RF-071 Study of the Influence of Anthropogenic Species in the Atmospheric Iodine Cycle on Global Warming（Abstract of the Final Report）

Contact person Yukio Nakano
Lecturer, Graduate School of Information Sciences,
Hiroshima City University,
Hiroshima, 731-3194, Japan
Tel:+81-082-830-1825 Fax: +81-082-830-1825
E-mail: yukio_n@hiroshima-cu.ac.jp

Total Budget for FY2007-FY2008 14,435,000Yen （**FY2008**; 6,935,000Yen）

Key Words iodine aerosol, alkyl iodides, NO_3 radical, formation mechanism, rate constant

[Abstract]

In this study, the influence of anthropogenic species on the atmospheric formation of iodine monoxide (IO) radical, which is considered to be a precursor of iodine aerosols, was investigated in order to contribute to improve the accuracy of the future estimation of the global warming. Specifically, we measured the reactions of nitrous radical (NO_3) with alkyl iodides that originate from natural sources and trifluoroiodomethane (CF_3I) which is a new candidate of a replacement for hydrochlorofluorocarbons and hydrobromofluorocarbons. Here, NO_3 radical is known to be atmospheric strong oxidizer emitted by human activities. Among alkyl iodides, iodomethane (CH_3I), iodoethane (C_2H_5I), chloroiodomethane (CH_2ClI) and bromoiodomethane (CH_2BrI) were examined in their reactions with NO_3 and the rate constants of these reactions were determined. To reveal the impact of the reactions of NO_3 with alkyl iodides on the atmospheric chemistry, model runs including NO_3 + CH_3I reaction were performed using a zero-dimensional box model. The durational variation of IO radical calculated by the model including the reaction of NO_3 with CH_3I shows about 10 times higher than that calculated by the model run not including the NO_3 + CH_3I reaction. This result indicates that the concentration of IO radicals in the atmosphere may be 10 times higher than that considered previously. We also measured the reaction of NO_3 with CF_3I. As a result, the reaction of NO_3 with CF_3I was found to be very slow. This result indicates that CF_3I in the atmosphere is mainly consumed by the sunlight photolysis and its concentration rises up during the nighttime. The results obtained in this work will contribute to the improvement of the accuracy of estimates of the reactive iodine compounds and iodine aerosols in the atmosphere by the model calculations.

1. Introduction

Aerosol, which is a suspension of fine solid particles or liquid droplets in a gas, has a potentially significant effect on global radiative forcing by absorbing and scattering the sunlight and infrared radiation from the earth surface, and consequently plays an important role in global warming. Because of low level of scientific understanding for aerosol, the estimated value of the radiative forcing of aerosols has a large uncertainty in radiative forcing which is comparable to the radiative forcing of carbon dioxide. Recent studies have suggested the importance of reactive iodine compounds, such as iodine monoxide radical (IO), for aerosol formation in the atmosphere. IO radical has been considered to be produced by the sunlight photolysis and the sequential reactions of alkyl iodides that are produced by various types of macroalgae and phytoplankton in the ocean and emitted into the atmosphere. The atmospheric formation of IO radical induces the formation of iodine aerosol particles in the atmosphere. Thus, the emission of alkyl iodides from marine environments had a potentially significant effect on global radiative forcing. If the phenomenon of the atmospheric formation of iodine aerosols occurs on a large scale, it could have significant effects on climate. Even the importance of IO radical in the atmosphere, model calculations of the concentration of IO radical could not reproduce the observed IO concentration. It is necessary to investigate the influence of anthropogenic species on the atmospheric concentration of IO radicals as new reaction pathways to form IO radicals. The candidates of new reaction pathways that form IO radicals in the atmosphere are the reactions of nitrous radical (NO_3) with alkyl iodides that originate from natural sources and trifluoroiodomethane (CF_3I) which is a new candidate of a replacement for hydrochlorofluorocarbons and hydrobromofluorocarbons. Here, NO_3 radical is known to be atmospheric strong oxidizer emitted by human activities. Those reactions have not been investigated previously, it is impossible at this time to estimate the influence of the formation of IO radicals via those reactions in the atmosphere

