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Shock wave studies of the reactions $HO+H_2O_2 \rightarrow H_2O+HO_2$ and $HO+HO_2 \rightarrow H_2O+O_2$ between 930 and 1680 K

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Monitoring resonance absorption at the $Q_1(4)$ line near 308.4 nm, HO concentration-time profiles were recorded during the thermal decomposition of H_2O_2 in shock waves between 930 and 1680 K. The results were analyzed with respect to the reactions $HO+H_2O_2 \rightarrow H_2O+HO_2$ (2) and $HO+HO_2 \rightarrow H_2O+O_2$ (3). Above 800 K, reaction (2) shows a strong increase of the rate constant with temperature. Over the range $240 \leqslant T \leqslant 1700$ K the apparent rate constant is represented as $k_2=[1.7\cdot 10^{18}\cdot \exp(-14\,800\ \mathrm{K}/T)+2.0\cdot 10^{12}\exp(-215\ \mathrm{K}/T)]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$. The rate constant k_3 decreases from a value of $2.0\cdot 10^{13}$ at 1100 K to a minimum value of $1.1\cdot 10^{13}$ at 1250 K, and rises again to a value of $4.5\cdot 10^{13}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ at 1600 K. The anomalous temperature dependences of k_2 and k_3 suggest mechanisms involving intermediate complex formation. © *1995 American Institute of Physics.*

I. INTRODUCTION

Because of their relevance to hydrogen and hydrocarbon oxidation in atmospheric chemistry and in combustion, the reactions

$$HO+H_2O_2 \rightarrow H_2O+HO_2 \tag{2}$$

and

$$HO+HO_2 \rightarrow H_2O+O_2 \tag{3}$$

have received considerable attention.[1,2] Near room temperature, a consistent set of data exists. Between 500 and 800 K, less information is available whereas at temperatures above 1000 K only few and controversial results have been reported. In previous work[3–7] we have investigated reactions (2) and (3) as secondary processes of the shock wave induced thermal dissociation of H_2O_2,

$$H_2O_2+M \rightarrow HO+HO+M. \tag{1}$$

In the lower part of the investigated temperature range 800–1100 K, reactions (1) and (2) and the subsequent self-reaction of HO_2 radicals

$$HO_2+HO_2 \rightarrow H_2O_2+O_2 \tag{4}$$

dominate whereas in the upper part also reaction (3) plays an important role. The simplicity of the mechanism and the possibility to monitor the concentrations of several species allow for a separate determination of all four rate constants k_1-k_4.

In our previous work we used uv absorption spectroscopy of H_2O_2 and HO_2 for detection. With this technique, k_1 and k_4 could be determined reliably, while data on k_2 and k_3 were more difficult to obtain. Nevertheless, our analysis[3] of HO_2 yields in the dissociation of H_2O_2 indicated a dramatic change of the temperature coefficient of reaction (2) near 800 K. While the apparent activation energy and the preexponential factor of k_2 were low at $T<800$ K, a change to much larger activation energy and anomalously high preexponential factor was observed at $T>800$ K. Using ring laser line absorption measurements of HO concentrations, a new and more sensitive access to the rate constants k_2 and k_3 became available such as indicated by our preliminary measurements near 1000 K.[7] It was the aim of the present work to extend these measurements and to confirm the earlier conclusions about an unusual temperature dependence of k_2. Likewise more extensive measurements on the important reaction (3) had to be performed, since the H_2O_2 decomposition system provides the most direct access to k_1-k_4 under high temperature conditions.

Our measurements of the temperature coefficients of reactions (2)–(4) led to quite differing behavior: While reaction (2) showed a change from a weakly to strongly positive temperature coefficient near 800 K, reaction (4) is characterized by a deep rate constant minimum near to the same temperature. On the other hand, reaction (3) shows a rate constant minimum near 1250 K. One may speculate on the origin of these interesting properties and tentatively attribute the results to the formation of H_3O_3, H_2O_3, and H_2O_4 intermediate complexes in reactions (2)–(4), respectively. Without *ab initio* calculations of reliable potential energy surfaces, detailed conclusions about the participation of such complexes cannot be drawn.[8] However, the present measurements provide considerable experimental material for an interpretation in terms of an intermediate complex mechanism, see below.

