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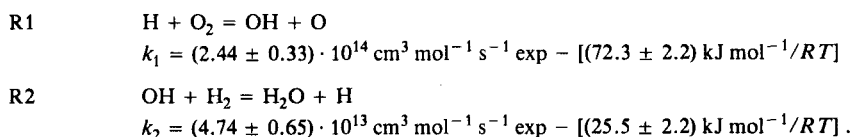
## High Temperature Reaction Rate for $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ and $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$

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### *Chemical Kinetics / Elementary Reactions / Shock Waves*

Shock heating together with atomic resonance absorption spectrometry (ARAS) was used to record simultaneously H- and O-atom concentration profiles in the post-shock region behind reflected shocks. The dissociation of  $\text{N}_2\text{O}$  together with the reaction  $\text{O} + \text{H}_2 = \text{OH} + \text{H}$  was used as a source of H and OH for the reactions  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  and  $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ . The test gas mixtures consisted of argon with relative concentrations of a few ppm  $\text{N}_2\text{O}$  and 100 to 500 ppm  $\text{H}_2$  and  $\text{O}_2$ . The experiments were conducted in the temperature range of 1700 to 2500 K at total densities of  $6 \cdot 10^{-6}$  to  $1.3 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ . The following rate coefficients were deduced:



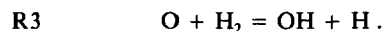
For temperatures below 2500 K nearly complete agreement with the value for the rate coefficient of reaction R1 as recommended by Baulch [1] was obtained. For reaction R2 a rate coefficient was deduced which is close to the value as given by Gardiner et al. [23].

### Introduction

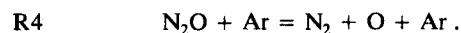
Hydrogen-oxygen reactions play a prominent role as part of the main chain-branching processes in the high-temperature combustion of hydrocarbons. It is well established that only a few reactions including R1, R2 are relevant for describing the ignition mechanism under flame conditions [3]. The most important rate controlling elementary step under most conditions is the reaction of H-atoms with molecular oxygen. In typical hydrocarbon-air-flames at pressures around 1 bar,  $\text{O}_2$  is mainly consumed by reaction R1. A study of the extensive literature and comprehensive reviews on hydrogen-oxygen reactions [1, 4, 5] reveals a considerable scatter in the data for the high-temperature rate coefficient of  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ . Due to the well known high sensitivity of many reaction systems under flame or shock tube conditions on this reaction (see e.g. Ref. [5–7]), a more precise determination of the rate coefficient of this elementary step seems desirable.

The aim of the present study is to measure the rate of the reaction

in a highly diluted system, so that the effect of subsequent reactions can be reduced considerably. The H-atoms were produced by the reaction of O-atoms with molecular hydrogen

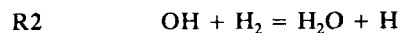


O-atoms were delivered by the thermal dissociation of small amounts of  $\text{N}_2\text{O}$

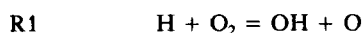


The rate coefficient for this reaction is well established in the pressure range of the present experiments [8–10]. The authors made recently a reinvestigation of this important reaction by applying two different methods of measurement. The results will be presented below.

It is to be expected [5] that the chain propagating reaction



will also have influence on the radical production in the system under investigation.



## Experimental

Details of the shock tube as well as the optical setup have been described elsewhere [9, 11] and only a short summary will be presented below:

The brass shock tube consists of a test section of about 7 m in length and a driver section of 4 m. The internal diameter is 7.5 cm. The test section is evacuated by a turbomolecular pump to less than  $10^{-7}$  mbar before each experiment. Mixtures are prepared and stored in a stirred 56-l stainless steel vessel which is bakeable up to  $250^\circ\text{C}$ . The measurements were performed behind the reflected shock front close to the end flange (5 mm). Atomic resonance absorption (ARAS) was used to monitor time-dependent H- and O-atom concentrations. As light sources for the absorption measurements, microwave-excited discharge lamps which contain  $\text{O}_2$  or  $\text{H}_2$  diluted in He, were used.

H- and O-concentrations can be measured simultaneously by using an oxygen spectral filter (for H-atoms at 121.5 nm) and a 1 m vuv-monochromator for O-atoms (at 130.5 nm). The spectral filter [9, 12] is combined with a solarblind photomultiplier and a  $L_\alpha$ -interference filter of 15 nm HBW. This filter was used to reduce lamp radiation originating from  $\text{H}_2$ -emission in the wavelength region around 160 nm. The transmitted intensity signals were recorded by a 2-channel transient recorder with 2 kB per channel and transferred to a HP 87 personal computer. A program computes an averaged signal and transfers the intensity via calibration curves into particle density versus time plots.

Because of the high sensitivity of the optical measurement technique ( $[\text{H}] > 5 \cdot 10^{11} \text{ cm}^{-3}$ ;  $[\text{O}] > 10^{12} \text{ cm}^{-3}$ ) very small initial concentrations of the reactants could be used. All gases were of ultrahigh purity:  $\text{H}_2 > 99.9997\%$ ,  $\text{O}_2 > 99.998\%$ ,  $\text{N}_2\text{O} > 99.99\%$ ,  $\text{Ar} > 99.9999\%$ . The range of the test gas mixtures used is given in Table I.

Table I  
Range of test gas mixtures in argon (in ppm)

Mixture:	A	B	C	D	E
$\text{N}_2\text{O}$	5	5	2.5	2	2
$\text{H}_2$	500	250	125	200	100
$\text{O}_2$	500	512	256	200	200

## Evaluation

### 1. Temperature

The speed of the incident shock near the end flange was obtained by linear extrapolation of the measured speeds between the four thin-film gauges. The temperature behind the reflected shock near the end flange was calculated by solving the appropriate conservation equations. It was assumed that the temperature so calculated agrees with the real gas temperature occurring immediately behind the reflected shock.