2. Research Objective

In this study, the influence of anthropogenic species on the atmospheric formations of IO radicals, which is considered to be a precursor of iodine aerosols, was investigated in order to contribute to improve the precession of the future estimation of the global warming. Because the candidates of new reaction pathways that form IO radicals in the atmosphere are the reactions of NO_3 radical with alkyl iodides that originate from natural sources and CF_3I, we performed the experiments for the following two research subjects.

1. Investigation of the formation process of atmospheric reactive iodine compounds by the reaction of NO_3 radical with naturally emitted alkyl iodides.

2. Investigation of the formation process of atmospheric reactive iodine compounds by the reaction of NO_3 radical with CF_3I.

The atmospheric importance of these research subjects are shown in Figs. 1 and 2, respectively.

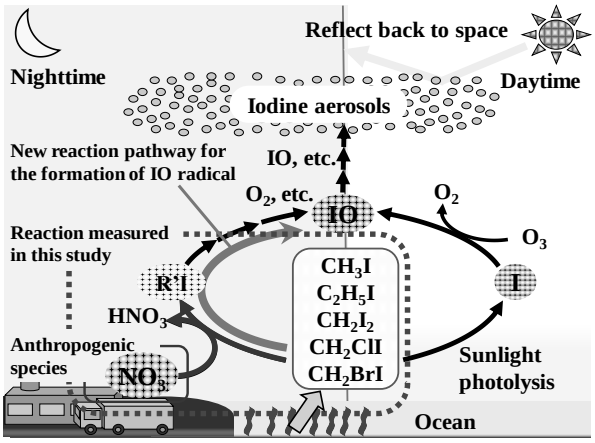

Fig.1 The formation process of atmospheric reactive iodine compounds by the reaction of NO_3 radical with naturally emitted alkyl iodides.

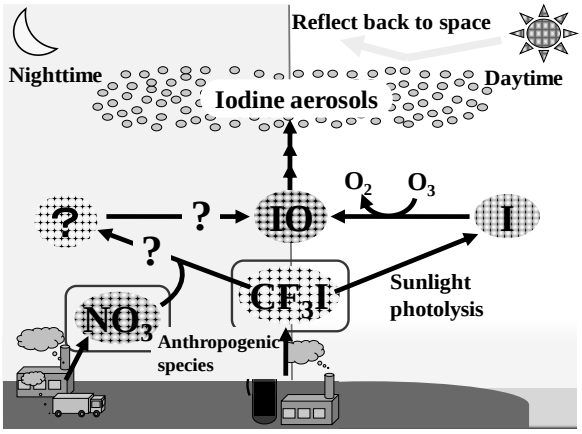

Fig.2 The formation process of atmospheric reactive iodine compounds by the reaction of NO_3 radical with CF_3I.

In the research subject 1, we measured the reactions of NO_3 radical with alkyl iodides that originate from natural sources. Here, NO_3 radical is known to be atmospheric strong oxidizer emitted by human activities. The reactions of NO_3 radical with alkyl iodides are shown in the following equation.

$$NO_3 + RI \rightarrow R'I + HNO_3 \quad (1)$$

Where RI indicates alkyl iodides and R'I indicates hydrogen abstracted forms of alkyl iodides. R'I are known to be converted into IO radical by the sequential reactions in the atmosphere. Iodomethane (CH_3I), iodoethane (C_2H_5I), diiodomethane (CH_2I_2), chloroiodomethane (CH_2ClI) and bromoiodomethane (CH_2BrI) are known to be major alkyl iodides that are produced by various types of macroalgae and phytoplankton in the ocean and emitted into the atmosphere. Among those alkyl iodides, CH_3I is most abundant in the atmosphere and its annual emission is estimated to be 300-1000 Gg $year^{-1}$. However, to completely understand the influence of the reaction of NO_3 radical with alkyl iodides on the atmospheric formations of IO radicals, not only CH_3I but also other alkyl iodides described above must be investigated. In this study the reactions of NO_3 radical with iodomethane (CH_3I), iodoethane (C_2H_5I), chloroiodomethane (CH_2ClI) and bromoiodomethane (CH_2BrI) were measured in this work and the rate constants of these reactions were determined.

