

B-3.2 Studies to Evaluate Budget of Atmospheric Trace Gases

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Abstract In order to estimate photodissociation rates of atmospheric trace gases at several altitudes, photoabsorption cross sections of these compounds have been measured in the ultraviolet region. The cross sections obtained show a temperature effect in the wavelength region longer than 200nm. The cross sections for CFC-112, CFC-113, and CFC-114 change through the substitution between Cl and F atoms among these molecules. Photodissociation rates were estimated using the observed cross section data and the calculated solar radiation intensities from the literature data. The life times for these molecules as well as CFC-12, CFC-13, and HCFC-123 are found to be longer than 10^5 years at the altitude of 10km, and those for CFC-113 and HCFC-123 are about 100 years at 20km. An infrared-ultraviolet double resonance laser-induced fluorescence method has been developed for observation of the OH radical in the troposphere, which exists in extremely low concentrations like 10^6 molecules/cm³, but plays a critical role in the atmospheric chemistry. The detection limit of this technique was experimentally determined and the monitoring in the atmospheric environment is discussed. A method for the selective detection of alkyl isomer radicals has been developed by using photo-ionization mass spectrometry. Site selectivities in reactions of O/OH+alkans and of O₂ with butyl radicals were investigated using this method.

Key Words Photoabsorption Cross Section, IR-UV LIF Method, OH Concentration,
Photoionization Mass Spectrometry, Alkyl Peroxy Radicals

I. Introduction

The concentration of CO₂ in the atmosphere is presumed to increase owing to expansion of human activities and of energy demand, which largely consume fossil fuels. Many scientists are afraid that this increase is provoking temperature rise and climate change in tens of years later. The temperature rise is also brought about by an increase in concentrations of several trace gases, for

example, CH₄ and chloro-fluoro-carbons. These compounds are inert and the height distributions of their concentrations are constant in the troposphere, indicating that their life times are very long. Many of those gases are expected to dissociate through absorption of solar ultraviolet radiation or to react with radicals in the stratosphere.¹⁾ The photodissociation rate is a very important factor in estimation of their lives, which play a critical role in determining a potential of green-house-effects.

The radical of OH plays an important role in the atmospheric chemistry. As a chemical life time of OH is about 1 s due to its high reactivity with the other trace gases, and a concentration of OH ([OH]) depends strongly upon ambient conditions, is less than 1×10^6 molecules/cm³. Space- and time-resolved "in situ" measurements are required for evaluating the chemical reaction model in the troposphere.²⁾ There appeared severe problems in measuring OH radicals by the laser-induced fluorescence (LIF) method. The first problem is artificial generation of OH, which is called "ozone interference". Ozone is photolyzed by ultraviolet light to monitor ambient OH and converted into artificial OH through O(¹D) + H₂O reaction. The second is nonresonant fluorescence background signals originating from the interaction/scattering of ultraviolet radiation with atmospheric gases and aerosol.

Formation of alkyl radicals and their reactions with O₂ are important for the oxidation processes of no-methane hydrocarbons in the atmosphere. In order to understand the detailed mechanism for the no-methane hydrocarbon reactions, it is necessary to develop the method for the selective detection of alkyl radical isomers which are expected to have different reactivities.

2. Research Objective

The present study was initiated in order to estimate precisely photodissociation rates of atmospheric trace gases. The estimation requires accurate data on photoabsorption cross sections of the compounds at a low temperature, ultraviolet solar radiation at several altitudes. These data have been measured using a long absorption cell connected with synchrotron radiation. In order to overcome the interferences on OH radical measurements, we developed an infrared-ultraviolet double resonance laser-induced fluorescence (IR-UV LIF) method to monitor the OH radical in the troposphere. Furthermore, the photo-ionization mass spectrometry developed by Washida and Bayes³⁾ has been adopted for the selective detection of alkyl radical isomers and the following subjects have been studied: 1) Direct determination of the product branching fractions for the O/OH+C₃H₈ reaction. 2) Rates and mechanism of the C₄H₉ radical isomers with O₂. 3) Unimolecular decomposition processes of the hydroperoxybutyl radicals.

