H_2-Laser Photolysis Study of the Quenching of $O_2(b^1\Sigma_g^+)$ by H_2 and D_2

K. Kohse-Höinghaus and F. Stuhl*)

Physikalische Chemie I, Ruhr-Universität, D-4630, Bochum, Germany

Isotopeneffekte / Laserspektroskopie / Photochemie

An H_2-laser ($\lambda \approx 160$ nm) was used to form metastable $O_2(b^1\Sigma_g^+)$ molecules in the photolysis of O_2. Monitoring the decay of the $O_2(b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$ emission in the presence of H_2 and D_2 yields rate constants of $k(H_2) = (8.3 \pm 1.2) \cdot 10^{-13}$ and of $k(D_2) = (1.4 \pm 0.2) \cdot 10^{-14}$ $cm^3 s^{-1}$ for the respective quenching process at 298 K. Preliminary results indicate similar temperature dependences (approximately 6.2 kJ mol^{-1} activation energy) for both reactions.

Ein H_2-Laser ($\lambda \approx 160$ nm) wurde benutzt, um in der Photolyse von O_2 metastabile $O_2(b^1\Sigma_g^+)$-Moleküle zu erzeugen. Das Verschwinden der metastabilen Moleküle wurde durch die Emission des verbotenen Überganges $O_2(b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$ verfolgt. Durch Zugabe von H_2 und D_2 wurden die Löschgeschwindigkeitskonstanten $k(H_2)$ und $k(D_2)$ bei 298 K zu $(8.3 \pm 1.2) \cdot 10^{-13}$ bzw. zu $(1.4 \pm 0.2) \cdot 10^{-14}$ $cm^3 s^{-1}$ bestimmt. Vorversuche zeigen für beide Reaktionen eine ähnliche Temperaturabhängigkeit (Aktivierungsenergie ca. 6.2 kJ mol^{-1}).

Introduction

In this note we wish to report on the application of an H_2-laser system to a photochemical study. For the initiation of chemical reactions, we have previously used pulsed vacuum-uv lamps ($\lambda > 110$ nm) [1–4] which in this investigation were replaced by a small vacuum uv H_2-laser ($\lambda \approx 160$ nm). Since we have been interested for some time in the quenching of metastable diatomic molecules in ($^1\Sigma$)-states [2–4] we have used the H_2-laser pulse in this study to generate small concentrations of $O_2(^1\Sigma)$ by photolysing O_2.

Table 1
Rate constants (in units cm^3 $molecule^{-1} s^{-1}$) for the quenching of $O_2(^1\Sigma)$ by H_2 and D_2 at 298 K

Rate constant, $k \cdot 10^{14}$		Experimental method	Ref.
$k(H_2)$	$k(D_2)$		
64 (preliminary)		Pulsed photolysis of O_2 Energy transfer from $O(^1D)$	[2]
40 ± 6	2.0 ± 0.5	Flow system Energy pooling of $O_2(^1\Delta)$	[5]
110		Pulsed photolysis of O_2 Energy transfer from $O(^1D)$	[6]
100 ± 20	1.8 ± 0.36	Pulsed photolysis of O_2 Energy transfer from $O(^1D)$	[3]
40*)	0.67*)	Static system Energy pooling of $O_2(^1\Delta)$	[7]
37 ± 3		Flow system Energy pooling of $O_2(^1\Delta)$	[8]
110 ± 1.6	1.7 ± 0.33	Flash photolysis of SO_2 Energy transfer from $SO_2^{\ddagger}$	[9]
92 ± 43		Photolysis of O_3/O_2 mixtures Energy transfer from $O(^1D)$	[10]
40		Flow system Energy pooling of $O_2(^1\Delta)$	[11]
82 ± 5		Pulsed photolysis of O_3 Energy transfer from $O(^1D)$	[12]
83 ± 12	1.4 ± 0.2	H_2-Laser photolysis, Energy transfer from $O(^1D)$	this work

*) Determination of relative values.