This assumption is supported by careful direct temperature measurements in this shock tube several years ago behind incident shocks [22]. In these experiments absolute temperatures by Na-line and  $\text{CO}_2$ -band emission-absorption methods were determined. The used black-body radiator (graphite) gave radiation temperatures which agreed within less than  $5^\circ$  with thermocouple measurements within the graphite radiator and with measurements using a calibrated pyrometer. The direct measurements immediately behind the incident shocks agreed with the calculated ones from the measured local shock speed within  $\pm 1.5\%$ . In most cases the agreement was even better.

Using the following error factors

- i) shock speed determination  $\pm 0.2\%$
- ii) measurement of absorption signal  $\pm 5\%$
- iii) time scale determination  $\pm 10 \mu\text{sec}$
- iv) rate coefficient for  $\text{N}_2\text{O}$ -decay  $\pm 20\%$

and a typical first order reaction such as  $\text{N}_2\text{O}$ -decay, we arrive at an uncertainty factor of  $\pm 1\%$  in the temperature of the reflected shock. This is in good agreement with the above mentioned results for the incident shock. The so calculated temperature is valid only for gas zones immediately behind the shock front. At long distances the temperature changes slightly. Experiments with  $\text{CO}_2$ -mixtures served as control experiments for the constancy of the temperature behind the

reflected shock. At  $4.41 \mu\text{m}$  the intensity profiles for optical thin conditions with time were monitored [15]. They revealed small deviations from the assumption of constant temperature in the post shock region behind reflected shocks. From these experiments, assuming adiabatic changes, an average temperature drop, linear in time, of  $2\%$  at  $400 \mu\text{sec}$  for total pressures around 2 bar has been derived. Temperature corrections are taken into account in all experiments including calibration experiments in which initiation reactions with relatively large activation energies like the  $\text{N}_2\text{O}$  decay are involved. For temperatures around  $1700 \text{ K}$  the O-atom formation from  $\text{N}_2\text{O}$  is very slow and therefore sensitive to slight temperature alterations, whereas at temperatures above  $1950 \text{ K}$  the temperature corrections are negligible with respect to the reaction system under investigation.

### 2. Calibration of H- and O-Concentrations

The H- and O-concentration profiles reported here are based on calibration measurements. The necessary H-atoms for calibration at  $T > 2100 \text{ K}$  are produced through the well known hydrogen dissociation reaction R10 (Table II). The value for  $k_{10}$ , as recommended by Baulch et al. [1], deviates in the temperature range between  $2100$  and  $2500 \text{ K}$  from that given by Myerson and Watt [13], who monitored the H-atom concentration via ARAS, only by less than  $5\%$ . Hence, either of the expressions can be used. Because of the slow thermal decay of  $\text{H}_2$  at temperatures below  $2000 \text{ K}$ , the calibration in the low temperature range of  $1600$  to  $2100 \text{ K}$  is performed by using the reaction of O-atoms (from the  $\text{N}_2\text{O}$ -dissociation) with  $\text{H}_2$  [14].

Table II  
Reaction mechanism and rate coefficient expressions

Reaction	A	n	$E_a$	Ref.
R1 $\text{H} + \text{O}_2 = \text{OH} + \text{O}$	$2.44 \cdot 10^{14}$	0.0	72.3	×
R2 $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	$4.74 \cdot 10^{13}$	0.0	25.5	×
R3 $\text{O} + \text{H}_2 = \text{OH} + \text{H}$	$1.85 \cdot 10^{14}$	0.0	58.0	×
R4 $\text{N}_2\text{O} + \text{Ar} = \text{N}_2 + \text{O} + \text{Ar}$	$9.30 \cdot 10^{14}$	0.0	248.8	×
R5 $\text{N}_2\text{O} + \text{O} = \text{NO} + \text{NO}$	$1.00 \cdot 10^{14}$	0.0	117.2	[1]
R6 $\text{N}_2\text{O} + \text{H} = \text{OH} + \text{N}_2$	$7.60 \cdot 10^{13}$	0.0	63.0	[1]
R7 $\text{H}_2\text{O} + \text{O} = \text{OH} + \text{OH}$	$1.50 \cdot 10^{10}$	1.14	72.0	[5]
R8 $\text{O}_2 + \text{Ar} = \text{O} + \text{O} + \text{Ar}$	$1.80 \cdot 10^{18}$	-1.0	494.0	[1]
R9 $\text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}$	$1.70 \cdot 10^{13}$	0.0	201.0	[18]
R10 $\text{H}_2 + \text{Ar} = \text{H} + \text{H} + \text{Ar}$	$2.20 \cdot 10^{14}$	0.0	402.0	[1]

× : this work

Rate coefficients are expressed in the form  $k = A \cdot T^n \cdot \exp(-E_a/RT)$ . Units are  $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and kJ.

The dissociation reaction of  $\text{N}_2\text{O}$  served also for obtaining O-atom calibration curves. At temperatures above  $2200 \text{ K}$ , partial equilibrium  $[\text{O}] = [\text{N}_2\text{O}]_0$  is achieved within the observation time. Above this temperature the evaluation of the O-atom calibration curves is free from errors caused possibly by the kinetics of the  $\text{N}_2\text{O}$ -dissociation.

The background absorption of  $\text{N}_2\text{O}$  and  $\text{H}_2$  at both wavelengths was taken into account if necessary. The temperature dependent absorption of  $\text{O}_2$  [17] at  $121.5 \text{ nm}$  was in all experiments less than  $3\%$ , yet it was considered. The used cross-sections for absorption were:

$$\sigma(\text{N}_2\text{O}) = 6 \cdot 10^{-18} \cdot (L_a); \text{ and } 5.5 \cdot 10^{-17} \cdot (\text{O-triplet})$$

$$\sigma(\text{H}_2) = 4.2 \cdot 10^{-17} \exp(-9986/T) \cdot (L_a)^*; \text{ and } \approx 0 \cdot (\text{O-triplet})$$

$$\sigma(\text{O}_2) = 7.1 \cdot 10^{-22} \cdot T - 6.3 \cdot 10^{-19} \cdot (L_a); \text{ and } 5 \cdot 10^{-19} \cdot (\text{O-triplet})$$

(All cross-sections are in  $\text{cm}^2$ ; \*: Ref. [15]).

