

A-7.1.2 Transformation and Decomposition of Substitutes for CFCs in the Troposphere

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Abstract

The tropospheric degradation mechanisms of CFCs substitutes are investigated from laboratory experiments about gas-phase homogeneous chemical reactions, gas-solid and gas-liquid heterogeneous chemical reactions. The rate constants and/or degradation products for the gas-phase reaction of OH with CFCs substitutes, have been determined by using a laser photolysis - laser induced fluorescent system and a Fourier transform infrared absorption spectrometer equipped with a long path cell. Possible tropospheric sink of CFCs substitutes as heterogeneous chemical reactions are suggested.

Key words CFC substitutes, Environmental acceptability, Lifetime, Degradation products

1. Introduction

To meet with the phase-out of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFC), hydrofluorocarbons (HFC) and other compounds to replace CFCs are being developed. Before practical use of these substitutes, their global and local environmental acceptability should be studied. It is necessary to evaluate lifetime of the substitutes in both stratosphere and troposphere as well as those of their degradation products in the troposphere.

In this research, the tropospheric degradation mechanisms of the CFCs alternatives such as HCFCs will be elaborated from laboratory experiments about gas-phase homogeneous chemical reactions (mainly with OH radicals), gas-solid and gas-liquid heterogeneous chemical reactions.

2. Experimental

(1) gas-phase homogeneous chemical reactions

The rate constants for the reaction of OH with the CFCs substitutes, are determined by use of a laser photolysis - laser induced fluorescent system (Figure 1). OH is produced by photolysis of H₂O₂ with KrF excimer laser.

Product analysis study of Cl atom initiated oxidation of HCFC and/or HFC is done using a photochemical chamber equipped with a Fourier transform infrared (FT-IR) absorption spectrometer (Figure 2). Cl atoms are used instead of OH radicals because Cl atoms are more easily generated than OH radicals and, in general, react via the same mechanism (hydrogen atom abstraction) with HCFC and/or HFC¹. The photochemical chamber is equipped with an in situ multiple reflection optical system.

(2) heterogeneous chemical reactions

Table 2 shows the degradation products of Cl atom initiated decomposition of HCFC and/or HFC. These products were ascertained based on IR absorption bands of C=O base, since these bands are shifted to high wavenumbers by bonding fluorine. HCFC and/or HFC are transformed into alkoxy radicals via alkyl peroxy radicals through OH initiated reactions. Alkoxy radicals are mainly decomposed through three pathways shown in Table 2, according to their chemical properties. Reaction pathways of alkoxy radicals are suggested as shown in Table 2, based on product analysis results.

Table 2. degradation products of Cl atom initiated decomposition of HCFC and/or HFC

HCFC and/or HFC	products	$\nu_{C=O}$ / cm^{-1}	reaction path of RO*
HCFC22	COF ₂	1930	[1]
HCFC123	COCICF ₃	1812	[1]
HCFC124	COFCF ₃	1899	[1]
HFC134a	COF ₂ , COHF, COFCF ₃	1930, 1836, 1899	[2] and [3]
HCFC141b	COCIF	1883	([2]→[3]) and/or [3]
HCFC142b	COF ₂	1930	([2]→[3]) and/or [3]
HCFC225ca	COCICF ₂ CF ₃	1816	[1]
HCFC225cb	COFCF ₂ CCIF ₂	1887	[1]

* : [1] elimination of Cl, [2] H atom abstraction by O₂, [3] fission of C-C bond

(2) heterogeneous chemical reactions

Elimination of hydrogen chloride, that is, $\text{CH}_3\text{CCl}_3 \rightarrow \text{CH}_2\text{CCl}_2 + \text{HCl}$, took place on both titanium dioxide and Allophane even in the dark. These reaction rates may be estimated to be comparable to the gas-phase removal process, with a simple model calculations. This reaction is inhibited by relative humidity and cannot proceed at higher relative humidity than 10%RH. Allophane got deactivated with the reaction proceeding, but TiO₂ kept its reactivity by removing HCl from the surface under photoillumination. Reaction probability and deactivation effects for the reaction should be further investigated.

Overall mass transfer rate of CCl₃COCl to water was determined as 1 - 2 cm s⁻¹ in the gas hydrodynamic conditions of 200 to 1000 rpm, indicating similar value and gas hydrodynamic dependence as NH₃.

4. Summary

The rate constants and/or degradation products for the gas-phase reaction of OH with CFCs substitutes, have been obtained by using a laser photolysis - laser induced fluorescent system and a FTIR equipped with a long path cell. Possible tropospheric sink of CFCs substitutes as heterogeneous chemical reactions are suggested. The heterogeneous chemical reactions are investigated also in the next project.

5. Reference

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