3. Research Methods

Synchrotron radiation is monochromatized using a monochromator of Seya-Namioka type,

providing an ultraviolet radiation source. The long cell has been designed and constructed, which is surrounded with cold bath. The temperature of the cell can be decreased to -60°C and be maintained at a pre-set value by a personal computer. The photoabsorption cross section at a temperature T and a wavelength λ is expressed with the following.

$$\sigma(\lambda, T) = n^{-1} \cdot L^{-1} \cdot \ln \{ I_0(\lambda, T) / I_1(\lambda, T) \},$$

where L denotes the length of the cell, and I_0 and I_1 indicate the intensities of the incident and transmitted lights, respectively.

The detection sensitivity and detection limit of IR-UV LIF method was determined experimentally. The rate constants of rotational relaxation in the $v=1$ state were determined for N_2 and Ar. The ν_{IR} light was generated in LiIO_3 (Inrad, IR-Auto Tracker) by the difference-frequency mixing of $1.06 \mu\text{m}$ from the Nd:YAG laser (Lumonics HY750) and 770 nm from one dye laser (Lumonics HD300). The ν_{UV} light was generated by the frequency-doubling of 700 nm from another dye laser using a non-linear crystal (Inrad, UV-Auto Tracker II). The OH radical in the known concentration was generated by a titration method ($\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$) using an excess amount of H atoms (produced by a microwave discharge of H_2/Ar) and the known concentration of NO_2 . The OH fluorescence was collected by quartz lens, selected by an interference filter (Corion, P10-310-F), and detected by a photomultiplier (Hamamatsu, 1P28). The output signal was averaged by a boxcar integrator (Stanford Research, SR-250/240/280), recorded by a chart recorder, and stored in a personal computer.

The ionization potential (IP) of $i\text{-C}_3\text{H}_7$ is equal to 7.57 eV , whereas IP of the $n\text{-C}_3\text{H}_7$ is equal to 8.13 eV . Therefore selective detection of $i\text{-C}_3\text{H}_7$ is possible with the use of the resonant radiation of Br atom at 7.9 eV for the ionization. The resonant radiation of Br was obtained by the microwave discharge of the Br_2/He mixture, which is slowly flowed in the discharge lamp. Sample gases (diluted in He) are also slowly flowed in the reaction cell and sampled through a pinhole into the ionization chamber of the mass spectrometer. Ions produced by the photoionization were detected by the time-resolved quadrupole mass spectrometry.

There are four different isomers for the butyl radical, and it is expected that these isomers have different reactivities with the molecular oxygen. In the present study, these butyl radical isomers have been produced by the ArF laser photolysis of corresponding $\text{C}_4\text{H}_9\text{Cl}$, and butyl radical isomers were detected with appropriate resonant lamps. For examples, $i\text{-C}_4\text{H}_9$ (IP= 8.01eV) was detected with O atom resonant line, and $t\text{-C}_4\text{H}_9$ (IP= 6.93eV) was detected with Br lamp.

Decomposition processes of the peroxy radicals formed by the reactions of alkyl radical + O_2 are important for the understanding of the oxidation mechanism of non-methane alkanes. It is believed that the hydroperoxy radical is produced by the isomerization of peroxy radical which is produced by the alkyl + O_2 reactions and that hydroperoxy radical is further decomposed to produce epoxide or

olefines. However there has been no direct evidence for this mechanism. Baldwin and Walker⁵⁾ found that butylene was produced by the reactions of *n*- and *s*-C₄H₉ at above 700K, whereas Batt et al.⁶⁾ reported that epoxide was the main product of the *t*-C₄H₉+O₂ reaction at below 400K. In the present study, *t*-hydroperoxybutyl radical was produced by the reaction of Cl+TBHP(*t*-butylhydroperoxide). Cl atom was generated by the ArF laser photolysis of CCl₄. It is noted that the Cl+TBHP reaction is exothermic by 5.2 kcal/mol. The butyl epoxide, C₄H₉O, could be detected as the product of the unimolecular decomposition of hydroperoxy butyl radical.