Data interpretation was performed with the aid of computer modeling. The rate coefficient for the reverse reaction was always computed from the forward rate coefficient and the equilibrium constant  $K_c$ . Thermochemical properties for calculating  $K_c$  were computed from polynomial fits to JANAF.

## Results

### $\text{N}_2\text{O}$ -Decomposition:

Since the  $\text{N}_2\text{O}$ -decomposition plays an important role in our experiments, the dissociation reaction of  $\text{N}_2\text{O}$  in argon has been reinvesti-

gated. Relative  $\text{N}_2\text{O}$  concentrations in the range from 0.25 to 500 ppm were applied.

At this point it should be mentioned that fortunately  $\text{N}_2\text{O}$  as well as  $\text{O}_2$  and  $\text{H}_2$ , show practically no wall adsorption when mixtures are prepared and filled into the shock tube. Fig. 1 shows the excellent agreement between  $\text{N}_2\text{O}$  mixtures, which differed in the initial concentrations by factors up to 500 but gave nearly identical results at closely neighbouring temperatures. The error in the  $\text{N}_2\text{O}$  concentration is given by the error of the pressure gauge and the applied multistep mixing procedure. This error never exceeded  $\pm 5\%$  for the  $\text{N}_2\text{O}$  concentration. That is marginal, considering the experimental scatter given by temperature uncertainties in calibration experiments with slow dissociation rates.

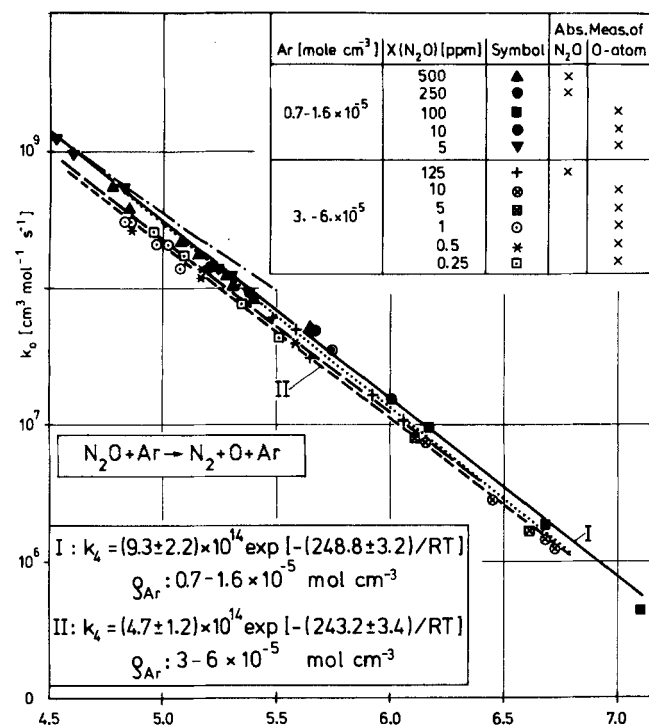


Fig. 1

Arrhenius diagram of evaluated values for the rate coefficients of  $\text{N}_2\text{O} + \text{Ar} = \text{N}_2 + \text{O} + \text{Ar}$ .

Full line: this work,  $[\text{Ar}] = 0.7 - 1.6 \cdot 10^{-5} \text{ mol cm}^{-3}$

-----: this work,  $[\text{Ar}] = 3.0 - 6.0 \cdot 10^{-5}$

.....: Ref. [8]  $[\text{Ar}] < 1.4 \cdot 10^{-5}$

---: Ref. [10]  $[\text{Ar}] < 6.0 \cdot 10^{-5}$

- - - - : Ref. [21]  $[\text{Ar}] < 3.0 \cdot 10^{-6}$

The temperature ranged from 1450 to 2220 K. Two different methods were used:

For the total density range of  $0.7 - 1.6 \cdot 10^{-5} \text{ mol cm}^{-3}$  with very small initial concentrations of  $\text{N}_2\text{O}$  (5 - 100 ppm), the rate of reaction was measured by monitoring the time-dependent O-atom concentration by ARAS.

The decrease of the  $\text{N}_2\text{O}$ -concentration in the same density range has been measured by monitoring the absorption of  $\text{N}_2\text{O}$  at 1282 Å. As the absorption of  $\text{N}_2\text{O}$  follows sufficiently good the Lambert-Beer-law, and the absorption coefficient of  $\text{N}_2\text{O}$  ( $\approx 6 \cdot 10^{-17} \text{ cm}^2$ ) at 1900 K) exceeds by more than a factor 30 the absorption cross-sections of  $\text{N}_2$  and NO, the evaluation of  $k_4$  could be performed by experiments, which were self-calibrating. Even for the highest values of the initial concentration ( $X(\text{N}_2\text{O}) = 500 \text{ ppm}$ ), it was found that the reaction mechanism of the  $\text{N}_2\text{O}$ -dissociation can be described by reaction R4 and the subsequent reaction R5,  $\text{N}_2\text{O} + \text{O} = \text{NO} + \text{NO}$  (or  $\text{N}_2 + \text{O}_2$ ), which fortunately under our conditions has a minor influence on the evaluation of  $k_4$ .

