

# MEASUREMENTS OF RATE CONSTANTS FOR HO<sub>2</sub> + NO AND NH<sub>2</sub> + NO REACTIONS BY TIME-RESOLVED PHOTOIONIZATION MASS SPECTROMETRY

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*(Received September 1, 1994)*

Absolute rate constants for HO<sub>2</sub> + NO and NH<sub>2</sub> + NO reactions were measured by a photoionization mass spectrometry coupled with a laser flash photolysis. HO<sub>2</sub> and NH<sub>2</sub> radicals were photoionized by an Ar resonance lamp and were detected as their parent ions (HO<sub>2</sub><sup>+</sup> and NH<sub>2</sub><sup>+</sup>). The rate constants were determined to be

$$k(\text{HO}_2 + \text{NO}) = (6.5 \pm 2.0)10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$k(\text{NH}_2 + \text{NO}) = (1.9 \pm 0.3)10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Both rates are consistent with those previously reported.

KEY WORDS: HO<sub>2</sub> radical, NH<sub>2</sub> radical, Rate constant, Photoionization mass spectrometry

## INTRODUCTION

Photoionization mass spectrometry (PIMS) is a method to detect reaction intermediates directly with adequate selectivity and sensitivity. PIMS is capable of combining with a laser flash photolysis technique as well as discharge flow and have been widely applied to kinetic studies of free radicals, atoms, and metastable molecules in the gas phase. Recently, in this laboratory, the detection sensitivity of PIMS has been improved by a factor of about 50 [1]. This enabled to detect the CH<sub>3</sub>O<sub>2</sub> as the parent ion (CH<sub>3</sub>O<sub>2</sub><sup>+</sup>) with sufficient sensitivity to measure the rate constant for the CH<sub>3</sub>O<sub>2</sub> + NO reaction. In this work, the detection of HO<sub>2</sub> radicals by PIMS was challenged.

The HO<sub>2</sub> is the simplest peroxy radicals and the reaction of HO<sub>2</sub> radicals with NO, reaction (1), is important to control the concentration of OH radicals in the atmosphere.



Laser magnetic resonance (LMR) spectroscopy is well known as a method to detect HO<sub>2</sub> directly with high sensitivity [2–4]. Discharge flow reactor coupled with a LMR spectrometer has been used to determine the rate of reaction (1) [3–7]. The rate constant recommended by the IUPAC Subcommittee is  $(8.3 \pm 2.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K [8]. There has been an attempt to detect HO<sub>2</sub> by PIMS, and it has been reported that the detection of HO<sub>2</sub> by PIMS was possible but the quantitative analysis of the HO<sub>2</sub><sup>+</sup> ion signal was difficult because the signal was extremely weak. In the present study, the intensity of the ionizing light of PIMS was greatly enhanced and hence the HO<sub>2</sub> radical was able to be detected directly as the parent ion of HO<sub>2</sub><sup>+</sup>.

The reaction of NH<sub>2</sub> radicals with NO, reaction (2), has been known as a thermal de-NO<sub>x</sub> process in combustion and atmospheric chemistry.



The rate constant for reaction (2) has been measured by several methods to measure NH<sub>2</sub> directly [9–17]. The rate constant recommended by the IUPAC Subcommittee is  $(1.6 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K [8]. There has been no measurement of NH<sub>2</sub> radicals by the method of PIMS.

In the present study, rate constants for reactions of HO<sub>2</sub> and NH<sub>2</sub> radicals with NO were measured by PIMS coupled with pulsed laser photolysis.

## EXPERIMENTAL

The experimental set-up of the photoionization mass spectrometer was described in detail elsewhere [1]. Briefly, NH<sub>3</sub> diluted in O<sub>2</sub> was flowed through a Pyrex tubular reactor and was coaxially irradiated by a 193 nm ArF excimer laser (Lambda Physik LPX120i) to generate H atoms and NH<sub>2</sub> radicals by reaction (3).



HO<sub>2</sub> radicals were produced by the association reaction of H atoms with O<sub>2</sub> by reaction (4).



The radicals, HO<sub>2</sub> and NH<sub>2</sub>, were sampled through a thin Pyrex pinhole ( $\phi = 0.3 \text{ mm}$ ) to ionization region and were photoionized by an Ar resonance lamp with a LiF window (11.62 and 11.83 eV). The Ar resonance lamp was powered by a microwave (2450 MHz) discharge. In order to achieve high sensitivity, the microwave cavity of the lamp was placed as close as possible (about 30 mm) to the ionization region. A typical sensitivity for the NO molecule was  $1 \times 10^6 \text{ counts mTorr}^{-1} \text{ s}^{-1}$  when 1 mTorr of NO (0.005% of NO/N<sub>2</sub> mixture) was in the reactor.