Recently a number of remarkable kinetic isotope effects in the quenching of metastable ($^1\Sigma$)-molecules have been observed [4]. For example, the rate constants previously determined for the quenching of $O_2(^1\Sigma)$ by H_2 and by D_2, $k(H_2)$ and $k(D_2)$, are displayed in Table 1. The literature values in Table 1 show that ratios of $k(H_2)/k(D_2)$ ranging from 20 [5] to 65 [9] have been measured. Furthermore, there apparently exist two different sets of values for $k(H_2)$, namely those close to $k(H_2) = 4 \cdot 10^{-13}$ [5, 7, 8, 11] and those close to $1 \cdot 10^{-12}$ cm^3 $molecule^{-1} s^{-1}$ [3, 6, 9, 10, 12]. Recently Derwent and Thrush [8], Thomas and Thrush [11] pointed out that higher values of $k(H_2)$ found in pulsed photolysis experiments can be attributed to quenching by hydrogen atoms formed through the reaction of $O(^1D)$ with H_2.

It therefore seems worthwhile to reinvestigate the quenching of $O_2(^1\Sigma)$ by H_2 and by D_2 and, at the same time, to study the feasibility of the H_2-laser system to kinetic experiments.

Experimental

The H_2-laser consists of a Blumlein discharge according to the design by Goujon et al. [13]. The laser channel is 20 cm long and the stored energy is about 3 J. The laser is operated at a repetition frequency of about 1 Hz. The energy of the laser pulse was found to be roughly 1 μJ. This energy of the laser radiation is 500 times smaller than that reported by Goujon et al. [13], ten times smaller than that reported by Knyazev et al. [14] and equal to that reported by Andreyev et al. [15]. The half-width times of the laser pulse reported fur such systems are 1 ns [13] and 0.5 ns [14]. The spectrum of the laser emission was registered in the wavelength region from 155 to 170 nm. The spectrum consists of several P-branch lines originating from different vibrational levels of the $H_2(b^1\Sigma_u^+)$ state. It is interesting to note that these emissions coincide well with the strong absorption region of the Schumann-Runge continuum of O_2.

Photolysing O_2 with the laser beam generates metastable $O_2(b^1\Sigma_g^+)$ molecules by [3]

$$O_2 + h\nu(\lambda \approx 160\,\text{nm}) \longrightarrow O(^1D) + O(^3P) \qquad (1)$$

$$O(^1D) + O_2 \longrightarrow O_2(b^1\Sigma_g^+) + O(^3P). \qquad (2)$$

The production of $O_2(^1\Sigma)$ occurs in about 0.5 μs at the concentration of O_2 used (≈ 2.5 mbar). The concentration of $O_2(^1\Sigma)$ generated by the laser pulse is estimated to be smaller than 10^{10} cm^{-3}. Metastable O_2 molecules are detected at right angles to the laser beam by their emission

$$O_2(b^1\Sigma_g^+) \longrightarrow O_2(X^3\Sigma_g^-) + h\nu \quad (\lambda \approx 762\,\text{nm}). \qquad (3)$$

---

*) On sabbatical leave at NOAA, Aeronomy Laboratory, and CIRES, University of Colorado, Boulder, Colorado, 80302.

Ber. Bunsenges. Phys. Chem. 82, 828–830 (1978) –

This emission is monitored either through an interference filter (761 ± 0.4 nm) or through a filter glass (λ > 715 nm) using a cooled photomultiplier tube. Stray light and electrical noises from the laser discharge were found not to interfere at reaction times longer than 700 ns. Using conventional photon counting and multiscaling techniques [4] the time dependence of the emission was accumulated up to 512 times.

The gases used had the following stated (Messer-Griesheim) minimum purities: O_2, 99.998%; He, 99.996%; H_2, 99.999%; D_2, 99.2%. The D_2 sample contained 0.64% HD and <0.16% H_2.

