B-8 Studies on the Impacts on Air Quality by Reactive Atmospheric Trace-Species which Control the Oxidizing Capacity of the Atmosphere and the Sink Processes of Green House Gases

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1. Introduction

It is required in the analysis of global warming to catch the effect of cooling by aerosols in addition to the warming effect according to greenhouse gases. In the new report of IPCC reported in 2001, aerosol occupies a significant part as a factor with indefinite nature, and, particularly, organic aerosols were newly added as an important factor.

East Asia is one of the biggest source region of emission of atmospheric pollutants and the emission gives a large impact on not only East Asia but also all over the world. The characteristics of this area is based on the presence of a large amount of natural substances, variety of climate from frigid to tropic, large contribution of sulfur oxides, increasing contribution of nitrogen oxides, and existence of aerosols such as yellow sand which can provide the place of heterogeneous reactions. There are very special chemical processes peculiar to this area. Such chemical processes are not yet well investigated in spite of its importance.

On the other hand, it is thought that the concentration of tropospheric ozone and changes of distribution as well as chemical composition of aerosol are an important factor for environmental changes in Asian region. The increase in nitrogen oxide concentrations mentioned above affects the chemical processes in the atmosphere. It is very important also for tropospheric chemistry to catch the spatial distribution of ozone and aerosol.

2. Research Objectives

From the above viewpoint, clarifying the atmospheric chemical processes peculiar to East Asia/Northwestern Pacific area and analyzing the present status of troposheric environment has urgent necessity. In this study two sub themes were set and research objectives are listed as follows.

(1) Studies on formation, transformation, and removal processes of NOy species

・Clarification of the formation, transformation, and removal processes of NOy in the troposphere, the most important species that governs atmospheric chemical process and atmospheric oxidizing

capacity.

- Prediction of the aggravating photochemical air pollution in the tropical area.
- Evaluation of the reactivity of NOy paying attention to reactions on the surface from a point of view of the characteristics of Asian region where effects of yellow sand and natural hydrocarbons are large.
- Detection of higher alkoxyl radicals and analyses of mechanisms for reactions with NO.
- Evaluation of the temperature dependence of aerosol formation from aromatic hydrocarbons.
- Analysis of aerosol formation processes from organic sulfur compounds.
- Elucidation of the reaction between halogen atoms and ozone.

(2) Ground-based observations of NOy, ozone, and aerosols on remote islands

- Clarification of the distribution of the troposheric NOy which controls the atmospheric oxidizing capacity.
- Clarification of the distribution of ozone which is an important oxidizing substance and is greenhouse gas and grasping the dynamics of hydrocarbons which are precursors of ozone.
- Particularly, understanding the impacts of continental air mass and oceanic air mass.

3. Experiments, Results, and Discussion

(1) Studies on formation, transformation, and removal processes of NOy species

1. Studies on formation and sink processes of peroxynitrate and photochemistry in the tropical region

i) The effect of temperature on the photochemical ozone formation in a toluene-NO_x-Air system was investigated in the temperature range of 17-70°C by using a 6-m^3 photochemical chamber. The reaction time to produce ozone was found shortened when the temperature increased as was observed in the propene system. This could be explained in terms that the HO_x radical concentration was enhanced mainly due to the acceleration of $HO_2NO_2 \rightarrow HO_2 + NO_2$ reaction. On the other hand, the maximum ozone concentration in the toluene system was found to decrease with increasing the temperature. This is different from the feature observed in the propene system in which the maximum ozone concentration was insensitive to the temperature. This could not be explained in terms that the two reaction channels in the OH + toluene (C_7H_8) reaction, *i.e.*, an addition to the aromatic ring and an H-atom abstraction from the CH_3 group, had a different ozone formation potential. Kinetic measurements suggested that the C–O_2 bond of OH-C_7H_8-O_2 radical should be very weak because of the resonance stabilization in the OH-C_7H_8 radical and that the OH-C_7H_8 and OH-C_7H_8-O_2 radicals were in the equilibrium. Hence, the thermo-chemical property of the reaction of OH- $C_7H_8 + O_2 \leftrightarrow$ OH-C_7H_8-O_2 is expected to be an important factor to control the temperature-dependent ozone formation.

ii) The secondary organic aerosol formation from toluene was also studied by using the chamber. The dependence of the initial toluene concentration on the aerosol mass concentration showed that the condensable products were second-generation rather than first-generation and that the ozone reaction with the primary products of toluene oxidation may be important for the production of the condensable species.

iii) The impact of the photooxidation of 2-methyl-3-buten-2-one (MBO) on the air quality was investigated. The OH-initiated oxidation of MBO in the presence of NOx produced acetone in addition to formaldehyde and glycolaldehyde. Since the yield of acetone was found to be about

50%, the oxidation of MBO could be a source of atmospheric acetone if the global emission rate of MBO is large. The ozone formation potential of MBO was found to be larger than that of isoprene. Therefore the MBO oxidation must contribute the photochemical ozone formation as isoprene does.