In the research subject 2, we measured the reaction of NO_3 radical with CF_3I. This reaction is shown in the following equation.

$$NO_3 + CF_3I \rightarrow \text{products} \quad (2)$$

CF_3I is the new compound which attracts the attention as a new candidate of a replacement for hydrochlorofluorocarbons and hydrobromofluorocarbons. Ozone-Depleting Potential (ODP) and Global Warming Potential (GWP) of CF_3I are about 1000 times lower than that of hydrochlorofluorocarbons and hydrobromofluorocarbons. By Montreal Protocol on Substances that Deplete the Ozone Layer, the productions of some of currently used hydrochlorofluorocarbons and hydrobromofluorocarbons were restricted. Thus, the expectation for the practical use of CF_3I has been rising. If CF_3I is widely used in near future, much amounts of CF_3I is emitted into the atmosphere. Because CF_3I includes iodine atom in its structure, it could become a new source of the atmospheric reactive iodide compounds. Here, one of possible reaction path way of the consumption of CF_3I to form IO radical in the atmosphere is the reaction with NO_3 radical. Because the reaction of NO_3 radical with CF_3I has not been investigated, it is impossible at this time to estimate the influence of the formation of IO radicals via this reaction in the atmosphere. Thus, the reaction of NO_3 radical with CF_3I was investigated as the research subject 2.

3. Results

In the research subject 1, we measured the reactions of NO_3 radical with alkyl iodides that originate from natural sources. CH_3I, C_2H_5I, CH_2I_2, CH_2ClI and CH_2BrI are known to be major alkyl iodides that are produced by various types of macroalgae and phytoplankton in the ocean and emitted into the atmosphere. Thus, the reactions of NO_3 with CH_3I, C_2H_5I CH_2ClI and CH_2BrI as alkyl iodides originating from natural sources were measured in this study. Consequently, we determined the rate constants of these reactions by using time-resolved cavity ring down spectroscopy method. By using the rate constants determined in this work, the atmospheric lifetimes of alkyl iodide originated from natural source were estimated. These results are summarized in Table. To reveal the impact of the reactions of NO_3 with naturally emitted alkyl iodides on the atmospheric chemistry more quantitatively, model runs including NO_3 + CH_3I reaction were performed using a zero-dimensional box model. The durational variation of IO radical calculated by the model including the reaction of NO_3 with CH_3I shows about 10 times higher than that calculated by the model run not including the NO_3 + CH_3I reaction. This result indicates that the concentration of IO radicals in the atmosphere may be 10 times higher than that considered previously.

In the research subject 2, the reaction of NO_3 radical with CF_3I was measured using FTIR smog chamber which is equipped with long path length gas cell and its rate constant was determined by a relative rate method. As the result, the rate constant for the reaction of NO_3 with CF_3I was determined to be $k_{NO3+CF3I} < 1.8 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. The determined rate constant and the atmospheric lifetime of CF_3I by the reaction with NO_3 radical are summarized in Table.

Table Atmospheric lifetimes of alkyl iodide originated from natural source and CF_3I by their reactions with NO_3 radical.