Results and Discussion

The concentration of $O_2(^1\Sigma)$ was monitored for approximately two orders of magnitude in decrease. The decay of $O_2(^1\Sigma)$ was always observed to be exponential. Thus with an excess of quenching gas over the concentration of $O_2(^1\Sigma)$ the decay rate, τ^{-1}, can be represented by

$$\tau^{-1} = \tau_0^{-1} + k[Q] \tag{4}$$

where τ and τ_0 are the lifetimes of $O_2(^1\Sigma)$ in the presence and in the absence of the quenching gas, Q, and k is the rate constant for the quenching process. In this system τ_0 is mainly determined by impurities (probably H_2O) contained in the reaction chamber. Pressures of O_2 from 0.5 to 5 mbar did not influence the lifetime of $O_2(^1\Sigma)$. According to Equation (4) the slope of a plot of τ^{-1} vs. [Q] determines k. Such a plot is shown in Fig. 1 for the addition of Q = H_2 and D_2 at 298 K. The resulting rate constants are $k(H_2) = (8.3 \pm 1.2) \cdot 10^{-13}$ and $k(D_2) = (1.4 \pm 0.2) \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} where the error limits are given by three times the standard deviation. The ratio of the rate constants is hence determined to be $k(H_2)/k(D_2) = 60$. These values are also included in Table 1.

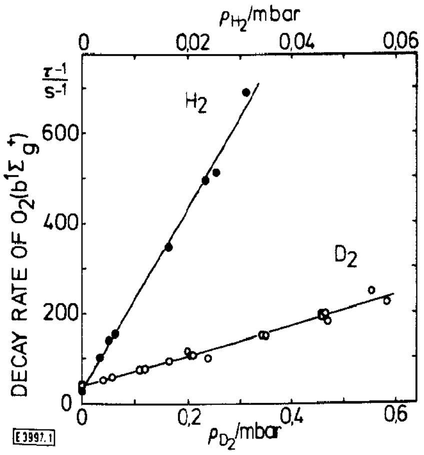

Fig. 1

Decay rates of $O_2(b^1\Sigma_g^+)$ as a function of pressure of H_2, P_{H_2}, and of D_2, P_{D_2}. Helium was added at a pressure of 100 mbar. $O_2(b^1\Sigma_g^+)$ was generated by photolysing 2.3 mbar O_2 (for the quenching by H_2) and 0.8 to 5.1 mbar O_2 (for the quenching by D_2). Note that the pressure scales are different for H_2 and for D_2

The present ratio of the rate constants $k(H_2)/k(D_2)$ is in accord with three previous determinations [3, 7, 9] but disagrees with a value obtained by a flow tube technique [5]. It is evident that the present value of $k(H_2)$ supports the larger values in Table 1. Previously the smaller values of $k(H_2)$ obtained in flow systems have been preferred [8, 11, 16] since photolytically produced H-atoms have been suspected to enhance the quenching rate in pulsed photolysis systems [8, 11]. In this H_2-laser study, however, the energy of the light pulse is about three orders of magnitude smaller than that of previous pulsed photolysis studies [3, 6] without any significant influence on the measured value of $k(H_2)$. Moreover, the absolute concentrations of possible photolysis products are sufficiently low ($\lesssim 10^{10}$ cm^{-3}) in this system to avoid reactions among them during the decay time of $O_2(^1\Sigma)$ ($\lesssim$ 20 ms). It thus seems to be unlikely that photolysis products affect the present value of $k(H_2)$. Furthermore, the large quenching rate constants of Table 1 cannot be attributed to a particular formation process of $O_2(^1\Sigma)$ since energy transfer from both $O(^1D)$ [2, 3, 6, 10, 12] and SO_2^* [9] has been used to generate $O_2(^1\Sigma)$ in the photolysis studies. $O(^1D)$ atoms were produced in the photolysis of either O_2 [2, 3, 6] or O_3 [10, 12].

On the other hand all the smaller values of $k(H_2)$ have been obtained by using the energy pooling reaction

$$2\,O_2(a^1\Delta_g) \longrightarrow O_2(b^1\Sigma_g^+) + O_2(X^3\Sigma_g^-) \tag{5}$$

as a source of $O_2(^1\Sigma)$. In this system it might be possible that products of the quenching process reproduce $O_2(^1\Sigma)$ in the presence of relatively high concentrations of $O_2(^1\Delta)$. It has been previously assumed that vibrationally [9, 12, 17] and rotationally [12, 17] excited H_2 are formed by

$$O_2(b^1\Sigma_g^+) + H_2(v = 0, J) \longrightarrow O_2(a^1\Delta_g) + H_2(v = 1, J + 2)\,. \tag{6}$$

However, it is not known whether the reverse reaction can occur and hence an explanation for the different sets of values for $k(H_2)$ in Table 1 cannot be given here.