The ions were mass selected by a quadrupole mass filter (Extrel, 4-270-9/150-QC) and detected as their parent ions (HO<sub>2</sub><sup>+</sup> and NH<sub>2</sub><sup>+</sup>) by a Daly-type ion detector. The ion signals were digitized in a digital oscilloscope (LeCroy 9400A) and transferred

to a microcomputer where the signals were discriminated, counted, and accumulated typically for 4000–20000 laser shots.

The initial radical concentration was determined from the depletion of NH<sub>3</sub><sup>+</sup> (m/e = 17) ion signals by the laser photolysis. The kinetic measurements were carried out under low initial radical concentration, such as (2–7) × 10<sup>11</sup> and (2–3) × 10<sup>11</sup> molecules•cm<sup>-3</sup> for HO<sub>2</sub> and NH<sub>2</sub>, respectively, in order to reduce the effect of secondary radical-radical reactions. The rate constants were determined by measuring the decay rate of the ion signal under various NO concentration. Total pressure was monitored by a capacitance manometer (MKS Baratron). The concentrations of gases and flow velocity were determined by a separate calibration of the flow rate as a function of pressure. The flow velocity was kept high enough to completely replace the gas in the photolysis reactor between laser shots at a repetition rate of 10–15 Hz.

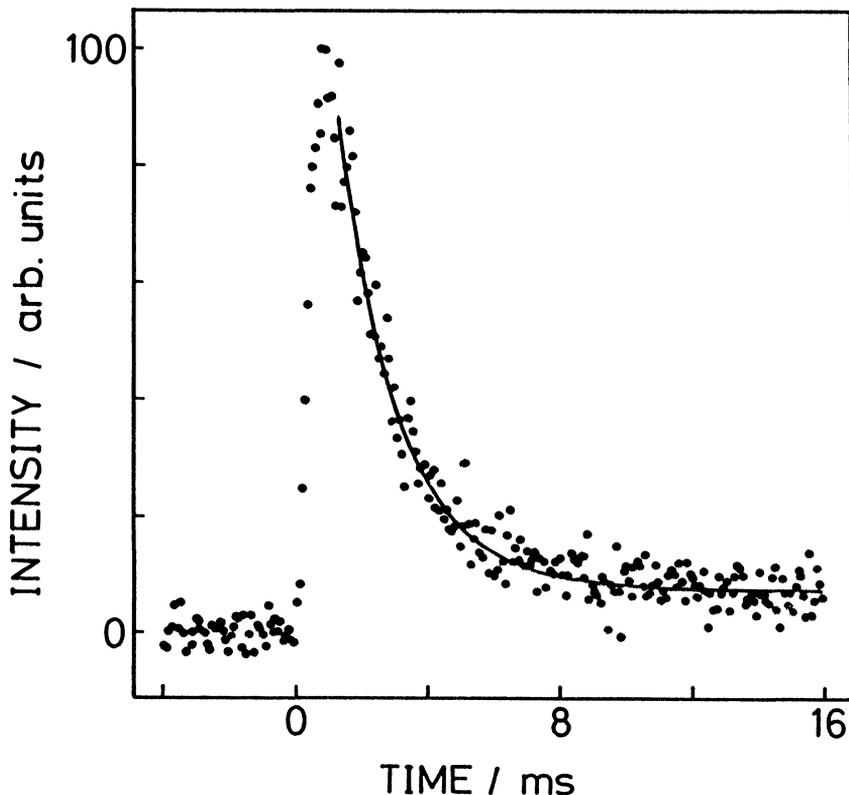
All experiments were carried out at 299 ± 2 K. NH<sub>3</sub> and O<sub>2</sub> were used without further purification. NO (0.953% diluted in He) was purified by passing through a trap with Ascarite (Arthur H. Thoumas).