II. EXPERIMENTAL TECHNIQUE

The thermal decomposition of H_2O_2 in the present work was studied in incident and reflected shock waves over the temperature range 930–1680 K. H_2O_2 concentrations of 1–1000 ppm in Ar and total gas concentrations of $(2-8)\cdot 10^{-6}\ \mathrm{mol\ cm^{-3}}$ were employed. The shock waves were generated in an aluminum shock tube of 20 cm inner diameter and a 7 m test section. For more details of our

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experimental setup, see Ref. 7. HO radicals were monitored by resonance absorption at the $Q_1(4)$ line at 308.4172 nm (wavelength in air). The radiation from an Ar-ion laser pumped cw-ring dye laser (Coherent CR-899-21) with intracavity frequency doubling served as light source. The light beam was split into an analysis beam and a reference beam. The absorption was determined with two photodiode detectors. Absorption-time profiles were converted into concentration-time profiles using Beer's law. The relevant absorption cross sections $\sigma(T,p)$ were calculated using oscillator strengths and additional parameters from Refs. 9 and 10. For the $Q_1(4)$-line, the results between 1000 and 2500 K can be represented (within 15% accuracy) by the expressions

$$\sigma/\mathrm{cm}^2 = 4.17\cdot10^{-16} - 3.89\cdot10^{-19}T + 1.48\cdot10^{-22}T^2 - 2.07\cdot10^{-26}T^3$$

for 0.5 bar of Ar and

$$\sigma/\mathrm{cm}^2 = 2.80\cdot10^{-16} - 1.84\cdot10^{-19}T + 4.26\cdot10^{-23}T^2 - 2.67\cdot10^{-27}T^3$$

for 1 bar of Ar. We tested the calculated cross-sections by following the unimolecular decomposition of HNO_3 and CH_3OH at temperatures above 1000 K, obtaining agreement within about $\pm$20%. Similar agreement had been found for measurements with the H_2/O_2 system in Ref. 11. Alternative expressions for $\sigma(p, T)$ have recently been used in Ref. 12 based on the oscillator strengths and calculations from Ref. 13, giving

$$\sigma/\mathrm{cm}^2 = 1.77\cdot10^{-16} - 6.13\cdot10^{-20}T - 4.77\cdot10^{-24}T^2 + 3.54\cdot10^{-27}T^3$$

for the $Q_1(4)$ line and $p=1$ bar. The deviation from our data at 1 bar is 12% at 1050 K and 8% at 2380 K. Like Ref. 12, other authors[14–18] basing their cross section on Ref. 13 estimate the uncertainty of the cross sections to be about 5%. Therefore, we estimate the precision of our HO concentrations to be better than $\pm$20%.

Reactions mixtures were prepared by passing a flow of Ar through a two-stage saturator filled with nearly 100% H_2O_2. The H_2O_2/Ar mixtures then were carried through an inlet in the end plate into the shock tube. In order to vary the H_2O_2 concentration over wider ranges, the H_2O_2/Ar stream could be mixed with a pure stream of Ar. Because of substantial adsorption and decomposition of H_2O_2 at the walls of the shock tube, the initial H_2O_2 concentration in the shock heated gas mixture was reconstructed from the HO signals: During the first microseconds, the decomposition of H_2O_2 is dominated by reaction (1). The rate of HO formation during this period, via the well known values of k_1[4,5] and the HO absorption cross section, led to the initial H_2O_2 concentration. A determination of the initial H_2O_2 concentration via the *in situ* uv absorption of H_2O_2 is by far too insensitive: The weak H_2O_2 and the much stronger HO_2 uv continua overlap over wide ranges[4,5] and the resulting signals for the here employed low concentrations are too small to be detected with similar sensitivity as HO. Therefore, the reconstruction of initial H_2O_2 concentrations via HO formation rates provided the by far most reliable access, leaving only the $\pm$20% uncertainty from the employed absorption cross section.

