A-2.5 .1 Tropospheric Lifetimes of CFC and Halon Substitutes

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1. Introduction

One of the most important evaluation of CFC and halon substitutes is the tropospheric lifetime of them. The main loss process of chemical substances in the troposphere is the reaction with OH radical because of its high reactivity and relatively large concentration as it is regenerate in a set of chain reactions. So, considerable scientific efforts over the past two decades have been made to obtain a reliable kinetic data concerning to the OH radicals reactions with partially and fully halogenated hydrocarbons, because of these substances could be potential substitutes for chlorofluorocarbons (CFC's) that destroy stratospheric ozone.

In general, the reaction rate of hydrocarbons with OH radical increases by substituting the hydrogen by Cl and Br because of their electron donating effect. The reaction rate of fluorinated hydrocarbons except CH_3F is smaller than the original hydrocarbon. From the empirical data, the reaction rate constants for a new chemical compound is possible if it belongs to the same type. However, the rate constant of a new type of compound can be obtained only experimentally.

Guidelines for estimation of photoabsorption and photo-dissociation primary processes are reported for chlorofluoro-carbons (CFCs), bromofluorocarbons (BFCs), hydrofluorocarbons HFCs) and their substituents, based on both experimental study of photoabsorption and photodissociation, and reference research of more than one hundred papers and thirty photoabsorption spectra of these compounds.

The observation of the trend of CFC's substitutions, HCFC or HFC, is important as the concentrations of them will increase in the atmosphere if the emission comes to be huge although the lifetime of them are shorter than CFCs. The comparison with the integrated emission and the increase of atmospheric concentration is a good validation experiment of the lifetime estimation.

2. Research Groups

The research group is consist of three groups,
(1) OH reaction rate group, Gen Inoue, NIES
(2) Photolysis rate group, M.Kawasaki, Hokkaido Univ.
(3) Atmospheric concentration group, Y.Makiide, Tokyo Univ.

3.OH reaction Rate of Halon and CFC Substitutes

3-1.Experimental

Some improvements have been made to the conventional reaction rate measurement system of laser photolysis-laser induced fluorescence technique in order to measure a very slow reaction. The back ground removal of OH radical was suppressed by increase of fluorescence detectivity, decrease of OH parent concentration, and decrease of photolysis laser power. The batch flow system reduced the diffusion rate to the wall, too. The back-ground lifetime of OH radical of 20ms was attained. One of the most important evaluation of freon and halon substitutes is the tropospheric
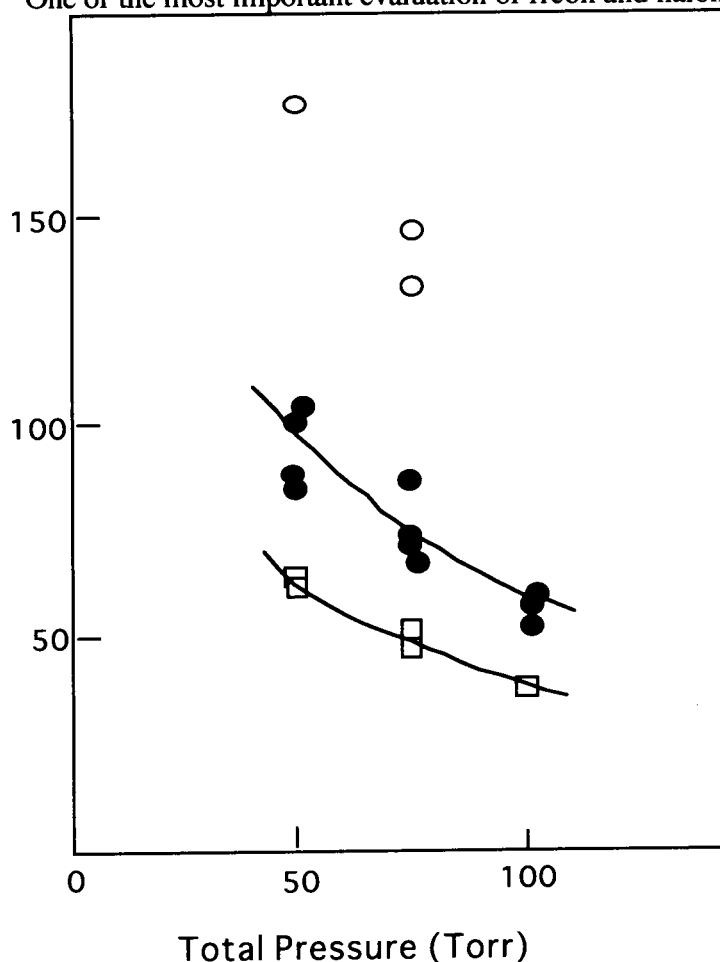

