

MEASUREMENTS OF RATE CONSTANTS FOR HO₂ + NO AND NH₂ + NO REACTIONS BY TIME-RESOLVED PHOTOIONIZATION MASS SPECTROMETRY

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Absolute rate constants for HO₂ + NO and NH₂ + NO reactions were measured by a photoionization mass spectrometry coupled with a laser flash photolysis. HO₂ and NH₂ radicals were photoionized by an Ar resonance lamp and were detected as their parent ions (HO₂⁺ and NH₂⁺). The rate constants were determined to be

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

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

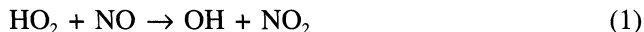
Both rates are consistent with those previously reported.

KEY WORDS: HO₂ radical, NH₂ 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 CH₃O₂ as the parent ion (CH₃O₂⁺) with sufficient sensitivity to measure the rate constant for the CH₃O₂ + NO reaction. In this work, the detection of HO₂ radicals by PIMS was challenged.

The HO₂ is the simplest peroxy radicals and the reaction of HO₂ 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 HO₂ 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 HO₂ by PIMS, and it has been reported that the detection of HO₂ by PIMS was possible but the quantitative analysis of the HO₂⁺ 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 HO₂ radical was able to be detected directly as the parent ion of HO₂⁺.

The reaction of NH₂ radicals with NO, reaction (2), has been known as a thermal de-NO_x process in combustion and atmospheric chemistry.



The rate constant for reaction (2) has been measured by several methods to measure NH₂ 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 NH₂ radicals by the method of PIMS.

In the present study, rate constants for reactions of HO₂ and NH₂ 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, NH₃ diluted in O₂ 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 NH₂ radicals by reaction (3).



HO₂ radicals were produced by the association reaction of H atoms with O₂ by reaction (4).



The radicals, HO₂ and NH₂, 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/N₂ 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 (HO₂⁺ and NH₂⁺) 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 NH₃⁺ (m/e = 17) ion signals by the laser photolysis. The kinetic measurements were carried out under low initial radical concentration, such as (2–7) × 10¹¹ and (2–3) × 10¹¹ molecules•cm⁻³ for HO₂ and NH₂, 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. NH₃ and O₂ 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) HO₂ + NO reaction

HO₂ 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 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 6 Torr of O₂ or N₂ [8]. The rise time of the HO₂ formation by reaction (4) is, then, calculated to be 0.5 ms at the O₂ pressure of 6 Torr. The rise time of the ion signals observed at m/e = 33 is consistent with the rate of the HO₂ 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 (HO₂⁺) of the HO₂. The adiabatic ionization energy of the HO₂ 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 HO₂ 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 HO₂ is about 5 times lower than that of CH₃O₂. The detection limit of HO₂ was about 1 × 10¹⁰ molecules•cm⁻³.

The decay rate obtained from the time profile of the HO₂⁺ ion signal without NO was 293 s⁻¹. Rapid decay of the HO₂⁺ signal was observed when NO was added to the reactor. The decay can be attributed to the depletion of HO₂ by the reaction with NO, reaction (1). The typical decay profile of HO₂ radicals with NO is shown in Fig. 1. In this case, the partial pressure of NO and the total pressure (mostly O₂) were 1.21 mTorr and 6.0 Torr, respectively.