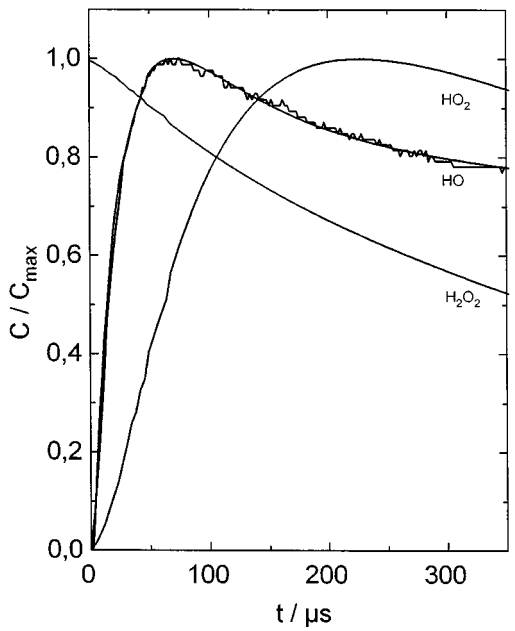

FIG. 1. Calculated concentration-time profiles of H_2O_2, HO, and HO_2 in the thermal dissociation of H_2O_2 (c=concentration, c_{max}=maximum concentration; T=1150 K, [Ar]=$5.6\cdot10^{-6}$ mol cm^{-3}, $[H_2O_2]_{t=0}=6.5\cdot10^{-9}$ mol cm^{-3}, $[HO]_{max}=2.4\cdot10^{-10}$ mol cm^{-3}, $[HO_2]_{max}=7.3\cdot10^{-10}$ mol cm^{-3}; simulated profiles with rate coefficients from Table II, curve with noise: measured HO profile).

III. EVALUATION OF CONCENTRATION–TIME PROFILES

At low initial H_2O_2 concentrations (1–5 ppm), the unimolecular decomposition of H_2O_2 could be completely isolated from secondary reactions. With higher relative concentrations of H_2O_2 (100–1000 ppm in Ar), reactions (2)–(4) then became more important. An orientation about the expected H_2O_2, HO, and HO_2 concentration–time profiles was provided by numerical simulation of the mechanism of reactions (1)–(4) using preliminary rate coefficients from Refs. 1 and 2. Whereas k_1 and k_4 have been accurately measured before,[3–7] the values of k_2 and k_3 were fine adjusted in the present work. Using our final set of rate parameters, Fig. 1 presents an example of calculated concentration–time profiles. A comparison of the calculated with a measured HO profile is also given, showing agreement in all details such that no evidence for other processes was present. The HO concentration reaches its maximum after a short time, remaining quasistationary at longer times during which [HO_2] reaches its maximum. While our earlier conclusions were based on measured H_2O_2 and HO_2 profiles,[3–7] the present investigations of HO profiles provide a more direct and more accurate access to the values of k_2 and k_3. We also did modeling including a variety of secondary reactions different from reactions (1)–(4) such as HO+HO→H_2O+O and other

TABLE I. Experimental conditions and derived rate constants k_2 and k_3.

T/ K	[Ar]/ 10^{-6} mol cm^{-3}	[H_2O_2]/ 10^{-10} mol cm^{-3}	k_2/ 10^{12} cm^3 mol^{-1} s^{-1}	k_3/ 10^{13} cm^3 mol^{-1} s^{-1}
931	8.2	84	1.6	
978	2.3	22	2.5	
979	2.3	20	2.0	
1012	7.2	53	4.0	
1015	5.1	49	4.0	
1025	2.4	6.5	4.0	
1030	6.7	22	3.2	
1078	2.4	3.6	5.0	
1091	2.4	1.9	5.0	
1110	6.5	33	6.3	
1118	6.2	33	6.3	2.2
1136	5.9	16	7.9	2.0
1152	5.6	65	6.0	1.6
1164	5.3	29	7.0	1.5
1190	5.2	25	7.5	1.3
1226	5.2	21	8.3	1.0
1246	5.1	52	9.0	1.1
1255	5.0	41	9.7	1.0
1278	4.8	34	10	1.1
1296	4.6	29	16	1.2
1362	4.4	11	22	1.6
1384	4.0	6.7	25	1.3
1420	3.9	13	39	2.6
1426	3.8	4.1	27	
1447	3.7	3.5	26	
1455	3.8	3.1	32	
1462	3.9	1.4	100	
1473	3.6	2.3	63	2.5
1481	3.4	3.0	63	
1488	3.5	6.9	130	
1494	3.1	6.1	86	
1502	3.5	2.2	73	2.8
1527	3.4	1.7	130	
1566	3.0	5.7	200	4.9
1678	2.8	1.5	200	

processes with rate parameters from Refs. 1 and 2. The influence of such reactions was always negligible under our conditions.