Fig. 1 shows an Arrhenius plot of  $k_4$  as second order rate constant for two different density ranges. The plot shows that especially for the

lower pressure range (full symbols in Fig. 1) - which corresponds to the range of the  $\text{N}_2\text{O}/\text{H}_2/\text{O}_2$ -experiments - there is very good agreement between O-atom-ARAS and  $\text{N}_2\text{O}$ -absorption measurements. The derived expression for  $k_4$  agrees very well with the expression given by Roth and Just [8] for temperatures above 1900 K, and is about 25% higher at 1500 K. The rate expression of Monat et al. [21] shows good agreement around 2000 K, whereas recent measurements of Louge and Hanson [25] are in good correspondence with our results between 1700 and 2000 K. The values reported by Olschewsky et al. [10] are slightly smaller at the lower pressures and fit the set of data for the higher pressure range very well. For this pressure range, the second order rate coefficients are about 30% smaller at 2000 K than for the lower pressure range, which may indicate, that the reaction proceeds already in the fall-off regime. This is in good agreement with the finding in Ref. [10] that the low pressure regime for  $\text{N}_2\text{O}$ -dissociation "ends" at about  $6 \cdot 10^{-5} \text{ mol cm}^{-3}$ .

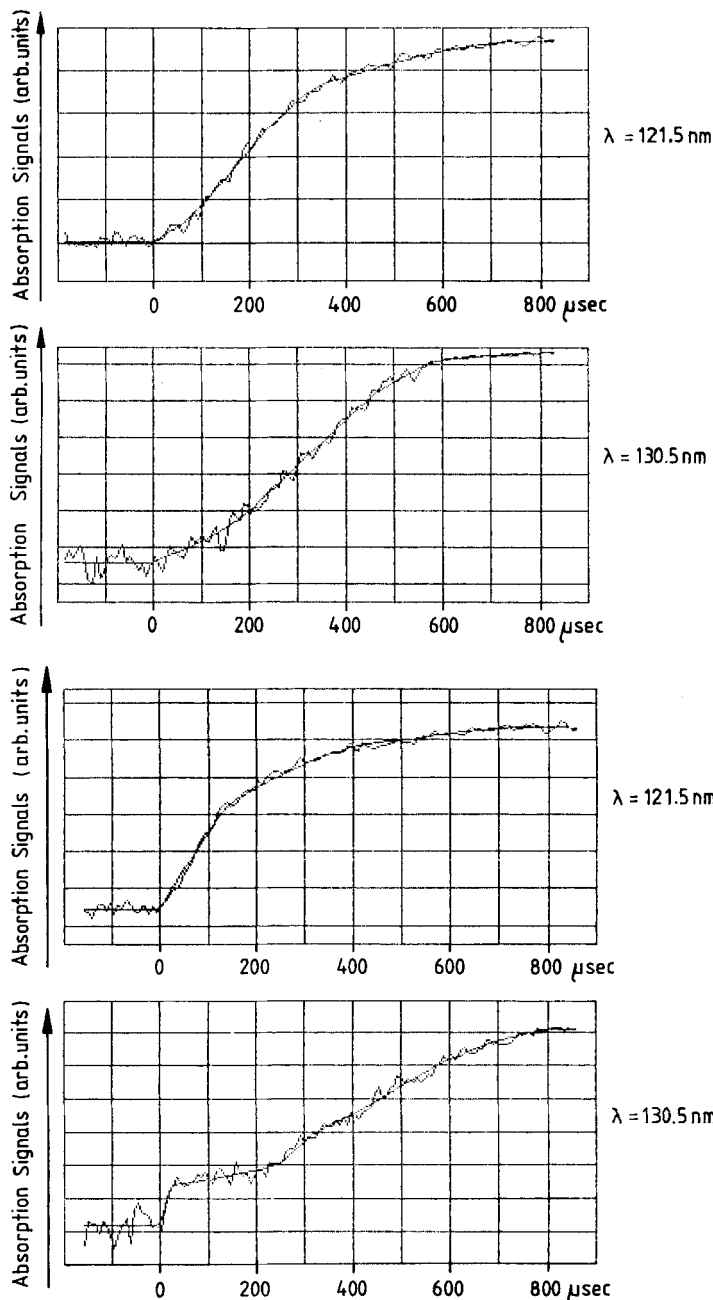


Fig. 2

Typical absorption signals of H- (upper print-out) and O-atoms (lower print-out).

a: mixture B,  $T = 1838 \text{ K}$

b: mixture E,  $T = 2430 \text{ K}$

**$N_2O-H_2-O_2$  Reactions:**

Fig. 2 shows typical absorption profiles of H- and O-atoms under two different conditions. The smoothed curve in each plot represents the averaged signal as calculated by the computer program. Point  $t = 0$   $\mu$ sec at the abscissa, the onset of the reaction, is calculated from the shock front speed, extrapolated to the observation station. In the cases where a steep signal increase immediately after the reflected shock front was observed, the calculated onset agreed always within  $\pm 10$   $\mu$ sec with the observed one. At lower temperatures (Fig. 2a, lower half) the O-atom production is slow, due to the small thermal dissociation of  $N_2O$ . With increasing time H-atoms, which are produced via the reaction of O-atoms with  $H_2$ , can now react with  $O_2$ . Hence, the rates of O-atom as well as H-atom production are increased by chain-branching. At high temperatures (Fig. 2b, lower half) O-atoms are formed nearly instantaneously in the post-shock region, which can clearly be seen by the step in the O-absorption profile. In the following 200  $\mu$ sec most of the additionally produced O-atoms are consumed by the reaction with  $H_2$ . This increases the H-atom concentration considerably. After this induction period for the O-atoms, the O-atom concentration increases mainly by the chain-branching reaction of  $O_2$  with H-atoms.

A ten-step reaction mechanism was adopted for calculating the particle density profiles as given in Table II.

For displaying the sensitivity of the computed H- and O-atom concentrations, a low and a high temperature (1693 and 2389 K) experiment with a mixing ratio of  $N_2O:H_2:O_2 = 1:50:100$  was selected (Fig. 3). At the chosen reaction time of 600  $\mu$ sec, the chain-branching and -propagating mechanism is completely switched on. The sensitivities of the particle density profiles on the rate coefficients  $k_1$  to  $k_4$  are considerable under these conditions.