Origin	Iodine compound	Reaction rate constant / cm^3 $molecule^{-1}$ s^{-1}	Lifetime[a)]
Natural	CH_3I	4.1×10^{-13}	2.7 hours
	C_2H_5I	2.0×10^{-14}	5.6 hours
	CH_2I_2	4.0×10^{-13}	2.8 hours
	CH_2ClI	1.1×10^{-13}	10 hours
	CH_2BrI	2.0×10^{-13}	5.6 hours
Anthropogenic	CF_3I	$<1.8 \times 10^{-15}$	>1 month

a) The concentration of NO_3 is estimated to be 2.5×10^8 molecules cm^{-3} and the concentration of OH is estimated to be 1.0×10^6 molecules cm^{-3}.

4. Discussions

From the experimental results obtained in the research subject 1, the atmospheric importance of the reaction of the alkyl iodides that originate from natural sources with NO_3 radical was summarized as follows. Iodomethane (CH_3I) and iodoethane (C_2H_5I), which one of the alkyl iodides originated from a natural source, are mainly consumed by the reaction with the NO_3 radical to form IO radical in the atmosphere. Because the formation of IO radicals in the atmosphere induces the formation of iodine aerosol particles in the atmosphere, the reactions of CH_3I and C_2H_5I with NO_3 radical can act important roles in the atmospheric iodine aerosol formation. For chloroiodomethane (CH_2ClI), bromoiodomethane (CH_2BrI) and diiodomethane (CH_2I_2), it is likely that the reactions with NO_3 radical don't affect on the losses of CH_2ClI, CH_2BrI and CH_2I_2 at daytime. However, during the nighttime, these reactions may have importance for the formation of IO radical.

From the experimental results obtained in the research subject 2, the influence of the reaction of CF_3I with NO_3 radical on the formation on the atmospheric formation of IO radical was summarized as follows. The reaction of NO_3 with CF_3I was found to be very slow in the atmosphere. Thus, CF_3I in the atmosphere is mainly consumed by the sunlight photolysis and its concentration rises up during the nighttime.

5. Scientific outcome

The scientific impact of the results obtained in this study is considered to be large because this study investigates the influence of anthropogenic species, especially NO_3 radical, on the atmospheric iodine cycle which has not considered previously. The results obtained in this study indicate that NO_3 radical can affect the atmospheric formations of iodine monoxide (IO) radicals,

which is considered to be a precursor of iodine aerosols. The level of scientific understanding of aerosol is low and the estimated radiative forcing values of aerosol have large uncertainties. Thus, our results contribute to the accuracy improvement of the estimated values of radiative forcing of aerosol. The results obtained in this work will also contribute to the improvement of the accuracy of estimates of reactive iodine compounds and iodine aerosols in the atmosphere by the model calculations.

6. Contribution to policy of global environmental issues for decision makers

Through the publication of our results in scholarly journal as articles, the rate constants determined in this study will be added to the kinetic databases for the atmospherically important reactions that are published by National Aeronautics and Space Administration/Jet Propulsion Laboratory (NASA/JPL), International Union of Pure and Applied Chemistry (IUPAC) and National Institute of Standards and Technology (NIST). Consequently, the results obtained in this study will be recognized as the important outocomes among atmospheric scientists whose major is environmental chemistry, physics, meteorology, computer modeling, oceanography, geology and volcanology and other disciplines, etc. Through this process, the results obtained in this work will be used for box model calculations and so on and those results will contribute to the improvement of the accuracy of estimates of reactive iodine compounds and iodine aerosols in the atmosphere by the model calculations. Finally, because the targets of present study are radiative forcing components whose levels of scientific understanding are low, our results will contribute to the accuracy improvement of the estimated values of radiative forcing in the report of Working Group I of the Intergovernmental Panel on Climate Change.

Major Publications

1) Yukio Nakano, Hiromi Ukeguchi, Takashi Ishiwata, Yugo Kanaya, Hiroto Tachikawa, Atsushi Ikeda, Shigeyoshi Sakaki, Masahiro Kawasaki “An experimental and theoretical study on temperature dependence of the reaction of NO_3 with CH_3I” *Bulletin of the Chemical Society of Japan*, **81**(8), 938-946 (2008)