2. Study on NOy species at atmosphere-solid interface

The final goal of this research project is the evaluation for the role of heterogeneous processes on the atmospheric fate of NOy at atmosphere-solid interface. Heterogeneous processes of relatively inactive NOy species, PAN and nitric acid, have been investigated for removal processes of them or formation of reactive species such as nitrous acid. Measurement of loss rates of PAN in water and in several aqueous salt solutions with a simple stripping experiment revealed that it is not a significant sink of PAN. DRS-UV measurement showed red shift of uv absorption of NO_3^- when it was adsorbed on clay minerals. Modified GDE and REMECH were used to simulate time-profile of chemical composition, particle number, average size, size distribution, and gaseous species including NOy under different reaction conditions such as relative humidity. The simulated results were useful to assess reactivity of aerosols and its interaction with NOy. Uptake of NOy on aerosols increased with increasing relative humidity.

3. Study on the reaction rate for Alkoxy Radicals and NO reactions

The reaction of vinoxy radical (CH_2CHO) with O_2 has been studied by using laser induced fluorescence method. Vinoxy radical has similar structure with alkoxy radicals, which is an oxy-type radical. In this study, the reaction rate constants and product yields were measured at room temperature. Pressure dependency of the rate constants was obtained in the experimental conditions, which was concerned to the fall-off region. The rate constants are consistent with comparable report by other group using similar experimental method, however, another report by using cavity ring-down spectroscopy is lower than our results. OH radicals were also observed as reaction products from this reaction. The rise rate constants of OH radicals are agreement with the reaction rate constants so that OH radicals are possible to be direct products from the reaction. The product yields of OH radicals were measured by comparing with reference reaction as $O(^1D)$ with H_2 which leads OH radicals from the unique product channel of OH + H. The product yields depends on the total pressures, which were determined as 0.2 to 0.1 for 10-40 Torr in He. The product yields were decreased at the side of high pressures, which was concluded that the OH product channel were competitive with the stabilization channel of formylmethyl peroxy radicals by third body effect. At the conclusive remarks, the reaction mechanism of vinoxy radical with O_2 is similar to the reactions of alkyl radicals rather than alkoxy radicals, however, it is surprising fact that reproducing channel of OH radicals as the reactive species is not unlikely exist even in the conditions of lower temperatures. The new product channel of this type will give some effects for modeling of atmospheric reactions.

4. Studies on the photochemical oxidation of organic sulfur compounds

In order to clarify the photooxidation processes of organic compounds in air both numerical model studies for photochemical reactions and smog-chamber studies were performed.

i) Photochemical reactions in propene-NOx-air systems both in the presence and absence of chlorine atoms were simulated by a box model. The model reproduced the results of the experiments. The

results of the simulation in this study could simulate the experimental results qualitatively.
ii) Aerosol production from the oxidation of dimethyl sulfide (DMS) - the main natural source of sulfur for the troposphere - was investigated next. Within this work particle formation in the gas-phase oxidation of DMS was studied in the absence and presence of NOx at 300±2 K. Significant formation of particles was observed under NOx-rich conditions. Particle formation was observed also when water concentration was low. This suggests that heterogeneous processes (hydrolysis) are not alone responsible for aerosol formation. Further chemistry of methylsulfonyl peroxynitrate seems to produce particles which agree with its decomposition producing SO_2 rather than methanesulfonic acid. Formation of methylsulfonyl peroxynitrate might occur in lightly polluted coastal regions.
iii) SO_2 is the most important as the source of new particles in the gas-phase oxidation of both DMS and DMSO. Oxidation of SO_2 proceeds via H_2SO_4 formation followed by homogeneous and/or heterogeneous nucleation. The effect of temperature on aerosol formation was also investigated. Suppression of particle formation was seen when temperature increased from 298 to 318 K in the absence of NOx. Physical features related to the nucleation process and partitioning of co-products (MSA, DMSO2) rather than chemistry account for these results.

The results give a possible image of the cloud condensation nuclei formation and growth in the marine boundary layer.

