H₂-Laser Photolysis Study of the Quenching of O₂(b¹Σ⁺) by H₂ and D₂

K. Kohse-Höinghaus and F. Stuhl

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

Isotopeneffekte / Laserspektroskopie / Photochemie

An H₂-laser (λ = 160 nm) was used to form metastable O₂(b¹Σ⁺) molecules in the photolysis of O₂. Monitoring the decay of the O₂(b¹Σ⁺ → X¹Σ⁺) emission in the presence of H₂ and D₂ yields rate constants of k(H₂) = (8.3 ± 1.2) x 10⁻¹¹ and of k(D₂) = (1.4 ± 0.2) x 10⁻¹⁴ cm³ 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 H₂-Laser (λ = 160 nm) wurde benutzt, um in der Photolyse von O₂ metastabile O₂(b¹Σ⁺)-Moleküle zu erzeugen. Das Verschwinden der metastabilen Moleküle wurde durch die Emission des verbotenen Überganges O₂(b¹Σ⁺ → X¹Σ⁺) verfolgt. Durch Zugabe von H₂ und D₂ wurden die Löschgeschwindigkeitskonstanten k(H₂) und k(D₂) bei 298 K zu (8.3 ± 1.2) x 10⁻¹¹ bzw. zu (1.4 ± 0.2) x 10⁻¹⁴ cm³ s⁻¹ bestimmt. Vorsichtsmaßnahmen wurden für beide Reaktionen eine ähnliche Temperaturabhängigkeit (Aktivierungsenergie ca. 6 kJ mol⁻¹).

Introduction

In this note we wish to report on the application of an H₂-laser system to a photochemical study. For the initiation of chemical reactions, we have previously used pulsed vacuum-uv lamps (λ > 110 nm) [1-4] which in this investigation were replaced by a small vacuum uv H₂-laser (λ ≈ 160 nm). Since we have been interested for some time in the quenching of metastable diatomic molecules in (¹Σ)-states [2-4] we have used the H₂-laser pulse in this study to generate small concentrations of O₂(¹Σ) by photolyzing O₂.

Recently a number of remarkable kinetic isotope effects in the quenching of metastable (¹Σ)-molecules have been observed [4]. For example, the rate constants previously determined for the quenching of O₂(¹Σ) by H₂ and by D₂, k(H₂) and k(D₂), are shown in Table 1. The literature values in Table 1 show that ratios of k(H₂)/k(D₂) ranging from 20 [5] to 65 [9] have been measured. Furthermore, there apparently exist two different sets of values for k(H₂), namely those close to k(H₂) = 4 x 10⁻¹¹ [5, 7, 8, 11] and those close to 1 x 10⁻¹² cm³ 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(H₂) found in pulsed photolysis experiments can be attributed to quenching by hydrogen atoms formed through the reaction of O(¹D) with H₂.

It therefore seems worthwhile to re-investigate the quenching of O₂(¹Σ) by H₂ and by D₂ and, at the same time, to study the feasibility of the H₂-laser system to kinetic experiments.

Experimental

The H₂-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 system 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 Kayazev et al. [14] and equal to that reported by Andreyev et al. [15]. The half-width times of the laser pulse was found for such systems to be 1 ns [13] and 0.5 ns [14]. The spectrum of the laser emission was recorded in the wavelength region from 155 to 170 nm. The spectrum consists of several P-branch lines originating from different vibrational levels of the H₂(b¹Σ⁺) state. It is interesting to note that these emissions coincide well with the strong absorption region of the Schumann-Runge continuum of O₂. Photolysing O₂ with the laser beam generates metastable O₂(b¹Σ⁺) molecules by [3]

O₂ + hν (λ ≈ 160 nm) → O(¹D) + O(¹P)

(1)

O(¹D) + O₂ → O₂(b¹Σ⁺) + O(¹P).

(2)

The production of O₂(¹Σ) occurs in about 0.5 μs at the concentration of O₂ used (~ 2.5 mbar). The concentration of O₂(¹Σ) generated by the laser pulse is estimated to be smaller than 10¹⁵ cm⁻³. Metastable O₂ molecules are detected at right angles to the laser beam by their emission

O₂(b¹Σ⁺) → O₂(X¹Σ⁺) + hν (λ ≈ 762 nm).

(3)
This emission is monitored either through an interference filter (761 \pm 0.4 nm) or through a filter glass (\lambda > 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: O₂, 99.998%; He, 99.996%; H₂, 99.999%; D₂, 99.2%. The D₂ sample contained 0.64% HD and <0.16% H₂.

