A-2.5.2 Heterogeneous Chemical Reactions of Alternatives to ODS in the Atmosphere (Final Report)

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Reaction rate and degradation products of heterogeneous reactions on some particles of $N(C_2F_5)_3$, $(CF_3)_2NCF_2CF_2H$ and $(CF_3)_2NCF=CF_2$ were examined to estimate their lifetime and/or degradation mechanisms in the atmosphere. Photodegradation of $(CF_3)_2NCF_2CF_3$ and $(CF_3)_2NCF=CF_2$ proceeded on some particles, while no decrease in $N(C_2F_5)_3$ concentration in gas phase was observed. The estimation of the lifetime of $(CF_3)_2NCF_2CF_3$ and $(CF_3)_2NCF=CF_2$ based on the experimental results revealed that photodecomposition on solid particles was negligible relative to gas phase removal process. For $N(C_2F_5)_3$, its possible removal through the reaction on particles could not be neglected because of its long lifetime in the troposphere. Degradation products were detected for the reaction of $N(C_2F_5)_3$ and $(CF_3)_2NCF_2CF_2H$ but they were not assigned.

INTRODUCTION

Lifetime of alternatives to ODS is directly related to the stratospheric ozone layer depletion[1] and the global warming[2]. While the lifetime is determined through the gas-phase reactions for most of chemical substances[3], it could depend on heterogeneous processes as dissolution into rain droplets[4] or photodegradation on aerosols[5]. This study is focused on heterogeneous reactions on particulate matters as a possible tropospheric sink of fluorinated amines which are candidates for alternatives to ODS.

EXPERIMENTAL

A closed circulation reactor shown in Figure 1 was used. It was made of Pyrex glass. The change in gas-phase concentration of the reactant and its degradation products was measured at ambient temperature using an FID-GC in dark during initial 70 minutes and under photoillumination during the following 280 minutes. A 300 W xenon lamp was used for photoillumination, cutting off UV light shorter than 290 nm using an optical filter.

The examined reactants were three kinds of fluorinated amines which were $N(C_2F_5)_3$, $(CF_3)_2NCF_2CF_2H$, and

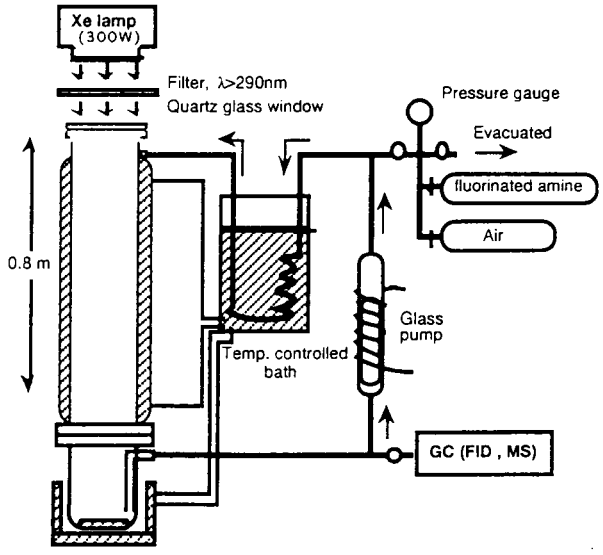

Figure 1. Schematic diagram of the experimental apparatus

$(CF_3)_2NCF=CF_2$. Each of them was diluted with synthetic air to about 50 or 200 ppmv. The examined particles were clays, metal oxides and model compounds for soils, sea salt or aerosols. The particles were placed in the reactor by 0.1 g and preheated at 623 K in air for one hour and in vacuum for one hour and cooled to room temperature before contacting with the reactant gas mixture.

RESULTS AND DISCUSSION

Definition of a decreasing rate

The decreasing rate of fluorinated amines is defined as follows. Figure 2 shows the time-course of $N(C_2F_5)_3$ concentration in the gas phase in the presence of Allophane which is a volcanic clay. Photoirradiation started 70 minutes after admitting the reaction gas mixture into the reactor. The data under photoillumination was analyzed by means of the least squares method. The decreasing rate was expressed by the slope of the straight line (k_L: % h^{-1}). Table 1 summarizes the values of k_L obtained for various particles. It also shows 95% confidence intervals of k_L. The negative value of k_L means the decrease in the gas-phase concentration.

