LABORATORY INVESTIGATIONS OF THE DEPOSITION OF OXIDATION PRODUCTS OF HYDROCHLOROFLUOROCARBONS (HCFCs) AND HYDROFLUOROCARBONS (HFCs) TO AQUEOUS SOLUTIONS

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Abstract. Laboratory experiments were conducted to investigate the deposition to aqueous media of the gas phase oxidation products of the following hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs): HCFC-22 (CCIF₂H), HFC-41 (CH₃F), HCFC-123 (CCl₂HCF₃), HCFC-124 (CCIFHCF₃), HFC-125 (CF₃CF₂H), HFC-134a (CF₃CFH₂), HCFC-141b (CCl₂FCH₃), HCFC-142b (CCIF₂CH₃), and HFC-152a (CF₂HCH₃). Single component experiments were conducted where the oxidation products CF₃CFO, COF₂, CF₃C(O)C₁ were exposed under laminar flow conditions to alkaline, acidic, and neutral solutions in a aluminum exposure trough. The anionic composition of the exposure solutions were used to determine the effective deposition velocity. Exposures to neutral solutions were also conducted for irradiated HFC and HCFC/Cl₂/air mixtures. The combined single component and irradiated mixture experiments were used to measure the effective deposition velocities of C(O)F₂, C(O)FC₁, HFC(O), CF₃C(O), and CF₃C(O). The deposition velocities differed by as much as a factor of two with the largest velocities found for C(O)F₂ and CF₃C(O). The data were insufficient to determine the extent to which gas and liquid phase resistance controlled the overall deposition. However, the data were used to estimate lower limits for the laboratory aqueous resistance and the results were found to be consistent with the recent conclusions of Wine and Chameides who reported the deposition of the oxidation products to oceans and cloudwater was sufficiently fast that there was little likelihood that the products would be transported to the stratosphere.

1. Introduction

Proposals for replacing O₃ depleting chlorofluorocarbons (CFCs) with hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have raised questions concerning the possible adverse effects these compounds and their oxidation products may have on the environment. HCFCs and HFCs differ from CFCs by the presence of reactive H atoms and thus are designed to degrade to a large degree in the troposphere by reaction with hydroxyl radicals (OH). This removal process alone, however, does not eliminate the possibility of the compounds contributing to stratospheric O₃ depletion, global warming, or other adverse effects, but rather shifts such questions to the role of the oxidation products. Recently we reported the results of Cl initiated photochemical oxidation studies of HCFCs and HFCs conducted using long path Fourier transform infrared spectroscopy (Edney et al., 1991a, b). The investigations showed that the acid halides CF₃CCl(O), CF₃CF(O), C(O)FCl, and C(O)F₂ as well as HFC(O) are among the major oxidation products expected from the OH initiated photooxidation of HCFCs and HFCs. With the
exception of HFC(O), the oxidation products contain no H atoms and are unlikely to undergo further tropospheric degradation by reactions with free radicals. Thus, heterogeneous removal mechanisms such as absorption into aqueous media are apt to be important in determining the fate of the products.

A review of the literature shows that although acid halides are expected to hydrolyze in aqueous solutions forming inorganic and organic halogenated acids, experimental data necessary to calculate or even establish lower limits of atmospheric deposition rates to such media are largely unavailable. Thus, there are insufficient data for unequivocally demonstrating whether the products are absorbed into tropospheric aqueous media including cloudwater and oceans or whether they buildup in the troposphere and contribute to global warming and eventually migrate to the stratosphere. Furthermore, such quantitative data are required to determine whether the product concentrations in dew, oceans, and precipitation could reach unacceptable levels.

As a first step in addressing these issues, a series of experiments were conducted where deposition rates of HCFC and HFC oxidation products to bulk quiescent aqueous solutions were measured. The experimental program included single component exposure studies where oxidation products were circulated through a square pipe under laminar flow conditions and then exposed to quiescent aqueous solutions whose chemical compositions were monitored as a function of time. Single component experiments consisted of exposing CF$_3$CCI(O), CF$_3$CF(O) and C(O)F$_2$ to deionized water (DI water) and to acidic and alkaline aqueous solutions. For comparative purposes, SO$_2$ deposition rates to DI water, an alkaline solution, and a 0.01 M H$_2$O$_2$ solution were determined. The second phase of the study involved irradiating HCFC/Cl$_2$ and HFC/Cl$_2$ mixtures in clean air and measuring the deposition rates of the irradiated mixtures to DI water. The laboratory derived deposition velocities for the oxidation products are presented and are discussed in terms of the information they provide for predicting ambient atmospheric deposition rates to aqueous media.

2. Experimental

2.1. Laboratory Chamber System

The laboratory chamber system consists of a long path photochemical reactor coupled to an auxiliary reactor, the heterogeneous reaction vessel (HRV), that is used to investigate the uptake of gases into bulk quiescent liquids. A schematic of the system is shown in Figure 1. The photochemical reactor consists of a cylindrical Pyrex glass long path cell, nine m in length, with a diameter of 0.3 m. The long path cell contains an eight-mirror optical system that allows in situ infrared analysis of the reactants and products at a path length of 144 m. The cell is surrounded by 96 fluorescent lamps, consisting of 72 black-light lamps and 24 sun lamps. The Fourier transform infrared spectrometer (Digilab Model 20/80) consists of a Nernst