## RESULTS AND DISCUSSION

### (1) HO<sub>2</sub> + NO reaction

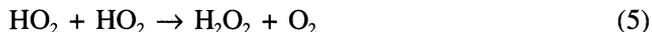
HO<sub>2</sub> radicals were produced by reactions (3) and (4). Transient ion signals were observed at m/e = 33 when the Ar resonance lines (11.83 and 11.62 eV) were used as the photoionization light source. The maximum intensity of the signals was observed within 1 ms after the photolysis laser (193 nm) flash. The rate constant for reaction (4) was reported to be 1.1 × 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 6 Torr of O<sub>2</sub> or N<sub>2</sub> [8]. The rise time of the HO<sub>2</sub> formation by reaction (4) is, then, calculated to be 0.5 ms at the O<sub>2</sub> pressure of 6 Torr. The rise time of the ion signals observed at m/e = 33 is consistent with the rate of the HO<sub>2</sub> formation considering the gas diffusion in the reactor and effusion to the ionization region. The ion detected at m/e = 33 could be attributed to the parent ion (HO<sub>2</sub><sup>+</sup>) of the HO<sub>2</sub>. The adiabatic ionization energy of the HO<sub>2</sub> has been reported to be 11.53 ± 0.2 eV from the electron impact ionization [18] and 11.35 ± 0.01 eV from the VUV photoelectron spectroscopy [19]. The detection of HO<sub>2</sub> radicals by photoionization using the Ar resonance lamp is consistent with above report. According to the signal intensity relative to the detection sensitivity for NO, it was estimated that the photoionization efficiency of HO<sub>2</sub> is about 5 times lower than that of CH<sub>3</sub>O<sub>2</sub>. The detection limit of HO<sub>2</sub> was about 1 × 10<sup>10</sup> molecules•cm<sup>-3</sup>.

The decay rate obtained from the time profile of the HO<sub>2</sub><sup>+</sup> ion signal without NO was 293 s<sup>-1</sup>. Rapid decay of the HO<sub>2</sub><sup>+</sup> signal was observed when NO was added to the reactor. The decay can be attributed to the depletion of HO<sub>2</sub> by the reaction with NO, reaction (1). The typical decay profile of HO<sub>2</sub> radicals with NO is shown in Fig. 1. In this case, the partial pressure of NO and the total pressure (mostly O<sub>2</sub>) were 1.21 mTorr and 6.0 Torr, respectively.



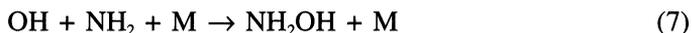
**Figure 1** Typical time profile of the ion signal at  $m/e = 33$ . The conditions were  $[\text{HO}_2]_0 = 2.4 \times 10^{11}$  molecules $\cdot\text{cm}^{-3}$ ,  $[\text{O}_2] = 6.0$  Torr, and  $[\text{NO}] = 1.21$  mTorr. The solid curve represents result of the best fitting of eq. (9).

As shown in Fig. 1, the  $\text{HO}_2^\ddagger$  signal did not converge to zero at long reaction time, and the time profile could not be fitted by a single exponential function owing to the presence of a residual signal. In the present study, the concentration of  $\text{HO}_2$  radicals should be kept low enough to reduce secondary radical-radical reactions. Therefore, reproduction of  $\text{HO}_2$  radicals through reactions (5) and (6) is not important by the following discussions.



OH radicals are mainly produced by reaction (1). The rate constants for reactions (5) and (6) were reported to be  $1.6 \times 10^{-12}$  and  $1.7 \times 10^{-12}$ , respectively, in unit of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [8]. Since the initial concentration of  $\text{HO}_2$  was low ( $\leq 7 \times 10^{11}$  molecules $\cdot\text{cm}^{-3}$ ), the reproduction of  $\text{HO}_2$  radicals through above reactions should be less than 0.1% of the initial rise.

Another possible ion to give  $m/e = 33$  might be NH<sub>2</sub>OH<sup>+</sup>. NH<sub>2</sub>OH could be produced by reactions (7) and/or (8).



The rate constants for reactions (7) and (8) and the photoionization efficiency of NH<sub>2</sub>OH relative to HO<sub>2</sub> are not known. Therefore, the contribution of NH<sub>2</sub>OH<sup>+</sup> to the signal at  $m/e = 33$  could not be calculated.

At this stage, assuming that the residual ion signal at  $m/e = 33$  increases at a rate equal to the decay of HO<sub>2</sub>, the decay profiles of the ion signals can be written by the following exponential decay equation having fitting parameters A and B,

$$I(t) = A \cdot \exp(-k' \cdot t) + B \quad (9)$$

where,

$$k' = k_0 + k_1 [\text{NO}] \quad (10)$$

Here  $k_1$  is the second order rate constant for reaction (1), and  $k_0$  is the sum of all other processes, including pumpout from the cell, loss on the walls and reactions with parent molecules or with impurities.