The numerical analysis of the recorded profiles and the fit of k_2 and k_3 is straight forward. However, a simplified analysis is already obtainable in the following way which shows that the analysis of HO concentration profiles allows for a nearly independent determination of the values of k_2 and k_3: With reactions (1)–(4), the maximum concentrations of HO are given by

$$[\mathrm{HO}]_{\max}=\frac{2k_1[\mathrm{Ar}]}{k_2+k_3[\mathrm{HO_2}]/[\mathrm{H_2O_2}]}. \tag{5}$$

The concentrations of HO_2 at times, when the HO maximum is reached, are generally still so low that $k_2 \gg k_3[\mathrm{HO_2}]/[\mathrm{H_2O_2}]$ in Eq. (5) and hence

$$k_2 \approx 2k_1[\mathrm{Ar}]/[\mathrm{HO}]_{\max}. \tag{6}$$

After having reached quasistationary state and passed through its maximum, [HO] decreases while [HO_2] still increases until it passes through a maximum. First estimations of k_2, therefore, were obtained from Eq. (6) while k_3 was derived from the later HO decay such as given by Eq. (5). Not much fine tuning of k_2 and k_3 was required to arrive at perfect agreement with the full HO profiles. This is, e.g., demonstrated in Fig. 1.

Table I summarizes conditions and derived values of the rate constants k_2 and k_3 for a selected set of our experiments (the values for k_1 and k_4 used in the analysis are given in the next section). Following the simplified analysis leading to Eqs. (5) and (6), one easily realizes that the accuracy of the derived values of k_2 neither depended on noise of the measured HO signals nor on the fitting procedure but on the ratio of $k_1/[\mathrm{HO}]_{\max}$; see Eq. (6). The uncertainty of k_2, hence, was that of the ratio $k_1/\sigma(\mathrm{HO})$. On the basis of the separate determinations of $k_1(\Delta k_1/k_1=25\%)$[4,5] and σ(HO) [$\Delta\sigma$(HO)/σ(HO)=20%] from Refs. 9 and 10, we estimate this ratio to be accurate within ±40%. The decay of [HO] after reaching the maximum is mainly determined by the ratio k_2/k_3. One may demonstrate the sensitivity of the observed [HO] profiles on the individual values of k_2 and k_2/k_3 (leaving k_1, k_4, $[\mathrm{H_2O_2}]_{t=0}$, and σ(HO) fixed). Figures 2 and 3 show concentration–time profiles for typical low and high temperature conditions used in our work. The simulation was done with optimum values of k_2 and k_2/k_3 and variations of ±40% of k_2 and a factor of 2 in the ratio k_2/k_3. The figures

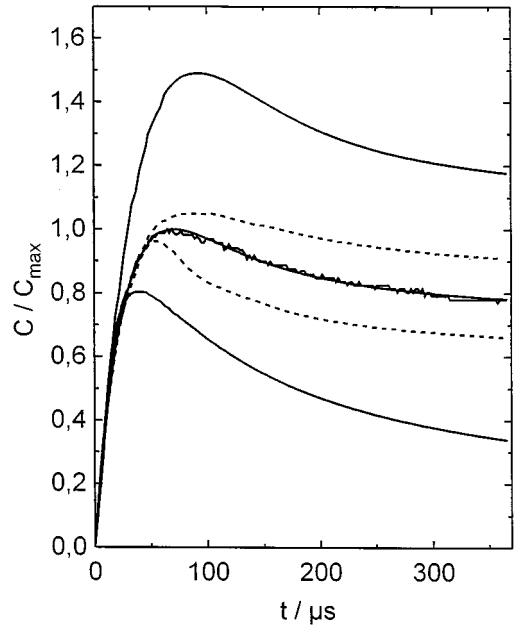

FIG. 2. Sensitivity of calculated concentration-time profiles of HO at 1150 K on k_2 and k_2/k_3 (full lines: k_2+40% (lower curve), k_2−40% (upper curve); dashed lines: $k_2/k_3\cdot 2$ (upper curve), $k_2/k_3\cdot 0.5$ (lower curve); line with noise: measured HO profile).