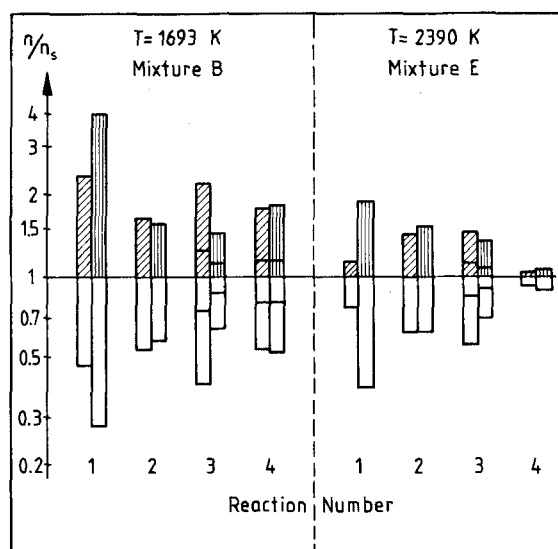


Fig. 3

Sensitivity of H- and O-concentration for  $N_2O:H_2:O_2 = 1:50:100$  mixtures.  $n/n_s$  represents changes in H (left box) – and O (right box) – concentrations at 600  $\mu$ sec by multiplying the rate expressions of Table II by 2 (dashed boxes) and 0.5 (open boxes). All noticeable changes are included. Bars in the boxes for reactions R3 and R4 correspond to changes of  $k_3$  and  $k_4$  by  $\pm 20\%$

The sensitivity analysis shows that besides the reactions of interest R1 and R2, in particular, reactions R3 and R4 have considerable influence on the profiles. The first step was therefore, to fix reliable limits for the rate coefficients for these two reactions:

The dissociation of  $N_2O$  is well investigated for the range of our experimental conditions [8, 10] and our own measurements for the density range of these experiments of both, the O-atom production and the  $N_2O$ -decay, gave a value for the rate coefficient which is very close to the data of Roth and Just [8], as discussed above. From these results we estimate the scatter in the rate coefficient for R4 to be less than  $\pm 20\%$ .

Reaction R3 has been investigated extensively by numerous authors [1, 15, 19, 24]. In a recent study, Pamidimukkala and Skinner [19] measured O-atom profiles of  $N_2O-H_2-Ar$  mixtures in the post-shock region and deduced a value for  $k_3$  which is very close to that of Schott et al. [24]. We have also performed such experiments with simultaneous measurements of H- and O-profiles (Figs. 4 and 5). A sensitivity analysis demonstrates that only reaction R3 and R4 influence the particle density profiles remarkably (Fig. 6). Concentration profiles have been calculated by varying  $k_3$  between the value given in Ref. [19] and a value close to that recommended by Baulch et al. [1]. The best fit was achieved if we reduce the value of Pamidimukkala and Skinner by 20% (Fig. 4 and 5). For comparison we have also computed the profiles if the  $N_2O$ -decay is changed by 20%, which corresponds to the scatter of our measurements for  $k_4$ . This results around 1850 K only in a moderate change in the concentration of the O-atoms. We conclude from our experiments that the value of the pre-exponential factor for the rate coefficient of R3 should be slightly smaller (about 10 to 20%) than given in Ref. [19]. We used this slightly reduced rate coefficient for the evaluation of the  $N_2O/H_2/O_2$ -experiments. With the limits of scatter fixed for the rate coefficients of reactions R3 and R4 to  $\pm 20\%$ ,

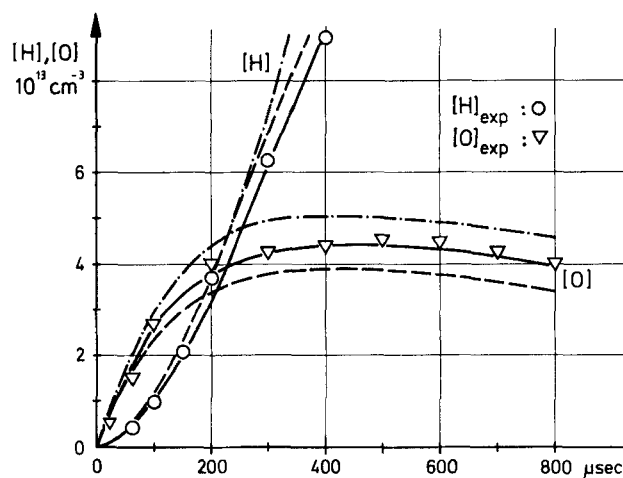


Fig. 4

Comparison between experimental results of H- and O-atom measurements and computational results.

$N_2O: 50$  ppm,  $H_2: 100$  ppm,  $T = 1845$  K,  $p = 1.75$  bar  
Full line: calculated with the  $k$ -values of Table II  
---: calc. with  $k_3$  (Ref. [19])  
- · - · -: calc. with  $k_4 \cdot 1.2$

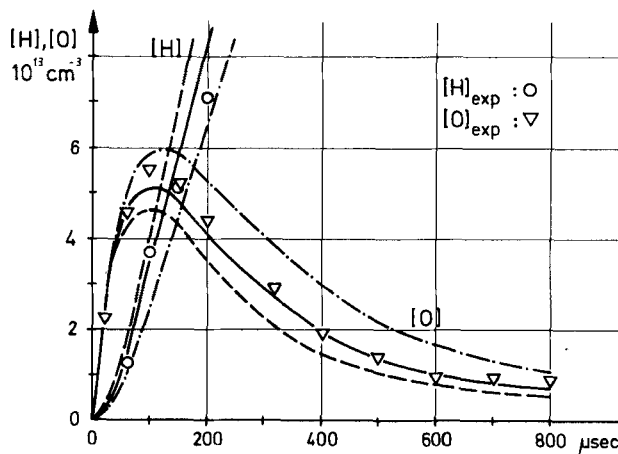


Fig. 5

Comparison between experimental results of H- and O-atom measurements and computational results.

