with the expected result that CF_3COO^- and F^- do not react with constituents in the bulk films. However, chemical analyses of the post evaporation DI rinses revealed significant losses for $HCOO^-$, CH_3COO^- , NO_2^- , NO_3^- , F^- , and CF_3COO^- , thus suggesting that acid halide deposition to aqueous media

that undergo evaporation may not serve as a permanent sink under all circumstances. The NO_3^- , NO_2^- , HCOO^- , CH_3COO^- , and F^- losses were congruous with volatilization of the corresponding acids. However, the evaporation data were insufficient to establish a loss mechanism for CF_3COO^- . Possible loss mechanisms included direct evaporation of the corresponding carboxylic acid and/or oxidative decarboxylation reactions of CF_3COOH with (1) dissolved metals ions from acid dissolution of the stainless steel panels or (2) other oxidants. If oxidative decarboxylation reactions occur, then the fate of CF_3COO^- could become an important issue. However, whether ambient hydrometeors undergo decarboxylation reactions has yet to be established. Nonetheless, even in the absence of such reactions, it appears likely that, under acidic conditions, evaporating ambient hydrometeors including dew, cloudwater, and precipitation could lose CF_3COO^- by volatilization of CF_3COOH .

Results and Discussion

To determine the risk associated with the release of HCFCs and HFCs the laboratory results were integrated into an elementary multimedia model. The model takes into account photochemical oxidation of the emitted compound and uptake of the products into cloudwater and oceans. The atmosphere is assumed to be completely mixed. The oceanic deposition process is described in terms of the transport through and reactions within the following three layers: a thin stagnant air layer directly above the ocean-air interface; a thin chemically inert stagnant aqueous layer just below the ocean-air interface; and the ocean mixed layer that covers the portion of the ocean from the bottom of the stagnant layer down to the thermocline. In the cloud model, the hydrolysis rate is assumed to be sufficiently slow and aqueous diffusion within the droplet is rapid enough so the dissolved product concentration remains in equilibrium with the gas phase concentration.

The modeling results showed that for $H = 1 \text{ M atm}^{-1}$, a liquid water content of 2×10^{-7} , an effective scale height of 10 km; and $T = 295 \text{ K}$, the criterion $k_h > 10^7 \text{ sec}^{-1}$ must be satisfied so the aqueous removal lifetime is less than two years. For the low k_h region, oceanic uptake was governed largely by the resistance of the mixed oceanic layer, whereas for $k_h > 10^6 \text{ sec}^{-1}$, removal by the oceans was determined by the aqueous stagnant layer and atmospheric resistances. Uptake to cloudwater was significant only if k_h exceeded 10^3 sec^{-1} .

For these same conditions and a global emission rate of $10^6 \text{ tonnes yr}^{-1}$, the model results showed that for an atmospheric lifetime (τ) of one year the steady state concentration of the emitted compound quickly reached 56 pptv, whereas for a lifetime of 20 years it took about 50 years to reach the steady concentration of 1120 pptv. The model simulations further showed that, for $\tau = 1 \text{ year}$ and $k_h < 10^7 \text{ sec}^{-1}$, the oxidation products were the dominant atmospheric species. Between $k_h = 10^6$ and 10^7 sec^{-1} , the product removal rate was controlled by the resistance of the mixed oceanic layer and product concentrations decreased an order of magnitude to a level similar to that of the reactants. Between 10^7 and 10^9 sec^{-1} , the product concentration decreased another order of magnitude, with the hydrolysis rate becoming sufficiently fast such that oceanic uptake of the product was eventually controlled by the resistances of the atmosphere and the aqueous stagnant layer. For $k_h > 10^9 \text{ sec}^{-1}$, the already low product levels decreased further. In this regime, the products hydrolyzed fast enough to be absorbed into cloudwater. For an atmospheric lifetime of 20 years, the reactant concentrations exceeded the product concentrations for all k_h .