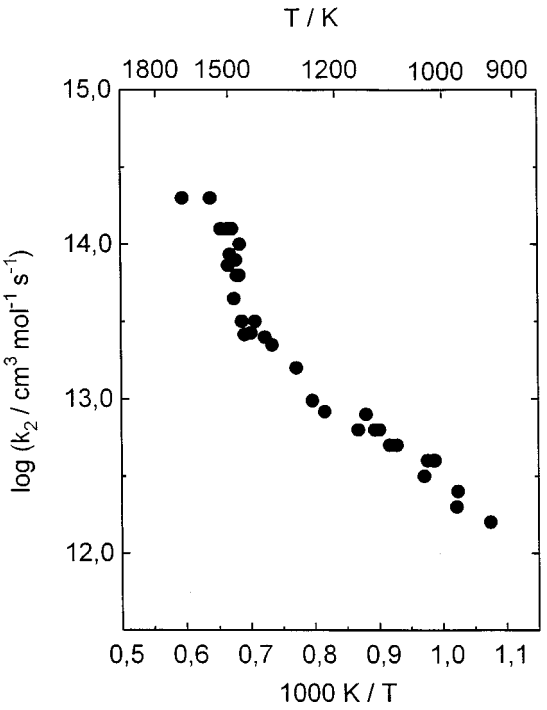

FIG. 4. Rate constants for the reaction HO+H_2O_2→H_2O+HO_2.

well illustrate that the fitting is more certain in k_2 than the basic uncertainty of ±40% of the ratio k_1/σ(HO). At the same time, the fitting of k_2/k_3 and, hence, of k_3 is more certain than a factor of 2.

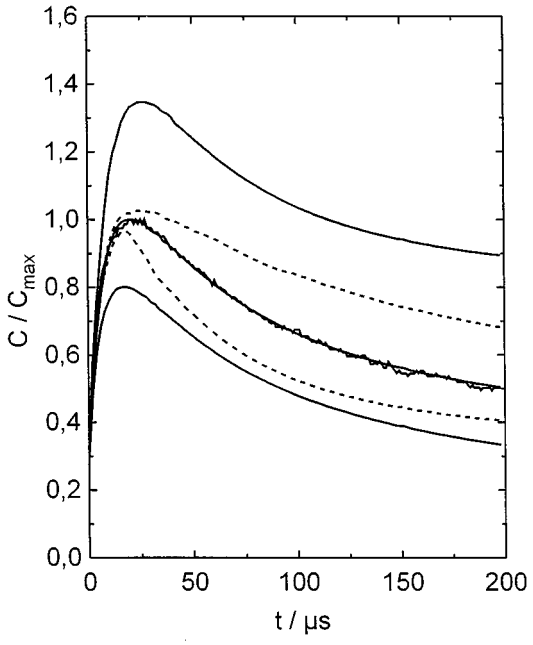

FIG. 3. Sensitivity of calculated concentration-time profiles of HO at 1566 K on k_2 and k_2/k_3 (full lines: k_2+40% (lower curve), k_2−40% (upper curve); dashed lines: $k_2/k_3\cdot 2$ (upper curve), $k_2/k_3\cdot 0.5$ (lower curve); line with noise: measured HO profile).

