

B-4.2 KINETIC MEASUREMENT ON GAS-PHASE REACTIONS RELATED TO GLOBAL WARMING

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Abstract In this research project, the intensity of the ionizing light of photoionization mass spectrometer was greatly enhanced, and hence the detection sensitivity for radicals was increased by a factor of about 50. The CH_3O_2 and HO_2 radicals were able to be detected directly as the parent ions at $m/e = 47$ and 33 , respectively. Reactions of CH_3O_2 and HO_2 with NO were studied by time-resolved measurements of the radical ion signals. The following rate constants were obtained at 298 ± 5 K:

$$k(\text{CH}_3\text{O}_2 + \text{NO}) = (11.2 \pm 1.4) 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1},$$

$$k(\text{HO}_2 + \text{NO}) = (6.3 \pm 2.1) 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}.$$

The value for $k(\text{CH}_3\text{O}_2 + \text{NO})$ is 50% larger than that previously reported.

The HOCO radical, which has been inferred to be an intermediate of the reaction of $\text{OH} + \text{CO}$, was successfully detected by the photoionization mass spectrometry in gas phase. Unimolecular processes of the radical were investigated in gas phase for the first time by time-resolved measurements. The rate constant for the reaction of HOCO with O_2 was determined, and appeared pressure-independent.

Key Words CH_3O_2 , HOCO, HO_2 , Photoionization mass spectrometry, Reaction rate constant

1. Introduction

The cause of the increase of greenhouse gases such as methane, nitrous oxide, and tropospheric ozone, is not straightforward because the concentration of atmospheric trace gases is controlled by a critical balance of their sources and sinks which are less understood. Detailed information on chemical reaction processes in the atmosphere is needed since they play important role in sources and sinks of the greenhouse gases. Atmospheric chemical reaction consists of a large number of elementary reactions. The rate constants for elementary reactions concerning to free radicals have been determined. In order to investigate these elementary reactions, sensitive and selective detection of free radicals are necessary. The development of methods to detect free radicals with high sensitivity and selectivity has also been involved.

2. Research Objective

In this research project, elementary reactions involving following important free radicals are investigated.

(1) Free radicals involved in the photooxidation of hydrocarbons

The reactions of CH_3O_2 and HO_2 radicals with NO , reactions (1) and (2), are one of the most important processes to convert NO to NO_2 in the atmosphere.





However, for RO₂ radicals only insensitive methods (e.g. ultraviolet absorption method) are known, and sensitive and selective detection methods are necessary for accurate measurement of rates of reactions involving RO₂ radicals.

In this research project, detection sensitivity of a photoionization mass spectrometry has been improved drastically, more than 50 times as sensitive as those of conventional equipments, and high sensitivity detection of RO₂ radicals has been accomplished. With this method, rate constants of reactions (1) and (2) were measured.

(2) Free radicals, reactions concerning in the source and sink of OH.

The reaction of hydroxyl (OH) radicals with carbon monoxide,



plays an important role in atmospheric chemistry. The reaction is known to be a major oxidation process to convert CO to CO₂ and a dominant sink (~70%) of OH radicals in the atmosphere. HOCO radical has long been inferred to be an important intermediate of reaction (3).

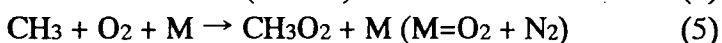
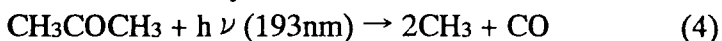
In the present study, the HOCO radical was directly detected by a photoionization mass spectrometry. Unimolecular processes of the radical were investigated in gas phase by time-resolved measurements. Two different methods to generate HOCO radical (with different excess energy) were used to investigate the effect of excess energy on the unimolecular dissociation. The rate constant for the reaction of HOCO with O₂, which is expected to be important at ambient pressures, has also been determined.

3. Results

(1) An improvement of a photoionization mass spectrometry –detection of peroxy radicals–

In this research project, the detection sensitivity has been drastically improved more than 50 times as sensitive as that of the older instrument. In order to achieve the high sensitivity, the ionizing light from the rare gas resonance lamp was greatly enhanced by placing the microwave cavity of the lamp as close as possible (approximately 5cm) to the ionization region. This improvement allowed us to detect RO₂, which has been considered to be difficult to detect with this method, with sufficiently high sensitivity.