Fig.1　Buffer-gas pressure and photolysis laser power dependence of the decay rate of OH concentration without reactant.　Laser power ratio ○ : ● : □=1 : 1/3 : 1/9

Total Pressure (Torr)

Table I.　Reaction rate constant with OH radical

reaction system	Reaction rate constants cm^3 molecule sec^{-1}	Pressure (Torr)
$CF_3CH_2OH + OH = CF_3CH_2O + H_2O$	9.44 ± 0.96　$\times 10^{-14}$	50
$CF_3CF_2CH_2OH + OH = C_3F_5H_2O + H_2O$	8.66 ± 0.68　$\times 10^{-14}$	50
	9.29 ± 0.56　$\times 10^{-14}$	75
	9.29 ± 0.77　$\times 10^{-14}$	100
$CF_3CF_2CF_2CH_2OH + OH = C_4F_7H_2O + H_2O$	10.44 ± 0.86　$\times 10^{-14}$	50
	12.0 ± 0.44　$\times 10^{-14}$	100
$(C_2F_6)_3N + OH = products$	< 6　$\times 10^{-16}$	50-100

lifetime of them. The main loss process of chemical substances in the troposphere is the reaction with OH radical because of its high reactivity and relatively large concentration as it is regenerate in a

set of chain reactions. So, considerable scientific efforts over the past two decades have been made to obtain a reliable kinetic data concerning to the OH radicals reactions with partially and fully halogenated hydrocarbons, because of these substances could be potential substitutes for chlorofluorocarbons (CFC's) that destroy stratospheric ozone.

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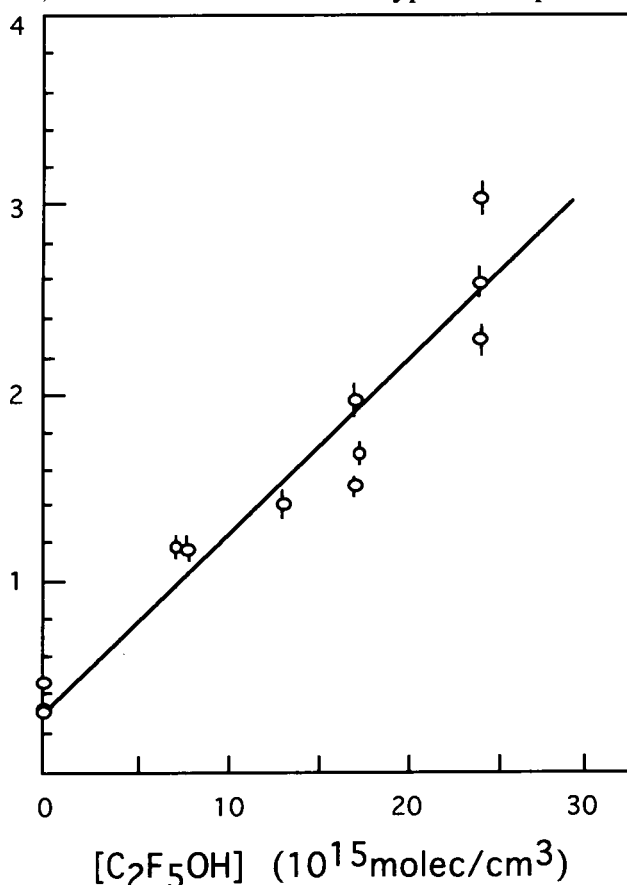

Fig.2. OH decay rate at various C_2F_5OH concentration. The reaction rate constant is calculated from the slope. to be $(2.3 \pm 0.3) \times 10^{-12}\ cm^3 molec^{-1} sec^{-1}$

$[C_2F_5OH]$ $(10^{15} molec/cm^3)$

3-3.Results and discussion

The rate constants obtained in this experiment is listed in Table I.

The reaction rates of OH with partially fluorinated alcohols were pressure independent as has been expected from their reaction mechanism; subtraction of hydrogen. The reaction rates was close to the estimated one from the empirical rules, and the measured rate constant for the reaction of OH with CF3CH2OH is in excellent agreement with the reported value by Wallingotn et al 1).

The pressure of $(C_2F_6)_3N$ could not increase more than 5 torr because of its amount synthesized and the large quenching rate of OH fluorescence. So, only the upper limit of the rate constant of $(C_2F_6)_3N$ was obtained. However, the lifetime of this molecule in the environment assuming the average OH concentration of 10^{-5} molecule cm-3 is more than 200years, and it is slower than the transportation rate to the stratosphere.