In the case shown in Fig. 1, the solid curve shows the best fit curve of the signal fitted to eq. (9), and the decay rate ( $k'$ ) determined is 546 s<sup>-1</sup>. The values of  $k'$  were determined under various NO concentrations and were plotted against the NO concentration as shown in Fig. 2. The value of  $k_1$  can be obtained from the slope of the Stern-Volmer plots according to eq. (10). Error bars of each point in Fig. 2 represent one standard deviation from the non-linear least squares fitting of each decay curve. The value of the slope of the Stern-Volmer plots shown in Fig. 2 is  $(6.5 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 6 Torr of O<sub>2</sub>. Error limits due to the scatter of the Stern-Volmer plots were calculated by least-squares fitting with 95% confidence limits.

The value of  $k_1$  obtained in this work is about 20% smaller than the value recommended by IUPAC, which is  $(8.3 \pm 2.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Considering the error limits of both values, however, values are in agreement. As mentioned before, the measurement of the rate constant for the reaction of CH<sub>3</sub>O<sub>2</sub> + NO was carried out by the laser flash photolysis-PIMS method in this laboratory [1].



The rate constant for reaction (11) determined was 50% larger than the value recommended by IUPAC. In the case of the CH<sub>3</sub>O<sub>2</sub> radical, most of previous measurements were carried out just by the pulse photolysis-UV absorption method. On the other hand, for the HO<sub>2</sub> radical, the rate constants for reaction (1) were measured by both pulse photolysis-UV absorption and discharge flow-LMR methods. Anyway, measurements of rate constants by a variety of methods are needed in order to cross check rate constants each other and to evaluate the rate constants to be recommended.

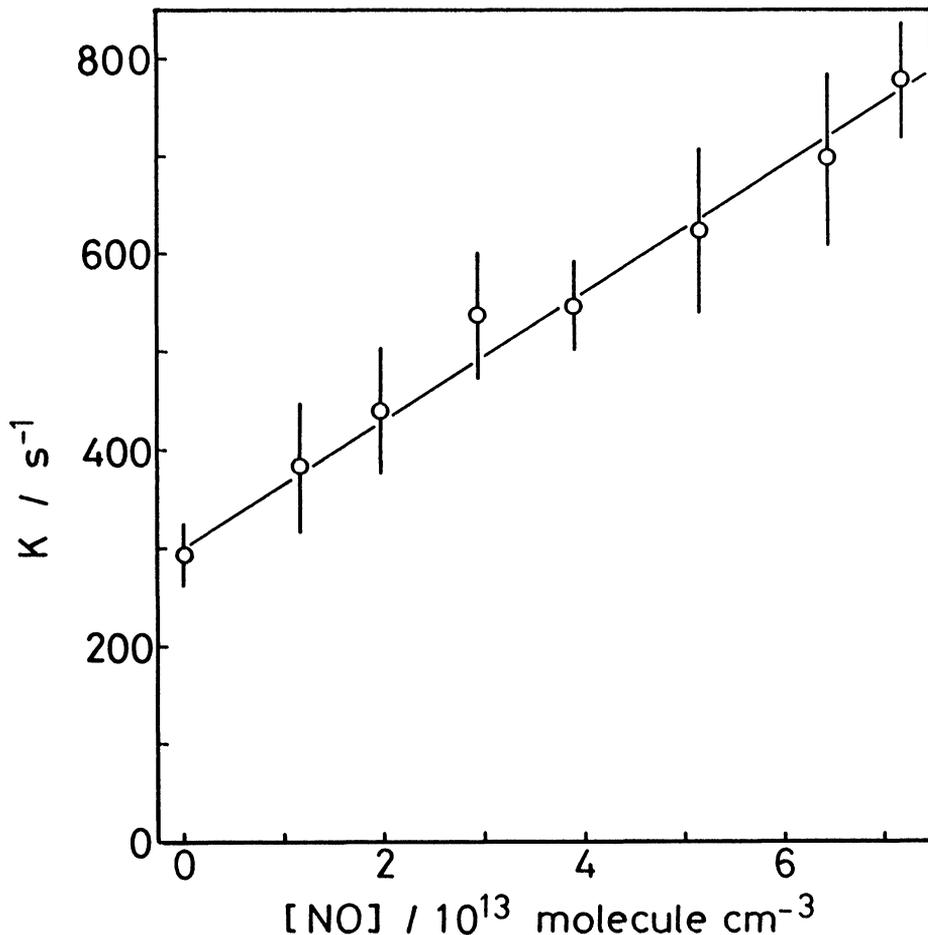


Figure 2 Decay rates of HO<sub>2</sub> radicals as a function of NO concentration.