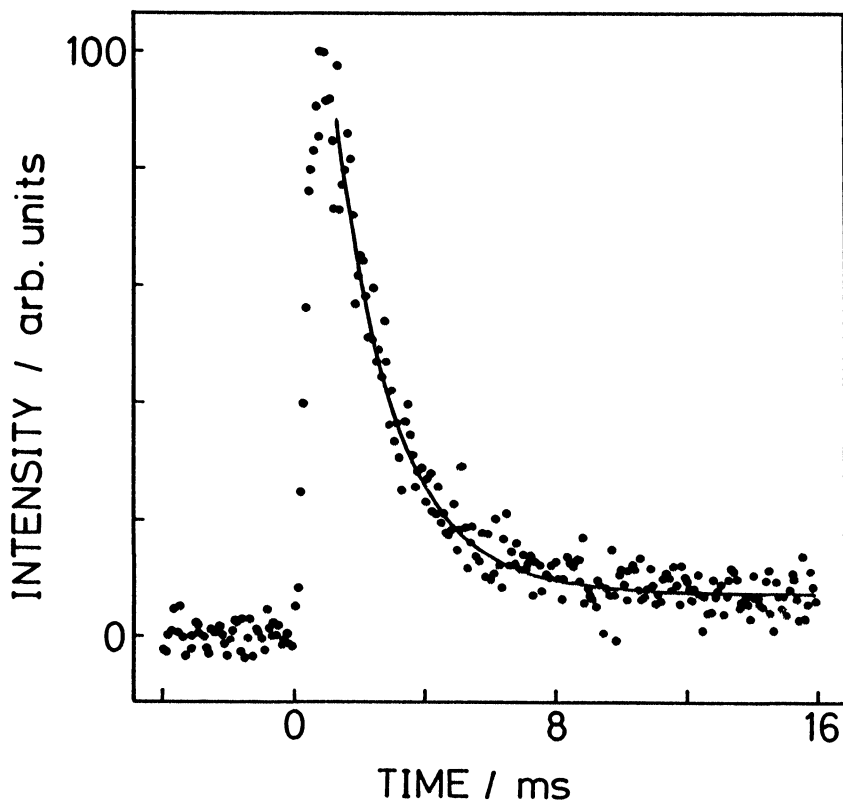
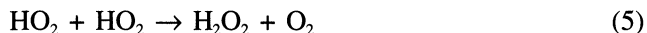


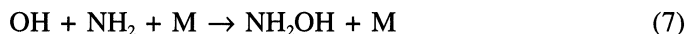
Figure 1 Typical time profile of the ion signal at $m/e = 33$. The conditions were $[\text{HO}_2]_0 = 2.4 \times 10^{11}$ molecules $\cdot\text{cm}^{-3}$, $[\text{O}_2] = 6.0$ Torr, and $[\text{NO}] = 1.21$ mTorr. The solid curve represents result of the best fitting of eq. (9).

As shown in Fig. 1, the 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 HO_2 radicals should be kept low enough to reduce secondary radical-radical reactions. Therefore, reproduction of 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 1.6×10^{-12} and 1.7×10^{-12} , respectively, in unit of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8]. Since the initial concentration of HO_2 was low ($\leq 7 \times 10^{11}$ molecules $\cdot\text{cm}^{-3}$), the reproduction of 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 NH₂OH⁺. NH₂OH could be produced by reactions (7) and/or (8).



The rate constants for reactions (7) and (8) and the photoionization efficiency of NH₂OH relative to HO₂ are not known. Therefore, the contribution of NH₂OH⁺ 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 HO₂, 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⁻¹. 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 $(6.5 \pm 2.0) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 6 Torr of O₂. 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 $(8.3 \pm 2.2) \times 10^{-12}$ cm³ molecule⁻¹ 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 CH₃O₂ + 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 CH₃O₂ radical, most of previous measurements were carried out just by the pulse photolysis-UV absorption method. On the other hand, for the HO₂ 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.