3-4.References

1) Wallingotn, T.J., Dagault, P., Kurylo, M.J.
"Correlation between Gas-Phase and Solution-Phase Reactivities of Hydroxy Radicals toward Saturated Organics Compounds" J.Phys.Chem. 1988, 92, 5024

4.Photodissociation of freons, halons and their substituents.

4-1.Experimental

Photoabsorption of substituent compounds for chlorofluoro-carbons were measured with a conventional spectrometer. Absolute cross sections were calculated from pressures of the compounds in a photoabsorption cell and their photoabsorption spectra. Compounds were kindly supplied from Nagoya Technical Institute of the Ministry of Trade and Industry, and used after bulb-to-bulb distillation. Photodissociation processes were investigated with a laser technique, directly detecting the photoproducts from the compounds. Resonance-enhanced multiphoton ionization technique and vacuum ultraviolet laser-induced fluorescence technique have been described in details elsewhere.

4-2.Results and discussion

4-2-1. Photoabsorption Spectra4

UV spectra distribution of the Sun ray ranges from 200 to 300 nm in the troposphere and stratosphere. Thus, the compounds that have not photoabsorption at >300 nm can go up to the stratosphere and are photodissociated to produce atoms and radicals. After reference research, we find the following rules for photoabsorption of CFCs and BFCs.

a) BFCs have strong photoabsorption at λ >200 nm. As the number of Br atoms in compounds increase, photoabsorption spectra shifts toward longer wavelength.

b) CFCs have weak photoabsorption at λ >200 nm. As the number of Cl atoms increases the spectra shift toward longer wave-length.

c) HFCs have photoabsorption only at λ <200 nm. As the number of F atoms increases, the spectra shift toward shorter wave-length.

d) Saturated hydrocarbons have no absorption at λ >160 nm, while unsaturated compounds have strong photoabsorption.

Most of the reported spectra were measured at room temperature, while the temperatures of the tropopause-stratosphere range from -70 to -30!n. It is not expected that absorption cross sections in these atmospheric conditions change very much from those reported at room temperature, because photoabsorption is induced mainly by electronic transition in the molecules.

Figure 3 shows an example of the spectra of substituent compounds for CFCs: CF3CF2N(CF2)4, (CF3CF2)3N and (CF3)2NCF2CF2H. photoabsorption is strong at >200 nm, extending up to 240 n

4-2-2. Photodissociation Primary Processes

CFCs produce Cl atoms as primary photoproducts when they are irradiated at near 200 nm. When photon energy is large enough, more than two Cl atoms may be produced.

$$\lambda \text{ (threshold)}$$

CF2Cl2 + hv------> CF2Cl + Cl   350 nm
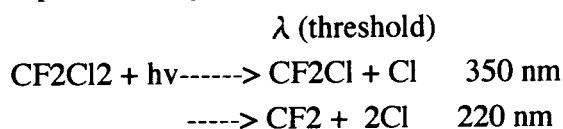
-----> CF2 + 2Cl   220 nm

Photo-produced Cl atoms have rather small kinetic energies. Their distributions are represented by translational temperatures of 2000K. HCFC compounds produce H atoms in their photo-