4. Results and Discussion

The photoabsorption cross sections of several freon molecules including CFC-112, CFC-113, CFC-114, and HCFC-123 have been determined in the ultraviolet radiation region. The cross sections decreased as the temperature of the cell was lowered, especially in wavelengths longer than 200nm. Systematic variation was found in the values of the cross sections against the substitution of Cl and F atoms in these molecules, as follows. The cross sections at 190nm are $1.7 \times 10^{-18} \text{ cm}^2$ for CFC-112, $7 \times 10^{-19} \text{ cm}^2$ for CFC-113, and $6 \times 10^{-20} \text{ cm}^2$ for CFC-114. The data at 220nm are $1.4 \times 10^{-20} \text{ cm}^2$ (CFC-112), $2.5 \times 10^{-21} \text{ cm}^2$ (CFC-113), and $1.3 \times 10^{-22} \text{ cm}^2$ (CFC-114). The molecule HCFC-123 is a promising candidate for alternative of CFC-11, because this molecule is supposed to disappear at about 1 year in the troposphere through a reaction with the OH radical. However a part of HCFC-123 is presumed to reach the tropopause, and then it is important to examine the photodissociation life time of this molecule through absorption of solar ultraviolet radiations. The obtained cross sections at room temperature are $1.2 \times 10^{-18} \text{ cm}^2$ at 185nm and $8 \times 10^{-22} \text{ cm}^2$ at 225nm. Those at a low temperature (-53 °C) are lower than those at room temperature in long wavelengths. The difference between the data at the two temperatures increases with the increasing wavelength.

Intensities of ultraviolet radiation at several altitudes were calculated in consideration of decrease by photoabsorption of O₂ and O₃ using the observed data of solar radiation at the upper atmosphere, photoabsorption cross sections of these gases, and mixing ratios of atmospheric components. Day-averaged intensities were derived on account of effective path length depending on the height of the solar position. Life times for the trace gases including HCFC-123 were found to be longer than 10⁵ years at the altitude of 10km. This finding means that the CFC compounds can reach the stratosphere without loss and that the life of HCFC-123 is determined by the reaction with the OH radical below 10km. At 20km, the lives of CFC-112, CFC-113, CFC-114, and HCFC-123 are longer than 20 years. However those become shorter than 5 years at 30km, except CFC-114.

A ν_{IR} -scanned IR-UV LIF spectrum was measured, where ν_{UV} was fixed at 28880.6 cm⁻¹ corresponding to the Q₁(3.5) transition of A(*v*=0)-X(*v*'=1). The ν_{IR} transition was assigned as a

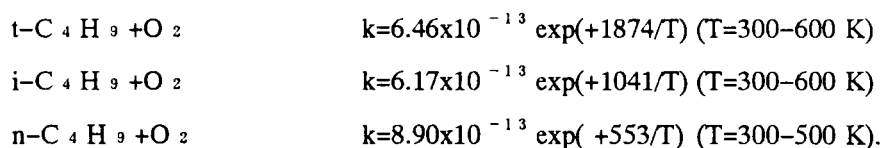
A doublet component of $P_1(4.5)$ transition of $X(v'=1)-(v''=0)$. The ν_{UV} -scanned IR-UV LIF spectrum obtained by fixing ν_{IR} at 3407.5 cm^{-1} corresponding to $P_1(4.5)$ of $X(v'=1)-(v''=0)$ and the observed line is assigned as $Q_1(3.5)$ of $A(v=0)-X(v'=1)$. We succeeded to detect OH in the low concentration around 10^{10} molecules/cm³ using the IR-UV LIF method. From the linear relationship between IR-UV LIF signals and [OH], the detection sensitivity of this technique was determined to be 1.3×10^9 molecules/cm³. The detection sensitivity ratio between the detection sensitivity of IR-UV LIF method and that of single photon LIF method was also determined to be 4.4×10^{-4} . The detection limit using our laser and fluorescence detection systems was estimated to be 1.3×10^9 molecules cm⁻³.