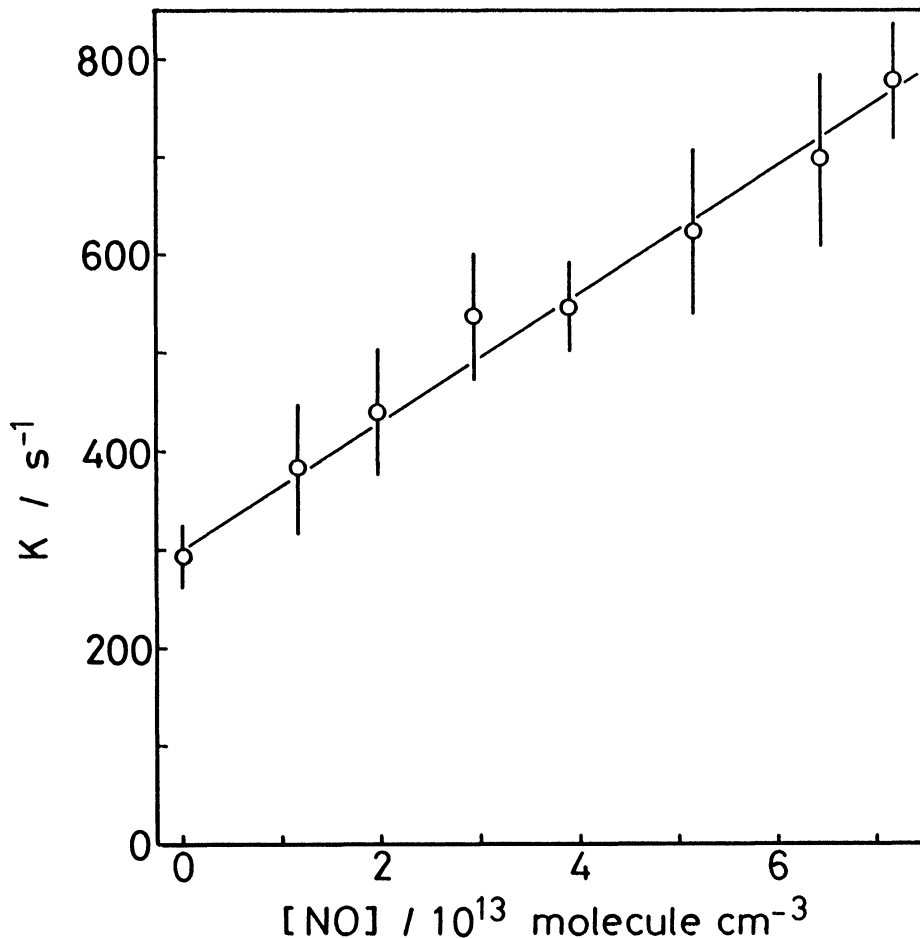


Figure 2 Decay rates of HO₂ radicals as a function of NO concentration.

(2) *NH₂ + NO reaction*

The photolysis of NH₃ at 193 nm generates NH₂ radicals via reaction (3). The quantum yield to produce NH₂ 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 NH₂ was reported to be 11.46 ± 0.01 eV [23], the ion signals observed at $m/e = 16$ should be attributed to the NH₂⁺. 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 O₂) of 6.0 Torr. In this case, since the NH₂⁺ 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).