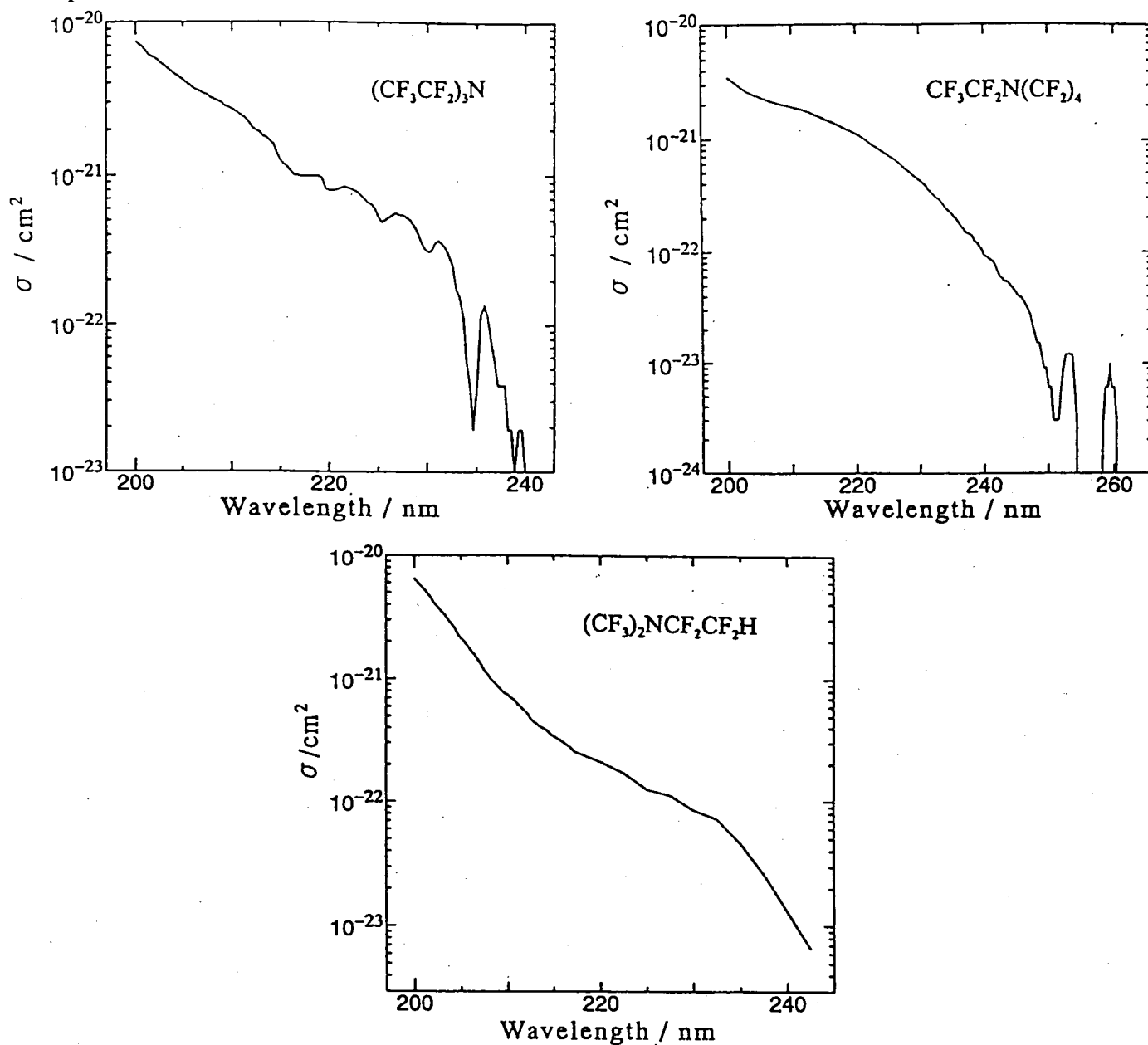dissociation processes. Quantum yields for the H production are always smaller than those for the Cl production.

Figure 3. Absorption spectra of CF3CF2N(CF2)4, (CF3CF2)3N and (CF3)2NCF2CF2H in room temperature.

4-2-3. Decomposition Processes of CFCs other than Photodissociation Processes

Reactive species in the stratosphere are O(1D) atoms and OH radicals. The reactions of O(1D) with CFCs are a) quenching of O(1D) to O(3P) and b) production of Cl atoms. Table II lists some of our results, which shows the quenching is main.

<u>4-3.References</u>

1) Y. Matsumi, S. M. Shamsuddin, M. Kawasaki, "Laser-induced Fluorescence Detection of ClO radicals at 167-180 nm", J. Chem. Phys., 51015, 8362 (1994).
Table I. Product Branching Ratios of O(3P) and ClO from the collision of O(1D) with chlorofluorocarbons.

Table II. Branching of O(1D) reaction to qunch to O(3P) and to produce ClO.

compounds	quenching to O(3P)	ClO production
CCl4	0.14	0.90
CFCl3	0.13	0.88
CF2Cl2	0.19	0.87
CF3Cl	0.16	0.85
CHFCl2	---	0.74
CHCl3	0.13	0.71
CH2Cl2	0.08	0.64

5.Atmospheric concentrations of freons, halons and their substituents.