In the present study, CH₃O₂ and HO₂ radicals were detected directly as the parent ions at m/e =47 and 33, respectively, and the rate constants for reactions (1) and (2) were determined by time-resolved measurements of the ion signals. CH₃COCH₃ or NH₃, O₂, and NO were introduced to a Pyrex tubular reactor (13 mm i.d.) with N₂ as carrier gas. Pulsed 193 nm radiation from an ArF excimer laser was directed along the axis of the reactor. Gas was sampled through a Pyrex pinhole (=0.3 mm) located in the wall of the reactor and was led into the ionization region of the mass spectrometer. The sampled molecules or radicals were photoionized by using a rare gas resonance lamp powered by microwave discharge (2450 MHz). The ions were mass selected by a quadrupole mass filter and were detected by a Daly-type scintillation detector. The CH₃O₂ radical was generated by laser pulse photolysis of CH₃COCH₃ followed by the reaction between CH₃ radicals and O₂.



When an Ar resonance lamp having a LiF window (11.62 and 11.83 eV) was used, appearance of the ion signal at m/e = 47 was observed. The signal, which is shown in Fig. 1(a), can be attributed to the formation of CH₃O₂. The decay rate obtained from the time profile of the CH₃O₂⁺ ion signal without NO was always less than 25 s⁻¹. Rapid decay was observed when NO was added to the reactor. A typical profile is shown in Fig. 1(b). The decay can be attributed to the depletion of CH₃O₂ by the reaction of CH₃O₂ with NO, reaction

(1). Since the initial concentration of the radical, $[\text{CH}_3\text{O}_2]_0$, was always low enough ($< 3 \times 10^{11}$ molecule cm^{-3}), other side reactions might be neglected. Hence, the decay can be represented as

$$[\text{CH}_3\text{O}_2] = [\text{CH}_3\text{O}_2]_0 \exp(-k't), \quad (6)$$

where

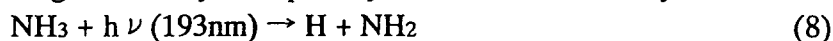
$$k' = k_1[\text{NO}] + k_0. \quad (7)$$

Here, k_1 stands for the overall rate constant for reaction (1) and k_0 represents other loss processes that are responsible for the decay shown in Fig. 1(a) ($< 25 \text{ s}^{-1}$). The decay was fitted to eq. (6), and the values of k' were calculated under various NO

concentrations. The values of k' were plotted against the NO concentration, and the value of k_1 was obtained from

the slope of the Stern–Volmer plots according to eq. (7). The rate constant for reaction (1) was determined to be $(11.2 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is about 50 % larger than the previous recommended value, $(7.6 \pm 1.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the present study, the time-resolved direct measurement of the CH_3O_2 radical was made under low radical concentrations. This method should be superior to the uv-absorption for the reaction rate measurements, since at least the radical–radical reaction can be disregarded.

The rate constant for reaction (2) was measured by the same method. The HO_2 radical was generated by laser photolysis of NH_3 followed by the reaction of $\text{H} + \text{O}_2$.



HO_2 radical was detected as a parent ion (HO_2^+ , $m/e=33$). The rate constant for reaction (2) was obtained to be $(6.3 \pm 2.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The value agreed with previous reported values within the error limit.

(2) Detection and reaction of HOCO radical in gas phase

The HOCO radical has been inferred to be an intermediate of the reaction of $\text{OH} + \text{CO}$. This reaction is known to be a major oxidation process to convert CO to CO_2 in the atmosphere. In the present study, the HOCO radical was successfully detected by the photoionization mass spectrometry.