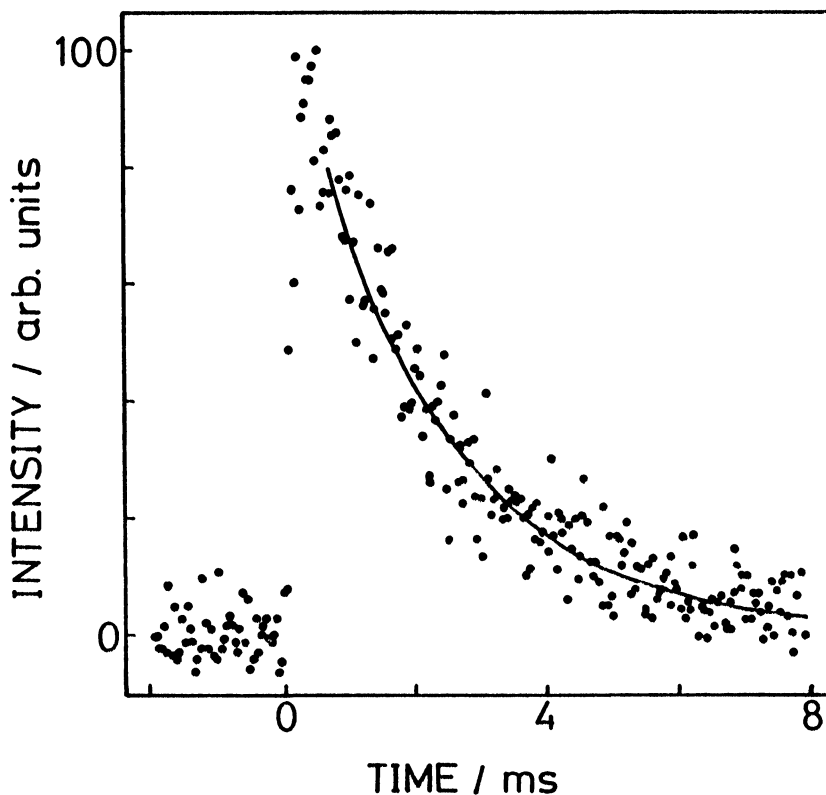


Figure 3 Typical time profile of the ion signal at $m/e = 16$. The conditions were $[\text{NH}_2]_0 = 2.4 \times 10^{11}$ molecules $\cdot\text{cm}^{-3}$, $[\text{O}_2] = 6.0$ Torr, and $[\text{NO}] = 0.39$ mTorr. The solid curve represents result of the best fitting using a single exponential function.

In the case shown in Fig. 3, since the decay of 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.



NO_2 and OH radicals are produced by reaction (1). The rate constants for reactions (13) and (14) were reported to be 1.9×10^{-11} and 1.6×10^{-13} , respectively, in unit of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8]. The decay rate of the NH_2 by reaction (13) is thought to increase with increasing the reaction time because the concentration of NO_2 rises with a rate equal to the decay of HO_2 . However, since the initial concentration of NH_2 and HO_2 radicals were low ($\leq 3 \times 10^{11}$ molecules $\cdot\text{cm}^{-3}$), the decay rate of the NH_2 by reaction (10) should be less than 2% of that by reaction (2) at the longest