(2) *NH<sub>2</sub> + NO reaction*

The photolysis of NH<sub>3</sub> at 193 nm generates NH<sub>2</sub> radicals via reaction (3). The quantum yield to produce NH<sub>2</sub> was reported to be almost unity [22]. When the Ar resonance lamp was used as the ionization light source, ion signals at  $m/e = 16$  were observed. As the ionization potential of the NH<sub>2</sub> was reported to be  $11.46 \pm 0.01$  eV [23], the ion signals observed at  $m/e = 16$  should be attributed to the NH<sub>2</sub><sup>+</sup>. Fig. 3 shows the typical time profile of the ion signals at  $m/e = 16$  measured at the partial NO pressure of 0.19 mTorr and at the total pressure (mostly O<sub>2</sub>) of 6.0 Torr. In this case, since the NH<sub>2</sub><sup>+</sup> ion signal converges to zero at long reaction time, the time profile observed could be fitted by a single exponential function shown by eq. (12),

$$[\text{NH}_2] = [\text{NH}_2]_0 \exp(-k't) \quad (12)$$

where  $k'$  is the decay rate defined by eq. (10).

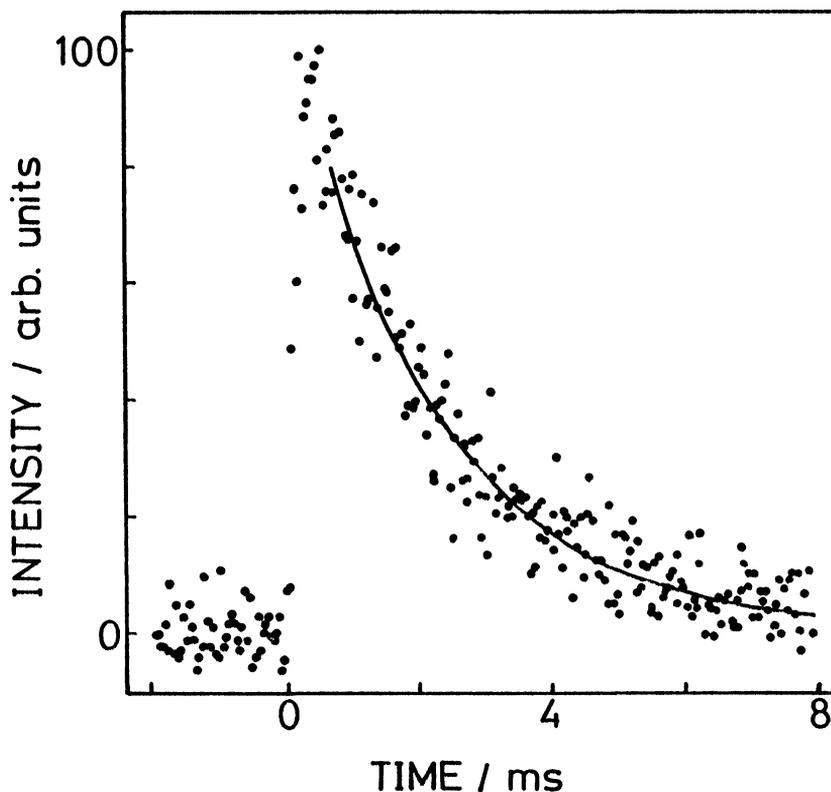


Figure 3 Typical time profile of the ion signal at  $m/e = 16$ . The conditions were  $[\text{NH}_2]_0 = 2.4 \times 10^{11}$  molecules $\cdot\text{cm}^{-3}$ ,  $[\text{O}_2] = 6.0$  Torr, and  $[\text{NO}] = 0.39$  mTorr. The solid curve represents result of the best fitting using a single exponential function.

In the case shown in Fig. 3, since the decay of  $\text{NH}_2$  was represented by the single exponential function, it is not necessary, in principle, to worry about the effect of the secondary radical-radical reactions. In order to make sure the effect, two possible reactions (13) and (14) will be discussed.