In order to estimate the detection sensitivity under the atmospheric environment, the rotational relaxation within the $X, v'=1$ state must be considered. We measured the rotational distributions of $OH(X, v'=1, N')$ after OH was excited to the $X, v'=1, N'=3$ level. On the assumption that the population of a $N'=3$ rotational level decreased to the thermal population exponentially, Stern-Volmer type analysis was performed and the rotational thermalization rate (k_{rot}) by N_2 and Ar were obtained to be 2×10^{-9} and $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The k_{rot} value by Ar corresponds to gas kinetic rate of $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The detection sensitivity ratio was also estimated by solving the sequential differential equation describing the absorption and induced-emission process between the ground state($X, v=0$), vibrationally excited state($X, v=1$), and electronically excited state($A, v=0$). The simulated value of 7.3×10^{-4} is consistent with the experimental value of 4.4×10^{-4} . There are some problems on the IR-UV LIF method. The high detection limit is caused by strong noise signal due to scattered light of a probe UV laser. To solve this problem, it is necessary to use the MCP-photomultiplier as a detector, which will improve the signal to noise ratio by at least 100 times. The pulse repetition frequency of the laser and the UV laser power are not appropriate for the field measurement. It is possible to improve the S/N ratio by 30000 times by the improvement of the laser and detection systems.

On the selective detection of propyl radical isomers, $i\text{-C}_3\text{H}_7$ and $n\text{-C}_3\text{H}_7$ produced by the ArF laser (193nm) photolysis of $i\text{-C}_3\text{H}_7$ and $n\text{-C}_3\text{H}_7$ were detected by using Br resonant lamp and it is confirmed that the detection sensitivity for $i\text{-C}_3\text{H}_7$ with Br lamp is about 44.4 times greater than that for $n\text{-C}_3\text{H}_7$. This method of selective detection of $i\text{-C}_3\text{H}_7$ has been adopted for the determination of the product branching fraction of $O/OH+C_3H_8$. Hydrogen abstraction by O and OH produced both $i\text{-}$ and $n\text{-C}_3\text{H}_7$ radicals, but only $i\text{-C}_3\text{H}_7$ could be detected with Br lamp. O atom was generated by the ArF laser photolysis of SO_2 and the initial concentrations of O atom were evaluated on the basis of the measured absorption coefficient and the quantum yield. Resulting product fraction for $i\text{-C}_3\text{H}_7$ in the $O/OH+C_3H_8$ reaction was found to be 1.2 (as a sum of $O+C_3H_8$ and $OH+C_3H_8$ reactions), which is in good agreement with the calculated results of Cohen⁷⁾ derived by

using a conventional transition state theory.

With respect to the reaction of butyl radicals, following rate constants were obtained (in unit of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):



In case of the $s\text{-C}_4\text{H}_9$ reaction, the time profiles of the $s\text{-C}_4\text{H}_9$ radical were not the single exponential decay, and the equilibrium between O_2 was observed. That is, residual signal of $s\text{-C}_4\text{H}_9$ at $t > 20\text{ms}$ caused by the $s\text{-C}_4\text{H}_9 + \text{O}_2 \rightleftharpoons \text{C}_4\text{H}_9\text{O}_2$ equilibrium was observed. The equilibrium constant was determined to be $K=1.51 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$ at $T=600\text{K}$ for the first time. This value is in good agreement with the estimation based on the Benson's bond additivity rule. Attempts have been tried to detect the products of butyl radical + O_2 reactions. $\text{C}_4\text{H}_9\text{O}$ (butyl epoxide) was detected. It is argued that this epoxide was produced by the unimolecular decomposition after the intramolecular hydrogen shift in the butyl peroxy radicals. Numerical simulations based on these mechanism well explained the time profiles of $\text{C}_4\text{H}_9\text{O}$ observed in the present experiments.

For the unimolecular decomposition process, the rate and the amount of $\text{C}_4\text{H}_9\text{O}$ showed clear pressure dependence, which indicated that $\text{C}_4\text{H}_9\text{O}$ is produced by the vibrationally excited hydroperoxy butyl radical (with the excess energy of 5.2 kcal/mol). Additional experiments with the addition of CF_4 (effective quencher for the hot molecules) also indicated that $\text{C}_4\text{H}_9\text{O}$ is produced by the unimolecular decomposition of hydroperoxy radical. These results indicated that the energy barrier for the unimolecular decomposition of hydroperoxy butyl radical to produce epoxide and OH is less than 5.2 kcal/mol.

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