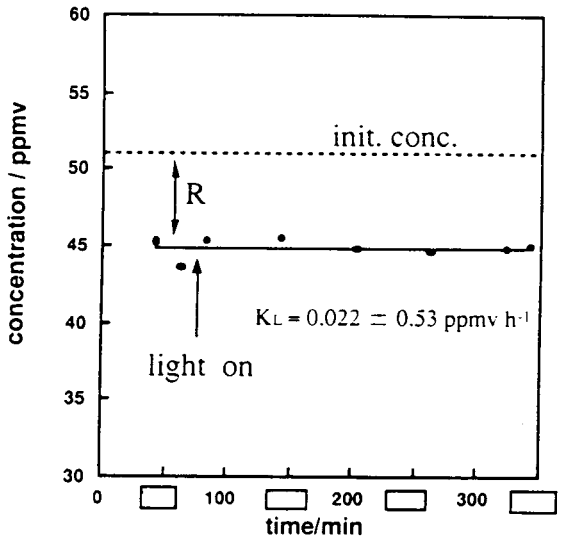

Figure 2. Change in $N(C_2F_5)_3$ concentration in gas phase through the reaction of $N(C_2F_5)_3$ - air - Allophane

Table 1. The decreasing rate of fluorinated ethers through the reaction on various particles under photoillumination

particle	kL / % h^{-1}		
	$N(C_2F_5)_3$	$(CF_3)_2NCF_2CF_2H$	$(CF_3)_2NCF=CF_2$
Blank	0.12 ± 0.88	-0.39 ± 0.43	0.099 ± 0.55
Allophane	-0.04 ± 1.0	-0.33 ± 0.34	-0.13 ± 0.34
Montmorillonite	0.082 ± 1.2	-0.70 ± 0.29	-0.32 ± 0.29
SiO_2	0.22 ± 1.7	-0.37 ± 0.43	-0.41 ± 0.43
Al_2O_3	-0.18 ± 3.2	-0.36 ± 0.44	-0.31 ± 0.44
Fe_2O_3	-0.18 ± 1.9	-0.59 ± 0.26	-0.25 ± 0.26
TiO_2(P25)	0.084±1.6	-8.5 ± 5.6	< -10
NaCl	0.32±1.0	-0.45 ± 0.38	-0.43 ± 0.70
KCl	0.050±0.71		
H_2SO_4	-0.41±0.94	-0.41 ± 0.29	-1.3 ± 0.71

$N(C_2F_5)_3$

The decrease of $N(C_2F_5)_3$ was not confirmed since the estimated 95 % confidence intervals of k_L value ranged over both positive and negative values. Upper limit of k_L is 3.4 % h^{-1}. Based on the model reported by Alyea et al.[61], the tropospheric lifetime of $N(C_2F_5)_3$ is calculated to be longer than several years. Considering very small reaction rate with OH in the gas phase, removal processes with only tens year of lifetime will make effects on the lifetime of $N(C_2F_5)_3$. Hence, no clear judgment can be made regarding its significant removal through photo-degradation on particles. Further experiments should be carried out with greater precision by one order of magnitude to determine whether its lifetime is shorter than several ten years or not.

Figure 3 shows a FID-gas chromatogram for blank, Al_2O_3 and NaCl before and after photoirradiation. A reaction product (A) were detected in the case of Al_2O_3. Products (A) and (B) were observed in the case of NaCl. Figure 4 and 5 shows mass spectra of (A) and (B), respectively. (B) is considered to be $(C_2F_5)_2NCF{=}CF_2$ which is produced by elimination of F_2 from the C_2F_5 base. (A) was not assigned.

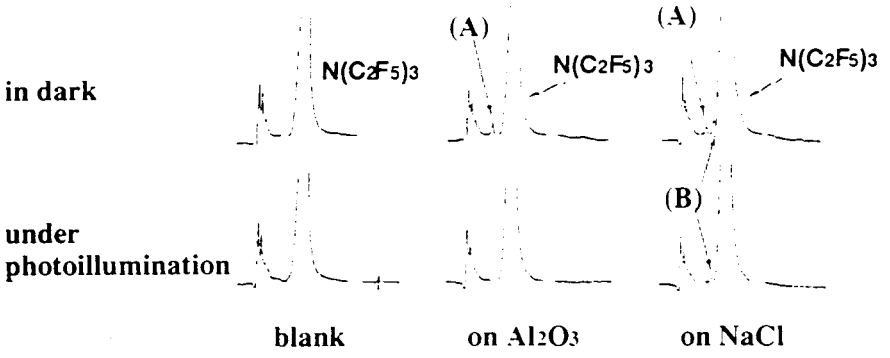

Figure 3. FID-gas chromatogram of $N(C_2F_5)_3$ - air , in the presence of Al_2O_3 or NaCl particles

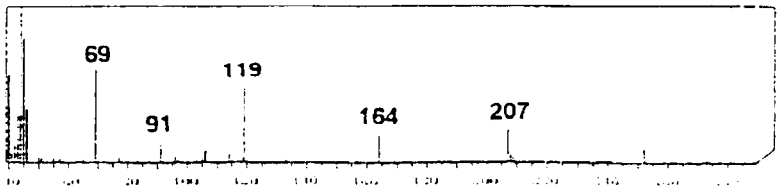

Figure 4. Mass spectrum of product (A)