(2) Ground-based observations of NOy, ozone, and aerosols on remote islands

1. Observations in the sub-tropical marine boundary layer

Ground based observation of atmospheric constituents has been conducted at Chi-chi Island of Ogasawara islands to investigate the effect of continentally originated pollutants on the pristine atmospheric nature over the North Pacific Ocean. In fiscal year 2001, we have analyzed the accumulated data at the Island. The effect of refractive index of particles on the readout of optical particle counter (OPC) is examined with the Mie calculation. Following such validation works, discrete readouts of particle size distribution by OPC are fitted to log-normal size distribution function and parameters describing mode diameter and standard deviation are determined. Those parameters are necessary in modeling the marine and continentally influenced types of aerosols. With a low-pressure impactor, the size distribution of soil particles and black carbon are further measured when they are transported simultaneously in spring.

Single scattering albedo of aerosols is determined from the absorption coefficient and scattering coefficient measured continuously. Single scattering albedo decreases greatly (~0.8) when polluted air masses are transported to the Island, which indicates that the Asian originated aerosols transported intermittently over the NW Pacific are greatly absorptive. Optical depths of aerosols, which is the integral of aerosol extinction coefficient from the surface to the top of atmosphere, fluctuate greatly with seasons and show maximum in spring, which differs from those of pollutants measured on the surface.

The fluctuation of black carbon is brought about by the passage of polluted air masses which have 4-6 day cycle. During the "high concentration period" from October to early June, the frequent passage of this polluted air mass is observed. While on the "clean period" under the influence of North Pacific Anticyclone in summer, the aerosols concentration are low although occasional arrival

of those polluted air mass still remains even in this season. From the analysis of OPC data, aerosols in these polluted air mass has a mode at about 0.2 μm when expressed in number size distribution.

2. Ground-based observation studies in the area of high anthropogenic impact and in the area where air masses show seasonal change

In this study, nitrogen oxides such as PAN and hydrocarbons, which are controlling the oxidizing capacity of air and the life time of greenhouse gases, were observed on Oki island and Okinawa island.

Among nitrogen oxides, peroxyacetyl nitrate (PAN) and organic nitrate ester are the carrier compounds which convey nitrogen oxide from polluted area to a clean area. Therefore, PAN is an important index substance for grasping the influence of nitrogen oxides from the East Asian continent on Pacific rim region and the Pacific Ocean. Moreover, nitrogen oxide is also a substance which plays a important role in tropospheric chemical reactions as a precursor of photochemical ozone production on global scale. In order to get insight into the dynamics of atmospheric PAN, an automatic concentration/analysis system was prepared, and continuous measurement was tried on Oki Island. For grasping the dynamics of hydrocarbons which promote tropospheric chemical reactions and are also the index substances of the atmospheric quality of anthropogenic contamination like nitrogen oxides, automatic sampling of air was carried out near Cape Hedo at the northernmost tip of Okinawa main island, and hydrocarbons were measured.

No significant diurnal variation was observed in the concentration of PAN on Oki Island. In urban photochemical smog near emission source PAN normally shows a maximum concentration in the afternoon. No such variation was seen on Oki Island, which means that the PAN observed there was not a local origin but was transported long range. During the season when northwest wind prevails (December-April) monthly average of PAN concentration was 20-30 ppt and the range of fluctuation was only 5-15 ppt. It suggests that relatively unpolluted air mass from North Asia reached Oki Island in winter, but more than 100 ppt of PAN was observed occasionally. Transport of polluted air mass from mid-latitude Asia cannot be ruled out. This high concentration of PAN was thought to be similar to the high concentration of PAN found by aerial observations over the Sea of Japan.

It turned out from the continuous measurements of light hydrocarbons at Cape Hedo in Okinawa main island that those hydrocarbons showed a seasonal variation such as low concentration in summer and high concentration in winter. From the backward trajectory analyses of the air masses inflow of the oceanic air from the central Pacific Ocean is dominant in summer, and inflow of the continental air from northwest is dominant in winter. Above seasonal variation of hydrocarbons was speculated to be caused by the seasonal difference of the origin of air masses and the seasonal differences in the photochemical activity of the atmosphere. Not only a seasonal variation but also a short (several days) periodic variation within the same season was observed based on the change of air masses. In addition, high concentration of ozone was also observed when high concentrations of hydrocarbons were transported with the out flow of continental air.

These observations supported the contention that the continental air which is rich in reactive gases has high oxidizing ability and, as a result, high ability of ozone formation.