IV. RESULTS AND DISCUSSION

A. Results for the reaction HO+H_2O_2→HO_2+H_2O

Figure 4 shows an Arrhenius representation of our results for k_2. With increasing temperature, one observes a steepening of the Arrhenius plot before the increase of k_2 levels off at the highest temperatures where k_2 exceeds 10^{14} $cm^3\,mol^{-1}\,s^{-1}$. The non-Arrhenius character of the rate constant becomes even more apparent when literature values[19–24] from lower temperatures are included, see Fig. 5. At low temperatures, reaction (2) has a small positive activation energy which changes to a much larger positive activation energy before a leveling off sets in. The marked change of the activation energy near 800 K, which we earlier derived from the analysis of HO_2 yields in the H_2O_2 decomposition,[3] is completely confirmed by the present analysis of HO profiles. Apart from the high temperature leveling off, the results can well be represented by the sum of two Arrhenius expressions

$$k_2=[1.7\cdot 10^{18}\ \exp(-14\ 800\ \ \mathrm{K/T})+2.0\cdot 10^{12}\times\exp(-215\ \ \mathrm{K/T})]\mathrm{cm}^3\ \mathrm{mol}^{-1}\,\mathrm{s}^{-1} \quad (7)$$

$$\text{for } 240\leqslant T\leqslant 1600\mathrm{K}.$$

For $T\geqslant 1600$ K, apparently a value of $k_2\approx 2.0\cdot 10^{14}$ $cm^3\,mol^{-1}\,s^{-1}$ is approached. Figure 5 includes the representation from Eq. (7).

One may ask for an interpretation of so strongly non-Arrhenius temperature dependences of rate constants as shown for k_2 in Fig. 5. One possible explanation could be the formation of intermediate complexes such that the overall rate of the ''elementary reaction'' is given by the rate of

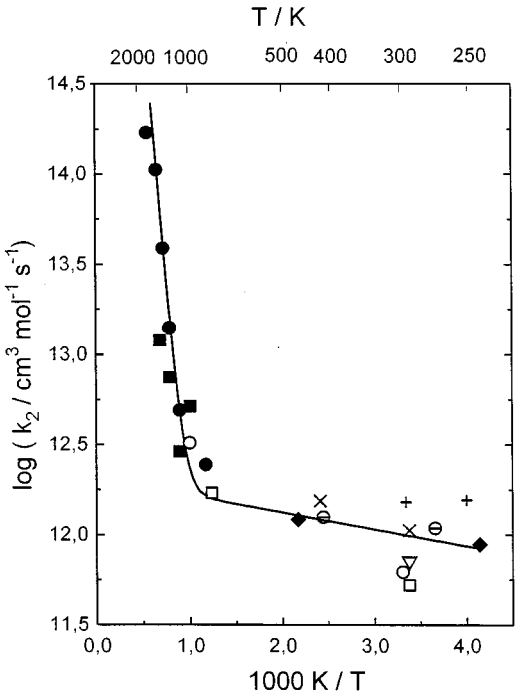

FIG. 5. Rate constants for the reaction HO+H_2O_2→H_2O+HO_2 (experiments in Ar at 400–600 mbar, this work: ●, full line from Eq. (7); measurements at 10–1000 mbar from Ref. 19: □, Ref. 20: ♦, Ref. 21: ○, Ref. 22: × and ⊖, Refs. 3, 7: ■, Ref. 23: +, Ref. 24: ▽).

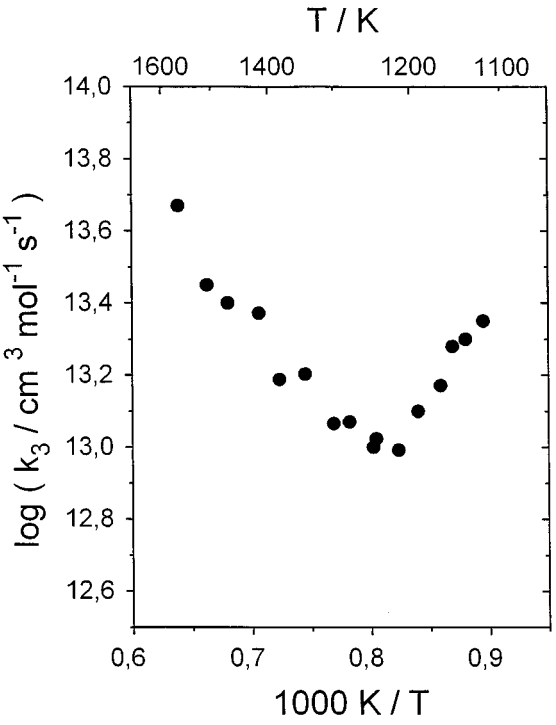

FIG. 7. Rate constants for the reaction HO+HO_2→H_2O+O_2.