### Results and Discussion

The concentration of O₂(1Σ) was monitored for approximately two orders of magnitude in decrease. The decay of O₂(1Σ) was always observed to be exponential. Thus with an excess of quenching gas over the concentration of O₂(1Σ) the decay rate, \( \tau^{-1} \), can be represented by

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

where \( \tau \) and \( \tau_0 \) are the lifetimes of O₂(1Σ) 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 \( \tau_0 \) is mainly determined by impurities (probably H₂O) contained in the reaction chamber. Pressures of O₂ from 0.5 to 5 mbar did not influence the lifetime of O₂(1Σ). According to Equation (4) the slope of a plot of \( \tau^{-1} \) vs. [Q] determines k. Such a plot is shown in Fig 1 for the addition of Q = H₂ and D₂ at 298 K. The resulting rate constants are \( k(H₂) = (8.3 \pm 1.2) \times 10^{-11} \) and \( k(D₂) = (1.4 \pm 0.2) \times 10^{-14} \) cm³ 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 \( k(H₂)/k(D₂) = 60 \). These values are also included in Table 1.

![Plot](image.png)

**Fig. 1**

Decay rates of O₂(b'1Σ⁺) as a function of pressure of H₂, P₀, and of D₂, P₀. Helium was added at a pressure of 100 mbar. O₂(b'1Σ⁺) was generated by photolyzing 2.3 mbar O₂ (for the quenching by H₂) and 0.8 to 5.1 mbar O₂ (for the quenching by D₂). Note that the pressure scales are different for H₂ and for D₂.

The present ratio of the rate constants \( k(H₂)/k(D₂) \) 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 \( k(H₂) \) supports the larger values in Table 1. Previously the smaller values of \( k(H₂) \) 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 H₂-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 \( k(H₂) \). Moreover, the absolute concentrations of possible photolysis products are sufficiently low (\( < 10^{15} \) cm⁻³) in this system to avoid reactions among them during the decay time of O₂(1Σ) (\( \leq 20 \) ms). It thus seems to be unlikely that photolysis products affect the present value of \( k(H₂) \). Furthermore, the large quenching rate constants of Table 1 cannot be attributed to a particular formation process of O₂(1Σ) since energy transfer from both O(1D) [2, 3, 6, 10, 12] and SO₂ [9] has been used to generate O₂(1Σ) in the photolysis studies. O(1D) atoms were produced in the photolysis of either O₂ [2, 3, 6] or O₁ [10, 12].

On the other hand all the smaller values of \( k(H₂) \) have been obtained by using the energy pooling reaction

\[
2O₂(a'1Δg) → O₂(b'1Σ⁺) + O₂(X'1Σ⁻)
\]

as a source of O₂(1Σ). In this system it might be possible that products of the quenching process reproduce O₂(1Σ) in the presence of relatively high concentrations of O₂(a'). It has been previously assumed that vibrationally [9, 12, 17] and rotationally [12, 17] excited H₂ are formed by

\[
O₂(b'1Σ⁺) + H₂(r = 0, J) → O₂(a'1Δg) + H₂(r = 1, J + 2).
\]

However, it is not known whether the reverse reaction can occur and hence an explanation for the different sets of values for \( k(H₂) \) in Table 1 cannot be given here.

The accuracy of the rate constant of the quenching by D₂ depends very much on the H₂ and HD impurities of the sample. With the stated impurities of the present sample the measured value of \( k(D₂) \) is likely to be about 10 to 20% too large. In view of the unknown content of H₂ and HD in previous D₂ samples, the present value of \( k(D₂) \) 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 \( k(H₂) \) and of \( k(D₂) \). When plotted in Arrhenius form the same activation energy of about 62 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 H₂. 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

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

C. Zetsch and I. Hansen

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

Emissionsspektren / Fluoreszenz / Freie Radikale / Photochemie / Reaktionskinetik

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

NH + O_2 \rightarrow \text{products}

was found to be (at 296 K):

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

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

NH + O_2 \rightarrow \text{Produkte}

die Geschwindigkeitskonstante (bei 296 K):

k = (8.5 \pm 0.9) \times 10^{-15} \text{ cm}^3 \text{s}^{-1}

Introduction

The absorption of NH(A^3 Π \rightarrow X^3 Σ^-) has been observed as a characteristic feature of the sun and of other stars [1]. The emission of NH(A^3 Π \rightarrow X^3 Σ^-) 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 sparse and there are 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 Π \rightarrow X^3 Σ^-) for detection of NH(X^3 Σ^-). For the rate constant of the reaction of NH with O_2 Hansen [5] derived the preliminary value of k_1 = 5 \times 10^{-15} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} whereas McConnell [6] quoted k_1 = 6 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{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 (λ > 105 nm), an NH(A^3 Π \rightarrow X^3 Σ^-) emission lamp, and a fluorescence detection system. These components are mounted at right angles to each other. Woods horns are 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 μF, L < 40 nH, b) type EC 304 – 20 M (Condenser products), C = 0.5 μF, L < 10 nH, c) type EC 503 – 25 M (Condenser products), C = 0.5 μF, L < 10 nH, d) type ESC-302 (Tobe Deutschmann), C = 0.1 μF, 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 Π \rightarrow X^3 Σ^-) was generated [4] by means of a microwave discharge in a flowing mixture of 0.4 Torr NH_3 and 2 Torr Ar and focused into the center of the