When a gas mixture of $\text{CCl}_4 / \text{HCOOH} / \text{He}$ was photolyzed by a 193-nm light, an ion signal at $m/e=45$ (HOCO^+) was successfully detected with a 10.03 eV ionization light [Fig.2(a)]. In the photolysis of a $\text{CCl}_4 / \text{HCOOD} / \text{He}$ mixture, a signal at $m/e=46$ (DOCO^+) was observed [Fig.2(b)]. These results suggest that the signal at $m/e = 45$ can be attributed to the HOCO radical formed by the reaction,



following photolysis of CCl_4 ,



The HOCO radical formed by reaction (10) was found to be stable at room temperature ($\tau > 10\text{ms}$).

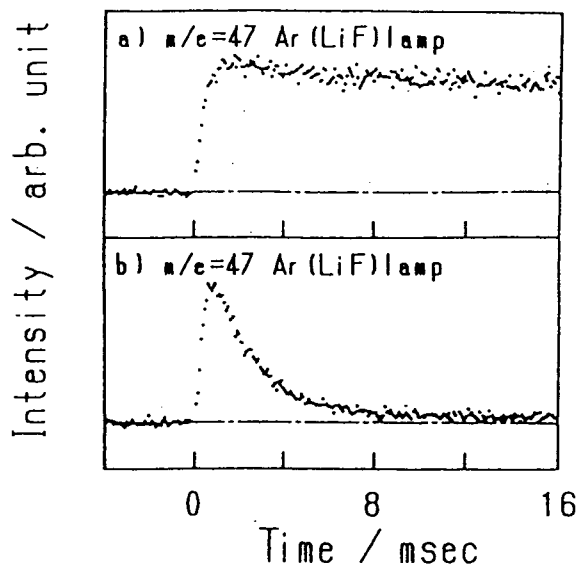


Fig. 1. Time profiles of CH_3O_2^+ observed at (a) $[\text{NO}]=0$ mTorr and (b) $[\text{NO}]=1.5$ mTorr.

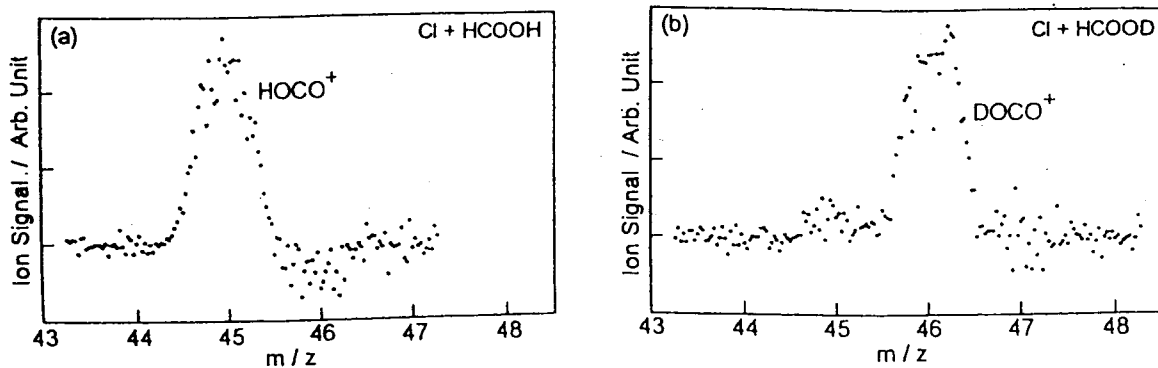
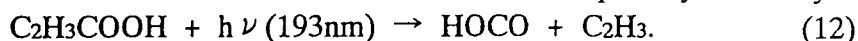


Fig. 2. Photoionization mass spectra of (a) HOCO and (b) DOCO radicals

The HOCO radicals were also detected in the photolysis of acrylic acid,



Contrary to the HOCO radical formed by reaction (10), the HOCO formed by reaction (12) exhibited fast, non-exponential, and total pressure dependent decay. This behavior was well interpreted by a competition of dissociation and relaxation of 'hot' radicals.

One of the most important reaction of the HOCO radical in the atmosphere is the reaction with ambient O_2 .



From the plots of pseudo first-order decay rates against $[\text{O}_2]$, the rate constant for reaction (13) was determined to be $(1.44 \pm 0.30) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constant was measured at two different total pressures (He as a buffer gas, 2.63 and 4.69 Torr), and no pressure dependence was observed.