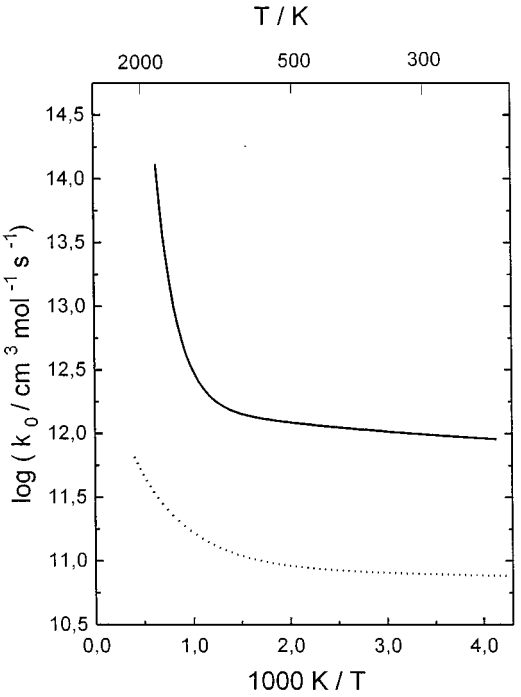

FIG. 6. Comparison of rate constants for the reaction HO+H_2O_2→H_2O+HO_2 (full line) with the reaction HO+CO→H+CO_2 (dashed line).

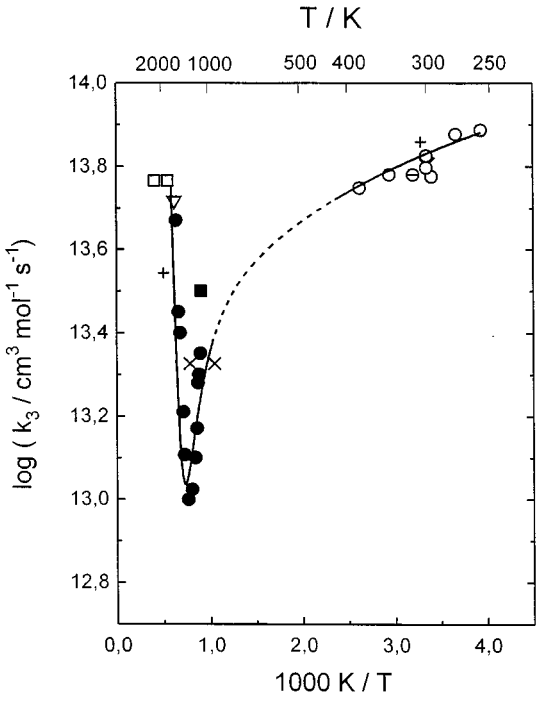

FIG. 8. Rate constants for the reaction HO+HO_2→H_2O+O_2 (this work: ●, full lines: measured high and low temperature dependence, dashed line: possible temperature dependence, measurements from Ref. 26: ▽, Ref. 27: ⊖, Ref. 28: ♦, Ref. 29: □, Ref. 30: Ref. 6: ◩, ○, Ref. 31: +, Ref. 3: ×).