The model was also used to predict product concentrations in precipitation. For a precipitation rate of 100 cm yr^{-1} , a global emission rate of $10^6 \text{ tonnes yr}^{-1}$, $H = 1 \text{ M atm}^{-1}$, and $\tau = 1 \text{ year}$, the condition $k_h > 10^3 \text{ sec}^{-1}$ was required for substantial uptake to precipitation. The resulting maximum precipitation concentration was 19 pmol ml^{-1} .

Conclusions and Recommendations

Buildup of HCFCs and HFCs will be limited by their OH based atmospheric lifetimes that range from about 1 to 30 years. For an emission rate of $10^6 \text{ tonnes yr}^{-1}$, the corresponding steady state concentrations vary from 56 to 1680 pptv. Acid halides will constitute a major portion of the oxidation products. The laboratory deposition data for COF_2 , COFCl , HFCO , CF_3CFO , and CF_3CClO agree with the proposition that acid halides will be taken up into aqueous media and hydrolyze, forming halogenated acids. The laboratory derived lower limit estimate for v_d , while adequate for estimating a room temperature limit for H/k_h , was not sufficient for estimating individual values for k_h and H , both required input parameters for the multimedia model. However, for $H = 0.1$, 1, and 10 M atm^{-1} and the corresponding values for k_h that were consistent with the lower limit for H/k_h , the atmospheric prod-

uct concentrations were all less than a few percent of the total concentrations. The limit data were not sufficient to establish the partitioning between product uptake to cloudwater versus oceans.

The partitioning of acid halides among aqueous media is an important issue because of concerns surrounding the possible toxicity of the long lived species CF_3COO^- , a common hydrolysis product of CF_3CFO and CF_3CClO . The model simulations showed that for an emission rate of $10^6 \text{ tonnes yr}^{-1}$ and precipitation levels of 100 cm yr^{-1} , CF_3COO^- precipitation concentrations as high as 20 pmol ml^{-1} are possible. However, this value is probably an upper limit because the CF_3COO^- producing HCFCs and HFC represent only a portion of total emissions and the average atmospheric yield from HFC-134a, the compound that is likely to have the most widespread use, is only 0.27. Furthermore, the possibility remains that a portion of CF_3COO^- precursors are taken up into oceans and other large aquatic bodies, thus reducing precipitation concentrations, but also increasing the accumulations in other possibly sensitive aquatic bodies.

The impact of evaporation should be considered in assessing the risks associated with the release of CFC substitutes. Most aqueous droplets that come in contact with ecological surfaces, for instance, plant leaves, undergo evaporation. The laboratory evaporation data suggest that loss of hydrolysis products can occur directly by evaporation of the corresponding acid and/or by volatilization of a reaction product from further reactions of the hydrolysis products. Thus, clouds could serve as processing centers where COF_2 is converted to HF and CO_2 , COFCl to HF, HCl and CO_2 , etc.

Further investigations are needed to establish the life cycles of HCFCs and HFCs. Chemical kinetic studies are needed to further clarify the degradation mechanisms for HCFC-141b, HCFC-142b, and HFC-152a, with special emphasis placed on establishing the gas and aqueous phase chemistry of halogenated PANs. Research is needed to determine the fate of CF_3O_2 in the presence of NO_x compounds. Further refinements of the deposition studies are needed to measure the individual values for k_h and H . The evaporation studies should be expanded to include studies to establish the key chemical and physical parameters controlling the fate of compounds during droplet evaporation. Emphasis should be placed on determining the fate of CF_3COO^- during evaporation. Finally, research is required to address general issues related to the development, implementation, and validation of multi-

media models. In particular, both gas and aqueous transport should be addressed in a rigorous fashion and the method used to parameterize aqueous uptake should be improved.

The EPA author E.O. Edney (also the EPA Project Officer, see below) is with the Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC 27711.

The complete report, entitled "Atmospheric Chemistry and Physical Fate of HCFCs and HFCs and Their Degradation Products," (Order No. PB93-131449/AS; Cost: \$17.50; subject to change) will be available only from:

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5285 Port Royal Road

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Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Atmospheric Research and Exposure Assessment Laboratory

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