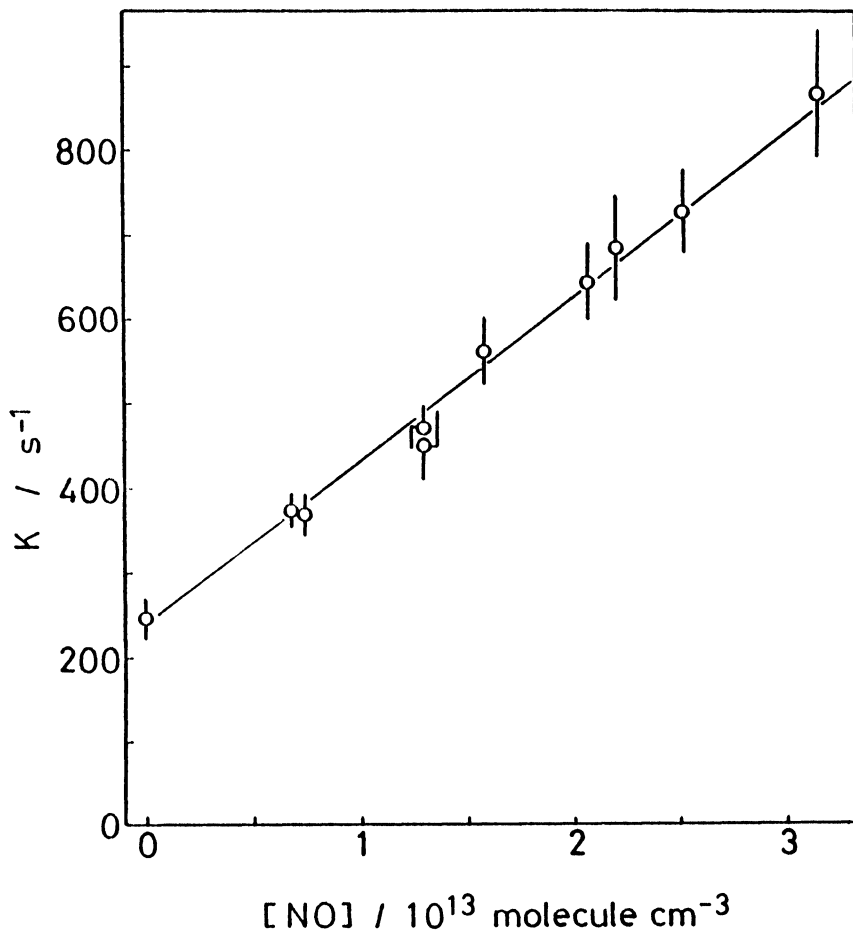


Figure 4 Decay rates of NH_2 radicals as a function of NO concentration.

reaction time of 16 ms. On the other hand, the reproduction of NH_2 radicals by reaction (14) could be estimated to be less than 1% of the initial rise.

The decay rates of NH_2 radicals (k') obtained at the total pressure (mostly 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 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 NH₂ + 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.

References

1. A. Masaki, S. Tsunashima and N. Washida, *Chem. Phys. Lett.*, **218**, 523 (1994).
2. M. S. Zahniser and C. J. Howard, *J. Chem. Phys.*, **73**, 1620 (1980).
3. C. J. Howard and K. M. Evenson, *Geophys. Res. Lett.*, **4**, 437 (1977).
4. C. J. Howard, *J. Chem. Phys.*, **71**, 2352 (1979).
5. W. Hack, A. W. Preuss, F. Temps, H. Gg. Wagner and K. Hoyermann, *Int. J. Chem. Kinet.*, **12**, 851 (1980).
6. B. A. Thrush and J. P. T. Wilkinson, *Chem. Phys. Lett.*, **81**, 1 (1981).
7. A. A. Jemi-Alade and B. A. Thrush, *J. Chem. Soc. Faraday Trans.*, **86**, 3355 (1990).
8. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data*, **21**, 1125 (1992).
9. G. Hancock, W. Lange, M. Lenzi and K. H. Welge, *Chem. Phys. Lett.*, **33**, 168 (1975).
10. R. Lesclaux, P. V. Khe, P. Dezaudier and J. C. Soullignac, *Chem. Phys. Lett.*, **35**, 493 (1975).
11. L. J. Stief, W. D. Brobst, D. F. Nava, P. R. Boekowski and J. V. Micheael, *J. Chem. Soc. Faraday Trans. II*, **78**, 1391 (1982).
12. A. R. Whyte and L. F. Phillips, *Chem. Phys. Lett.*, **102**, 451 (1983).
13. B. Atakan, A. Jacobs, M. Wahl, R. Weller and J. Wolfrum, *Chem. Phys. Lett.*, **155**, 609 (1989).
14. V. P. Bulatov, A. A. Ioffe, V. A. Lozovsky and O. M. Sarkisov, *Chem. Phys. Lett.*, **161**, 141 (1989).
15. J. A. Silver and C. E. Kolb, *J. Phys. Chem.*, **86**, 3240 (1982).
16. J. B. Jeffries, J. A. McCaulley and F. Kaufman, *Chem. Phys. Lett.*, **106**, 111 (1984).
17. T. Yu and M. C. Lin, *J. Phys. Chem.*, **98**, 2105 (1994).
18. S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962), **36**, 2676 (1962).
19. J. M. Dyke, N. B. H. Jonathan, A. Morris and M. J. Winter, *Mol. Phys.*, **44**, 1059 (1981).
20. I. Galashick-schimpf, A. Leiss, P. B. Monkhouse, U. Schurath, K. H. Becker and E. H. Fink, *Chem. Phys. Lett.*, **67**, 318 (1978).
21. M. T. Leu, *J. Chem. Phys.*, **70**, 1662 (1979).
22. V. M. Donell, A. P. Baronavski and J. R. McDonald, *Chem. Phys.*, **43**, 271 (1979).
23. S. J. Dunlavy, J. M. Dyke, N. B. H. Jonathan and A. Morris, *Mol. Phys.*, **39**, 1211 (1980).