$N_2O: 20$  ppm,  $H_2: 100$  ppm,  $T = 2240$  K,  $p = 1.64$  bar  
Full line: calculated with the  $k$ -values of Table II  
---: calc. with  $k_3$  (Ref. [19])  
- · - · -: calc. with  $k_3$  (Ref. [1])

the sensitivity analysis (Fig. 3, bars in the boxes for R3 and R4) shows that the change in the H- and especially O-profiles depends mainly on the value of  $k_1$ .

Fig. 7 shows measured H- and O-atom concentrations for a typical low temperature experiment. Due to the small amount of O-atoms in the earlier stages of the reaction, the increase in the production of both species H and O, is only moderate within the observation time. The best fit in this example is achieved with a  $k_1$  from Table II times 0.9. For comparison calculated profiles are shown, if a value for the reaction R1 is used as given by Schott [2]. This corresponds at this temperature to  $k_1$  (Schott) =  $k_1 \cdot 0.65$ . If the value for reaction R2 is increased by a factor of 3 in order to fit the measured O-atom profile again, the calculated H-atom concentrations are then definitely much too large with respect to the measured ones.

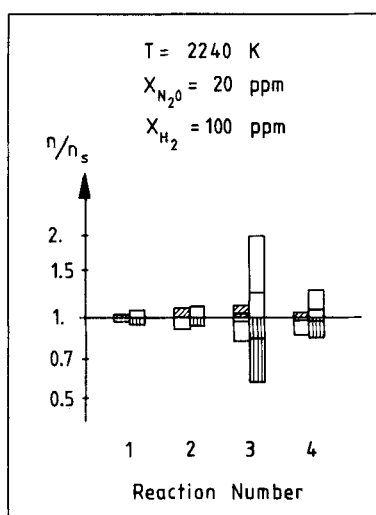


Fig. 6

Sensitivity of H- and O-profiles at 2240 K for  $\text{N}_2\text{O}/\text{H}_2$ -mixtures.  $n/n_s$  represents changes in H (left box) – and O (right box) – concentrations at 400  $\mu\text{sec}$  by multiplying the rate expressions of Table II by 2 (dashed boxes) and 0.5 (open boxes). All noticeable changes are included. Bars in the boxes for reactions R3 and R4 correspond to changes of  $k_3$  and  $k_4$  by  $\pm 20\%$

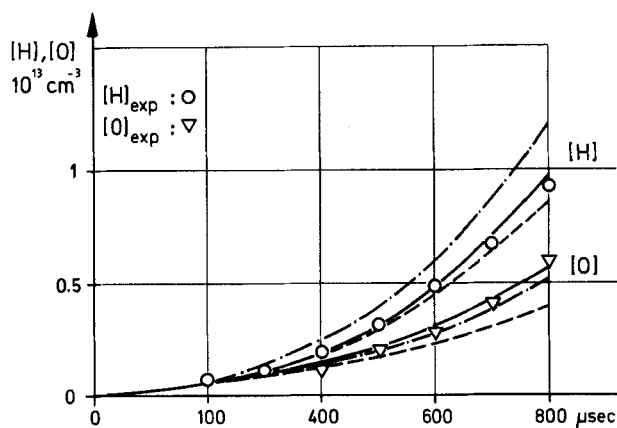


Fig. 7

Comparison between H- and O-atom measurements in  $\text{N}_2\text{O}/\text{H}_2/\text{O}_2$ -mixtures and computational results obtained by different sets of rate coefficients.

Mixture: C,  $T = 1710 \text{ K}$ ,  $p = 1.74 \text{ bar}$

Full line: calculated with  $k_1 \cdot 0.9$

--- : calc. with  $k_1$  (Ref. [2])

- · - · - : calc. with  $k_1$  (Ref. [2]),  $k_2 \cdot 3$

At temperatures above 2000 K there is a pronounced acceleration of the O-atom production during the second part of the observation period. For the presented experiment (Fig. 8) the best fit is achieved if

one of the rate coefficients for R2 or R3 is slightly increased (factor 1.2–1.3). These variations in the rate coefficients lay all within the range of the experimental scatter. If the value for  $k_1$  of Ref. [2] is used again for the reaction R1:  $k_1 \cdot 0.5$ , a very pronounced deviation from the measured O-atom profiles is observed.

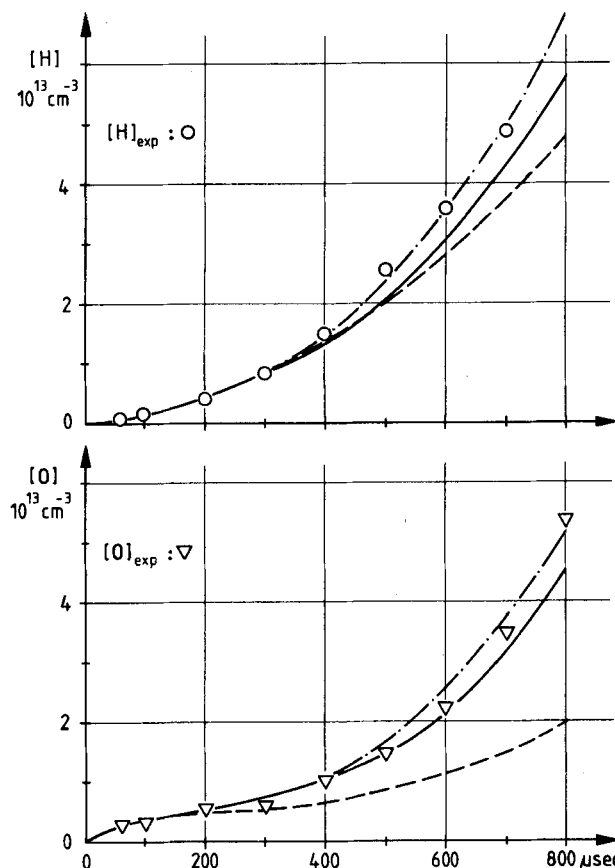


Fig. 8

Comparison between H- and O-atom measurements in  $\text{N}_2\text{O}/\text{H}_2/\text{O}_2$ -mixtures and computational results obtained by different sets of rate coefficients.