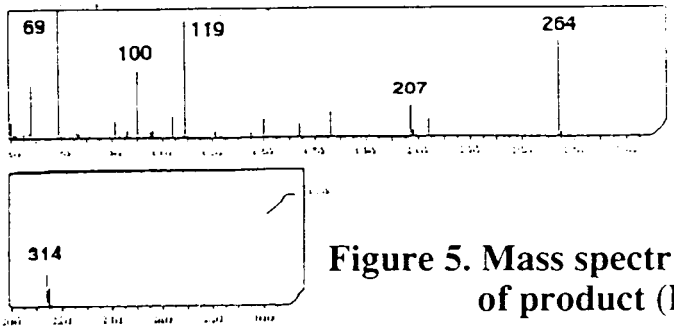

Figure 5. Mass spectrum of product (B)

$(CF_3)_2NCF_2CF_2H$

The decrease of $(CF_3)_2NCF_2CF_2H$ is confirmed in the case of Montmorillonite, Fe_2O_3, TiO_2, NaCl and H_2SO_4. The largest decreasing rate is observed in the case of TiO_2. Reaction products are observed only in the case of TiO_2. Figure 6 shows total ion chromatogram in the range of m/z between 40 and 310. Figure 7 shows a mass spectrum of each reaction product. Neither of them could be identified.

The lifetime of $(CF_3)_2NCF_2CF_2H$ through photodecomposition on TiO_2 is calculated to be about seventy years when one percent of the surface is filled with TiO_2. Considering that the lifetime of $(CF_3)_2NCF_2CF_2H$ through the reaction with OH is several years, the impact on the estimated lifetime seems to be small even for TiO_2 which shows the largest reaction rate. It means that heterogeneous reactions of $(CF_3)_2NCF_2CF_2H$ on particulate matters may be neglected relative to the gas phase reaction.

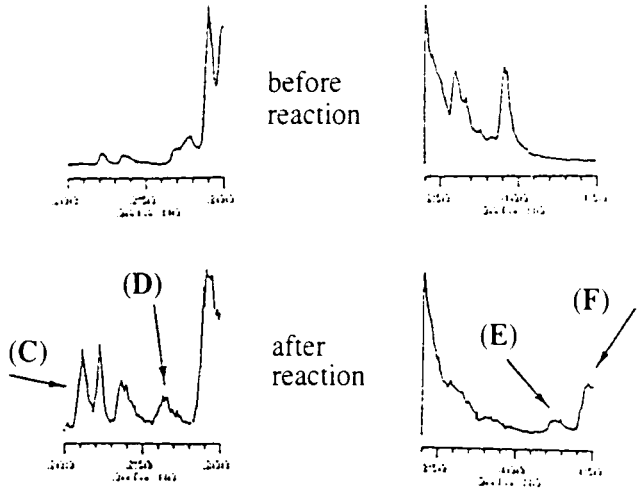

Figure 6. TIC chromatogram for $(CF_3)_2NCF_2CF_2H$ - air - TiO_2

$(CF_3)_2NCF=CF_2$

The decrease was observed in the case of Montmorillonite, TiO_2 and H_2SO_4. The decrease might be brought about mainly due to the reaction with Cl which was formed through photodecomposition of a contaminant such as CH_2Cl_2, and hence its lifetime was not estimated.

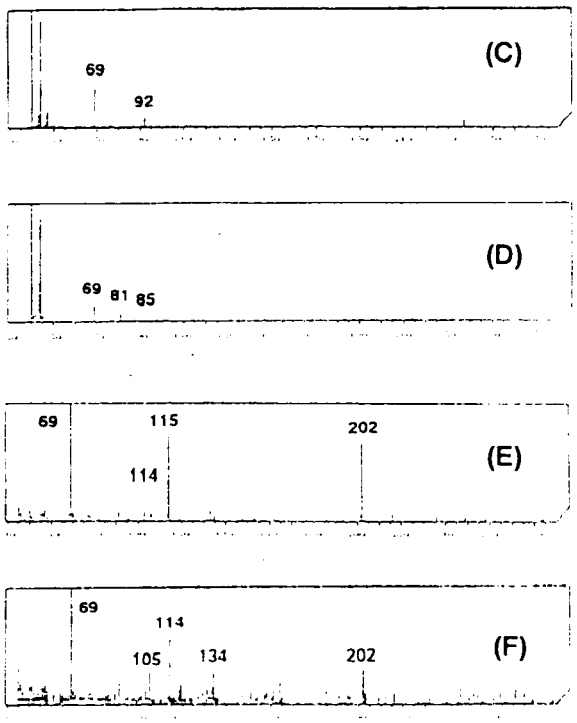

Figure 7. Mass spectrum of products for $(CF_3)_2NCF_2CF_2H$ - air - TiO_2

Summary

Heterogeneous reactions of three kinds of fluorinated amines, which are candidates for alternatives to ODS, on various particles are examined. The lifetime through phodegradation on particles is longer than several years for all examined particles. The tropospheric sink through the reaction on particles has not been confirmed all fluorinated amines examined in this study, though $(CF_3)_2NCF_2CF_2H$ is photodecomposed on some particles. Degradation products are detected for $N(C_2F_5)_3$ and $(CF_3)_2NCF_2CF_2H$.

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