5-1.Measurement of HCFC-22 by a sensitized ECD

The sensitivity of conventional ECD is very poor for HCFC-22 (CHClF2) in comparison with CFC-11, 12, 113, Methyl chloroform and tetrachloromethane by the factor of several hundred, and the detection with sufficient accuracy without a large volume condensation process was impossible. But the pretreatment requires a lot of time and the accuracy is lost, in general. The remarkable improvement has been achieved by adding a trace amount of oxygen to the carrier nitrogen of GC between the exit of column and the ECD. By this method, the accuracy of 1-2% has been achieved for the background atmospheric HCFC-22 in 200 ml sample (Fig.4).
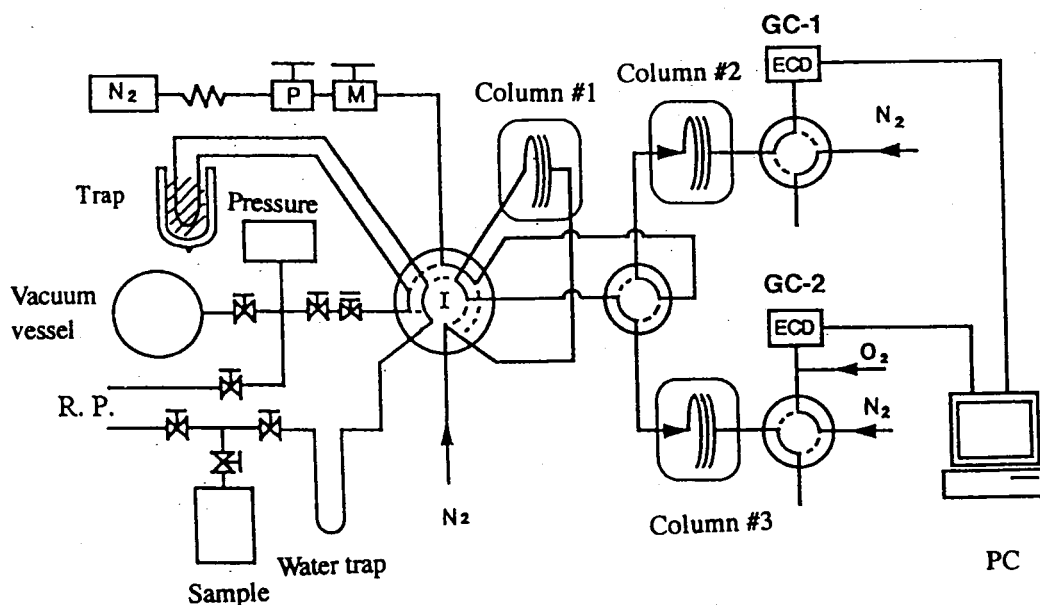

Fig.4. The low temperature condensation-GC-sensitized ECD system to analyze HCFC-12.

5-2. Analysis of stocked air samples

The stocked samples obtained at Cape Nossappu, Wakkanai in Hokkaido (since 1980), the northern island of Japan, and Sowa (since 1985), in Antarctica, were analyzed to know the change of past HCFC-22 concentration. The result is show in Fig.5, where the slow increase of 5.2 pptv/yr in 1980-87 followed by a remarkable increase of 10.3pptv/yr in 1988-1993 can be seen. This rapid growth of the concentration has been induced by Montriol Protocol, which decided the stop of production of CFCs, and the increase of HCFCs production.
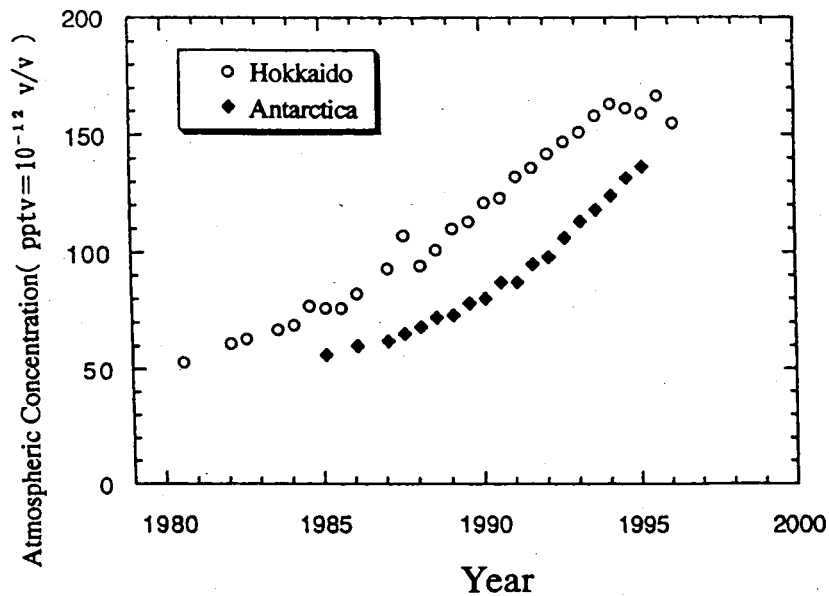

Fig.5. The annual change of background atmospheric HCFC-22 concentration in Northern and Southern Hemisphere. (a) ○ : Hokkaido, ◇ : Antarctica. The solid line is the 2-box model calculation based on the estimated emission database. The dotted line is the result when the emission was multiplied by 1.2 times. (b) Global average.