$\text{NO}_2$  and  $\text{OH}$  radicals are produced by reaction (1). The rate constants for reactions (13) and (14) were reported to be  $1.9 \times 10^{-11}$  and  $1.6 \times 10^{-13}$ , respectively, in unit of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [8]. The decay rate of the  $\text{NH}_2$  by reaction (13) is thought to increase with increasing the reaction time because the concentration of  $\text{NO}_2$  rises with a rate equal to the decay of  $\text{HO}_2$ . However, since the initial concentration of  $\text{NH}_2$  and  $\text{HO}_2$  radicals were low ( $\leq 3 \times 10^{11}$  molecules $\cdot\text{cm}^{-3}$ ), the decay rate of the  $\text{NH}_2$  by reaction (10) should be less than 2% of that by reaction (2) at the longest

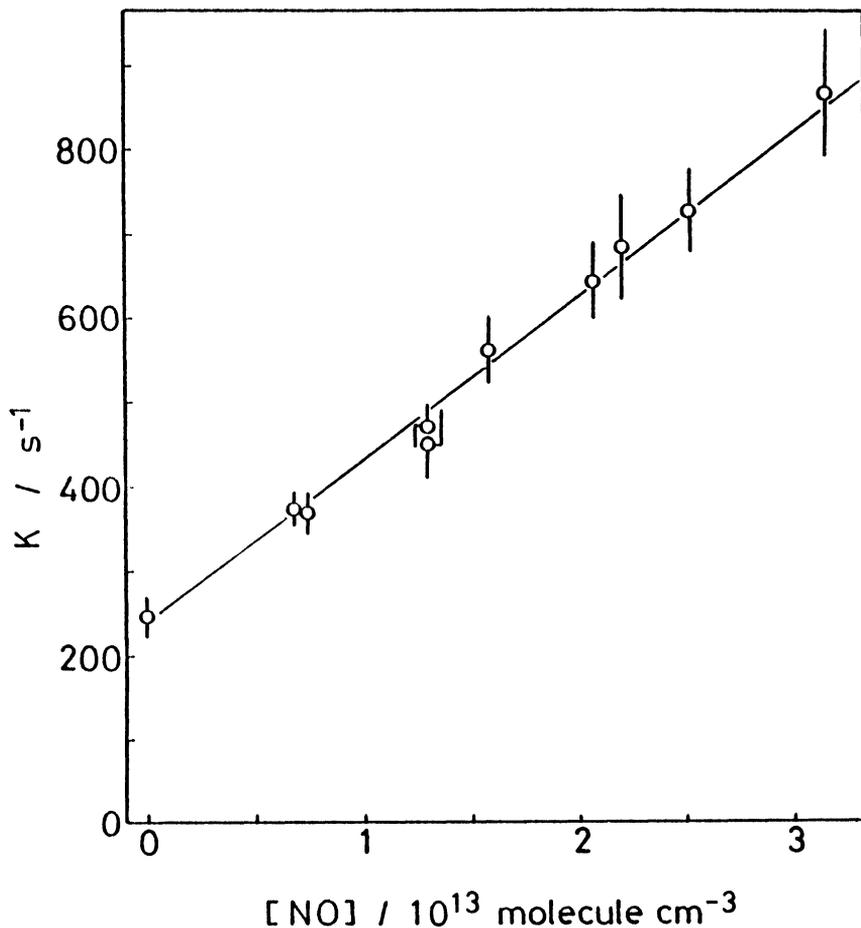


Figure 4 Decay rates of  $\text{NH}_2$  radicals as a function of NO concentration.

reaction time of 16 ms. On the other hand, the reproduction of  $\text{NH}_2$  radicals by reaction (14) could be estimated to be less than 1% of the initial rise.

The decay rates of  $\text{NH}_2$  radicals ( $k'$ ) obtained at the total pressure (mostly  $\text{O}_2$ ) of 6 Torr are plotted in Fig. 4 as a function of the NO concentration. From the slope of the plots, the value  $(1.9 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained as the rate constant for reaction (2). The rate constant for reaction (2) obtained in this work is in good agreement with the previous recommended value,  $(1.6 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

In conclusion, the rate constant for the reaction of  $\text{HO}_2 + \text{NO}$  was measured by monitoring the  $\text{HO}_2$  directly by PIMS coupled with the laser flash photolysis. The rate constant was determined to be  $(6.5 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is in agreement with those obtained by discharge flow technique within the error limit.

The rate constant for the reaction of NH<sub>2</sub> + NO was also determined to be  $(1.9 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This is good agreement with the previous recommended value.

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