Mixture: E,  $T = 2070 \text{ K}$ ,  $p = 1.60 \text{ bar}$

Full line: calculated with the  $k$ -values of Table II

--- : calc. with  $k_1$  (Ref. [2]),  $k_2 \cdot 1.3$

- · - · - : calc. with  $k_2 \cdot 1.3$  or  $k_3 \cdot 1.2$

The same behaviour is also shown in Fig. 9. Here, at a temperature near 2400 K, the O-atoms are produced nearly instantaneously by the  $\text{N}_2\text{O}$ -decay. After an induction period, the O-atom concentration increases rapidly. Using the value for  $k_1$  as given in Ref. [2],  $k_1$  (Schott) =  $k_1 \cdot 0.5$ , the calculated profiles show very low O-atom concentrations and also smaller H-atom concentrations in the later stages of the observation time. For  $k_2 \cdot 5$ , an O-atom concentration is calculated, which is still too small, whereas the H-atom concentrations already exceed the measured values considerably.

## Discussion

The kinetic behaviour of the system can be represented – under the present experimental conditions – by a reaction scheme, whose major features can be described by just four elementary reactions. Two of them, the  $\text{N}_2\text{O}$ -decay R4 and the reaction of  $\text{H}_2$  with atomic oxygen R3, have been investigated separately by different authors and by us. The scatter of the rate coefficients are within  $\pm 20\%$  including the recent  $\text{N}_2\text{O}$ -results of Louge and Hanson [25] at lower temperatures and the values for  $k_3$  of Ref. [19]. The influence of these inaccuracies

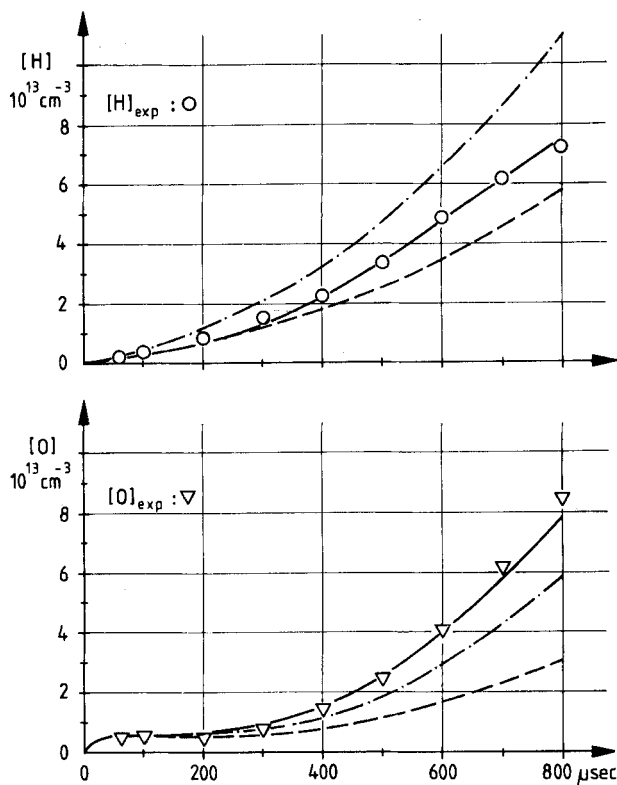


Fig. 9

Comparison between H- and O-atom measurements in  $\text{N}_2\text{O}/\text{H}_2/\text{O}_2$ -mixtures and computational results obtained by different sets of rate coefficients.

Mixture: E,  $T = 2368 \text{ K}$ ,  $p = 1.42 \text{ bar}$

Full line: calculated with the  $k$ -values of Table II

---: calc. with  $k_1$  (Ref. [2])

- · - · -: calc. with  $k_1$  (Ref. [2]),  $k_2 \cdot 5$

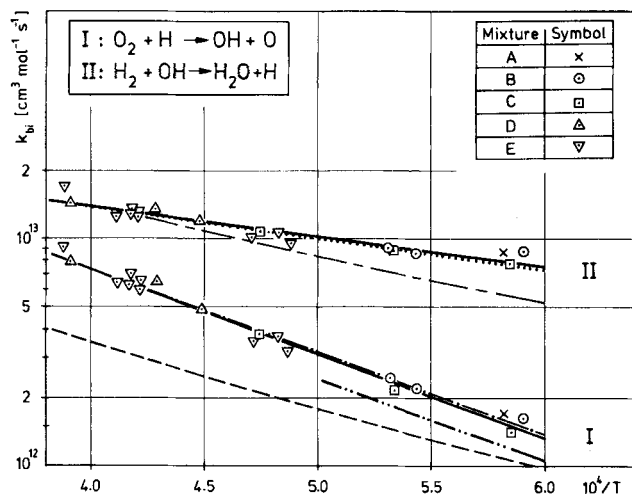


Fig. 10

Arrhenius diagram of evaluated values for the rate coefficients of  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  (curve I) and  $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$  (curve II).

Full line: this work      · · · · ·: Ref. [23] (extrapolated)

- · - · -: Ref. [1]      - - - - -: Ref. [2]

- · - · -: Ref. [26]      - - - - -: Ref. [5]

( $\pm 20\%$ ) in  $k_3$  and  $k_4$  on the evaluation of  $k_1$  is in all experiments equal or less than these scatter limits.

The sensitivity analysis shows, that the dependence of the rate of reaction R1 on the value for the rate coefficient of

reaction R2 should be moderate in highly diluted mixtures. As the value of  $k_1$  is much more sensitive with respect to the O-atom concentration than to the H-atoms (see Fig. 3), whereas reaction R2 influences the concentration of both species in the same order, we can clearly deduce  $k_1$  from the O-atom profiles. For  $k_2$  it is difficult from the present experiments to evaluate a very accurate Arrhenius expression, because this evaluation has to be based mainly on the measurement of H-atom concentrations in the later stages of the observation period. Under the chosen experimental conditions the measured H-atom concentrations between 600 and 800  $\mu\text{sec}$  are near the upper limit of the validity range of our calibration curve, which results in a reduced accuracy.