The accuracy of the rate constant of the quenching by D_2 depends very much on the H_2 and HD impurities of the sample. With the stated impurities of the present sample the measured value of $k(D_2)$ is likely to be about 10 to 20% too large. In view of the unknown content of H_2 and of HD in previous D_2 samples, the present value of $k(D_2)$ appears to be in good agreement with the literature data [3, 5, 9]. The relative values reported by Becker et al. [7] would agree excellently with the values of the present study if multiplied by a factor of two.

In preliminary experiments we have also studied the temperature dependence of $k(H_2)$ and of $k(D_2)$. When plotted in Arrhenius form the same activation energy of about 6.2 kJ mol^{-1} is obtained for both quenching processes. An activation energy of 4.6 kJ mol^{-1} has been reported previously [12] for the quenching by H_2. These results and further isotope effects will be reported elsewhere.

This work was supported by the Deutsche Forschungsgemeinschaft under the program "Laserspektroskopie". We thank H. W. Zwingmann for technical help.

References

[1] F. Stuhl, J. Chem. Phys. *59*, 635 (1973).
[2] F. Stuhl and K. H. Welge, Can. J. Chem. *47*, 1870 (1969).
[3] F. Stuhl and H. Niki, Chem. Phys. Lett. *7*, 473 (1970).
[4] C. Zetzsch and F. Stuhl, J. Chem. Phys. *66*, 3107 (1977).

[5] R. J. O'Brien, Jr. and G. H. Myers, J. Chem. Phys. *53*, 3832 (1970).

[6] S. V. Filseth, A. Zia, and K. H. Welge, J. Chem. Phys. *52*, 5502 (1970).

[7] K. H. Becker, W. Groth, and U. Schurath, Chem. Phys. Lett. *8*, 259 (1971) and Institut f. Phys. Chem., Universität Bonn, SHA/6 (1970).

[8] R. G. Derwent and B. A. Thrush, Trans. Faraday Soc. *67*, 2036 (1971).

[9] J. A. Davidson, K. E. Kear, and E. W. Abrahamson, J. Photochem. *1*, 307 (1972) and K. E. Kear and E. W. Abrahamson, J. Photochem. *3*, 409 (1974).

[10] M. J. E. Gauthier and D. R. Snelling, J. Photochem. *4*, 27 (1975).

[11] R. G. O. Thomas and B. A. Thrush, J. Chem. Soc., Faraday Trans. 2, *71*, 664 (1975).

[12] M. Braithwaite, E. A. Ogryzlo, J. A. Davidson, and H. I. Schiff, J. Chem. Soc., Faraday Trans. 2, *72*, 2075 (1976).

[13] P. Goujon, A. Petit, and M. Clerc, B.I.S.T. Commissariat à l'Energie Atomique *205*, 31 (1975) and P. Goujon, Ph. D Thesis, Université de Paris-Sud, Centre d'Orsay 1975.

[14] I. N. Knyazev, V. S. Letokhov, and V. G. Movshev, IEEE J. Quantum Electronics *QE-11*, 805 (1975).

[15] S. V. Andreyev, V. S. Antonov, I. N. Knyazev, and V. S. Letokhov, Chem. Phys. Lett. *45*, 166 (1977).

[16] J. R. Hislop and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, *73*, 506 (1977).

[17] M. Braithwaite, J. A. Davidson, and E. A. Ogryzlo, J. Chem. Phys. *65*, 771 (1976).