The Arrhenius plot, as given in Fig. 10 (curve I) for  $k_1$  gives an analytical expression, which is nearly identical with the value given in the Baulch collection [1]. It differs from the values of Ref. [2] by more than a factor 1.8 at temperatures above 2000 K and even at temperatures around 1700 K, there exists a deviation of about 50%. Two experimental studies [26, 27] at temperatures below 2000 K give values for  $k_1$  which are smaller by 30% and more compared to our results.

Our experimental findings, that there is no noticeable "negative" curvature ( $\sim T^{-0.91}$ ) of the Arrhenius curve for reaction R1 in the temperature range between 1600 and 2500 K agree well with a recent theoretical work on  $k_1$  [20].

For reaction R2 from the Arrhenius plot (Fig. 10, curve II) an expression is deduced, which is close to that of Gardiner et al. [23], but it should be pointed out, that the sensitivity of the measured profiles, with respect to the value of  $k_2$ , is not as good as in the case of R1. We estimate from our modeling of the experimental profiles a scatter of less than  $\pm 40\%$  in the evaluation of  $k_2$ . This corresponds fairly well to the observed scatter of our evaluated data points (Fig. 10).

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## Kinetics of the Reactions of CH<sub>2</sub>OH Radicals with O<sub>2</sub> and HO<sub>2</sub>

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### Chemical Kinetics / Mass Spectrometry / Radicals

The rate coefficient of the reaction CH<sub>2</sub>OH + O<sub>2</sub> → HO<sub>2</sub> + CH<sub>2</sub>O (1) has been measured by discharge flow mass spectrometry-technique under first order conditions with excess oxygen at room temperature to be  $k_1 = (9.5 \pm 2.5) \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Reaction (1) is followed by CH<sub>2</sub>OH + HO<sub>2</sub> → products (4). The rate coefficients  $k_4$  could be inferred from HO<sub>2</sub> measurements to be  $6 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , the uncertainty factor being 2.

### Introduction

The reaction of hydroxymethyl radicals with molecular oxygen is believed to play an important role not only in the chemistry of methanol flames [1] but also in the ethylene removal within polluted atmospheres [2]. To our knowledge the work of Radford [3] is the only previous one dealing with this elementary reaction. He found the "unexpectedly large value" of  $k = (2 \pm 1) \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , which had been verified by LMR measurements of the product HO<sub>2</sub> after having failed to find any LMR spectra of CH<sub>2</sub>OH. Therefore, we attempted to study this reaction more directly by mass spectrometric measurements of the CH<sub>2</sub>OH radical under O<sub>2</sub> excess conditions.

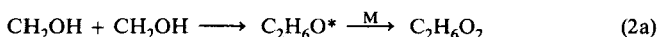
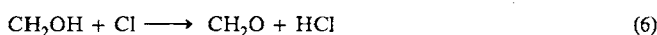
### Experimental

We carried out the experiments at room temperature, pressures ranging from 0.4 to 1.2 mbar and flow velocities up to 30 ms<sup>-1</sup>. Different fast flow reactors were used with diameters of approximately 4 cm, lengths 25 or 50 cm, made of teflon or quartz (HF washed or coated with halocarbon wax) with a movable inlet. In the case of the HO<sub>2</sub> experiments, we used a double injector, the two jets being separated by 3 cm and constructed such as to optimize mixing. All gas flow meters have been calibrated. Gas samples were taken by means of a molecular beam sampling system and analyzed by a TOF mass spectrometer.

### CH<sub>2</sub>OH Production

CH<sub>2</sub>OH radicals were produced by the fast reaction of CH<sub>3</sub>OH + Cl which generates [4] CH<sub>2</sub>OH in large excess over CH<sub>3</sub>O radicals. The latter has been confirmed by our mass spectrometric experiments with deuterated methanols, i.e. CH<sub>3</sub>OD and CD<sub>3</sub>OH, as well as by LIF ex-

periments [5]. In order to obtain the CH<sub>2</sub>OH concentration at the O<sub>2</sub> injection point, one has to account for the following reaction sequence:



The products of reaction (2b) were  $\dot{\text{C}}\text{HOH}$  and CH<sub>3</sub>OH which was found by experiments with deuterated methanols.

The rate coefficients  $k_5$  and  $k_{2a+b}$  have been measured in a separate study [6] to be  $1.4 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $1.5 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , (2b) is the minor channel. Based on this reaction sequence we roughly estimated the [CH<sub>2</sub>OH]<sub>0</sub> values in Figs. 1 and 2. Whenever a better knowledge of [CH<sub>2</sub>OH]<sub>0</sub> was needed it has been determined by computer simulation and/or calibration (see below). CH<sub>3</sub>OH usually was in a 100–1000 fold excess over Cl.

CH<sub>2</sub>OH measurements were carried out at ionization energies below 11 eV, thus nearly suppressing the occurrence of the 31 amu fragmentation peak of the excess methanol, which was less than 5% of the CH<sub>2</sub>OH signal.

### Results

#### CH<sub>2</sub>OH + O<sub>2</sub>

O<sub>2</sub> was added to the CH<sub>3</sub>OH/CH<sub>2</sub>OH-flow by a movable injector. This portion of the flow was shown to be free from Cl atoms but not entirely free from Cl<sub>2</sub> molecules. Continuous displacement of the O<sub>2</sub> injector led to CH<sub>2</sub>OH vs.  $t$  profiles as shown in Fig. 1. Especially in the low pressure regime the resulting slopes must be corrected for viscous pressure drop and axial diffusion. This has been done according to the well known expressions [7] which led to corrections of up to 5% for the pressure drop and 15% for the diffusion in the case of lowest pressure and highest O<sub>2</sub> concentrations. The resulting data from various experiments are shown in Fig. 2. A least squares fit yields an

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