(Eingegangen am 5. April 1978) E 3997

Rate Constant for the Reaction of NH($X^3\Sigma^-$) with O_2 Determined by Pulsed Vacuum UV Photolysis of NH_3 and Resonance Fluorescence Detection of NH

C. Zetzsch and I. Hansen

Ruhr-Universität, Physikalische Chemie I, D-4630 Bochum, Germany

Emissionsspektren / Fluoreszenz / Freie Radikale / Photochemie / Reaktionskinetik

The kinetics of NH($X^3\Sigma^-$) was studied using resonance fluorescence of NH($A^3\Pi \leftrightarrow X^3\Sigma^-$). From the pulsed vacuum uv photolysis of mixtures containing NH_3, O_2, and He the rate constant for the reaction

$$NH + O_2 \longrightarrow \text{products}$$

was found to be (at 296 K):

$$k = (8.5 \pm 0.9) \cdot 10^{-15}\ \text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$$

Mit Hilfe der Resonanzfluoreszenz NH($A^3\Pi \leftrightarrow X^3\Sigma^-$) wurde die Kinetik von NH($X^3\Sigma^-$) untersucht. Die gepulste Vakuum-UV-Photolyse von Gemischen aus NH_3, O_2 und He ergab für die Reaktion

$$NH + O_2 \longrightarrow \text{Produkte}$$

die Geschwindigkeitskonstante (bei 296 K):

$$k = (8{,}5 \pm 0{,}9) \cdot 10^{-15}\ \text{cm}^3\,\text{s}^{-1}.$$

Introduction

The absorption of NH($A^3\Pi \leftarrow X^3\Sigma^-$) has been observed as a characteristic feature of the spectrum of the sun and of other stars [1]. The emission of NH($A^3\Pi \rightarrow X^3\Sigma^-$) occurs in cometary spectra [2] and it has been discussed in terms of resonance fluorescence, excited by sunlight [3]. NH radicals have also been observed in the vacuum uv photolysis of many N–H containing molecules and in flames. Kinetic data on NH is sparce and there are a few estimates on rate constants only. In a recent study [4] the rate constant for the reaction of NH with NO was measured using pulsed vacuum uv photolysis of NH_3 for production and resonance fluorescence of the transition NH($A^3\Pi - X^3\Sigma^-$) for detection of NH($X^3\Sigma^-$). For the rate constant of the reaction of NH with O_2 Hansen [5] derived the preliminary value of $k_1 = 5 \cdot 10^{-15}$ cm^3 molecule^{-1} s^{-1} whereas McConnell [6] quoted $k_1 = 6 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} based on an estimate of the absolute rate constant for the reaction of NH with C_2H_4 [7] and based on an estimate of relative rate constants for the reactions of NH with O_2 and C_2H_4 [8]. In the present study the reaction of NH with O_2 was investigated under a wide range of experimental conditions.

Experimental

The apparatus has been described previously [4, 9], and mainly the modifications will be described here. It consists of a pulsed vacuum uv light source ($\lambda > 105$ nm), an NH($A^3\Pi \rightarrow X^3\Sigma^-$) emission lamp, and a fluorescence detection system. These components are mounted at right angles to each other. Woods horns at the opposite of each component serve to minimize stray light. The signal from the photomultiplier is fed to a photon counting multichannel scaler.

The following low inductance capacitors were used at voltages ranging from 5–15 kV corresponding to discharge energies from 0.12–64 J: a) type KO/MPS 2/0.5 K 25000/2 (Bosch), $C = 0.5\ \mu$F, $L < 40$ nH, b) type EC 504–20 M (Condenser products), $C = 0.5\ \mu$F, $L < 10$ nH, c) type EC 503–25 M (Condenser products), $C = 0.05\ \mu$F, $L < 10$ nH, d) type ESC-302 (Tobe Deutschmann), $C = 0.01\ \mu$F, $L < 3$ nH. The halfwidths of the light pulses ranged from 0.2 to 1.5 µs, depending on the capacitor used. The light pulses were short compared with the decay time of the fluorescence signals. Emission of the transition NH($A^3\Pi - X^3\Sigma^-$) was generated [4] by means of a microwave discharge in a flowing mixture of 0.4 Torr NH_3 and 2 Torr Ar and focussed into the center of the

Ber. Bunsenges. Phys. Chem. *82*, 830–833 (1978) – © Verlag Chemie, D-6940 Weinheim, 1978.