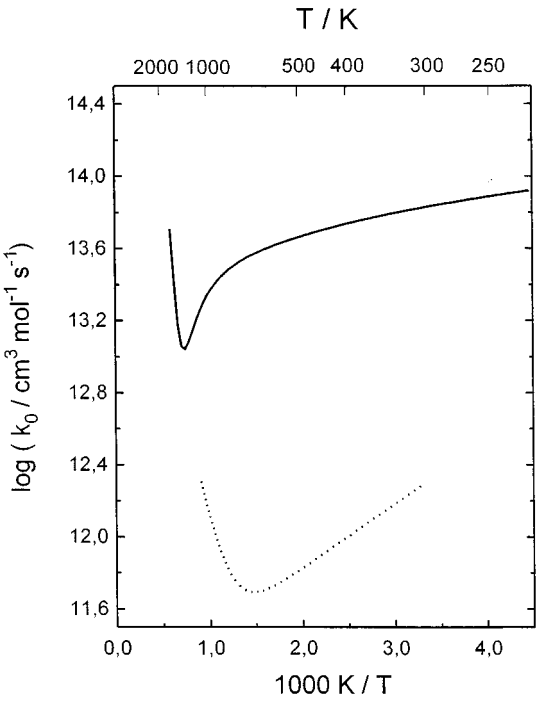

FIG. 9. Comparison of rate constants for the reaction HO+HO_2→H_2O+O_2 (full line, see Fig. 8) with the reaction HO_2+HO_2→H_2O_2+O_2 (dashed line).

formation of the complex and the subsequent competition between forward and backward dissociations. It was shown in Ref. 8 that a multitude of possible temperature dependences arises in this class of reactions, apparent activation energies and preexponential factors not being related to barrier heights and gas kinetic collision frequencies in a simple way. Besides anomalous temperature dependences, this class of reactions sometimes also reveals its very nature by pressure dependences of the apparent second-order rate constants. However, the latter effect is only observed when the dissociation rates of the complex become smaller than the collisional stabilization rates. A particularly complete picture of this type of behavior recently was observed[25] for the reaction

$$HO+CO \rightarrow H+CO_2 \tag{8}$$

which involves the well known HOCO intermediate. In Fig. 6 we compare the limiting low pressure rate constant $k_{8,0}$ of this reaction with k_2. The temperature dependences of the two reactions are of similar strongly non-Arrhenius character. One, therefore, may speculate whether reaction (2) also involves intermediate complex formation. In this case, however, the intermediate H_3O_3 species has not yet been well characterized. A pressure dependence has also not been observed as yet. However, this would just indicate that the dissociation rate of excited $H_3O_3^*$ with the applied pressures below a few bar was not matched by a collisional stabilization rate, i.e., the well depth of the complex would have to be considerably smaller than the 130 kJ mol^{-1} derived for HOCO.[25] Experiments at higher pressures and lower temperatures or direct trapping of the intermediate would provide the proof. As long as this is not available, at least we take the similarity of the non-Arrhenius temperature dependence of k_2 and $k_{8,0}$ as strong evidence for the implication of H_3O_3 intermediate complex formation.

B. Results for the reaction HO+HO_2→H_2O+O_2

The temperature dependence of k_3 is weaker than that of k_2 and it is characteristically different. Figure 7 shows our results. There is a rate constant minimum near 1250 K which is located at higher temperatures than that for reaction (4) which was found near to 800 K.[7] The rate constant k_3 decreases from a value of $2.0\cdot10^{13}$ at 1100 K to a minimum value of $1.1\cdot10^{13}$ at 1250 K, and rises again to a value of $4.5\cdot10^{13}$ cm^3 mol^{-1} s^{-1} at 1600 K. Again a non-Arrhenius temperature dependence is observed, in particular when our high temperature results are compared with literature data[26–31] for lower temperatures; see Fig. 8. The initially observed pressure dependence near room temperature apparently was an artifact, see Ref. 30.

In Fig. 9 we compare the temperature dependences of the low pressure rate constants $k_{4,0}$ and $k_{3,0}$. For reactions (3) and (4) one observes rate constant minima which, however, are developed to different extent. Furthermore, for reaction (4) a pressure dependence of k_4 was observed near room temperature[32,33] which apparently was not present below 1 bar in reaction (3). If one again attributes the pressure and non-Arrhenius temperature dependence of k_4 to a reaction involving an H_2O_4 intermediate complex, one is tempted to draw similar conclusions on reaction (3), i.e., to postulate an H_2O_3 intermediate complex. The absence of a pressure effect below 1 bar for reaction (3) at 300 K then again has to be attributed to a shorter lifetime of excited $H_2O_3^*$ in comparison to excited $H_2O_4^*$.

The conclusions on a mechanism involving intermediate complex formation in reactions (2)–(4) are still tentative. They are based on anomalous temperature dependences and,

TABLE II. Summary of rate constants for reactions (1)–(4).

Reaction	T (K)	k (cm^3 mol^{-1} s^{-1})	Reference
(1) H_2O_2+Ar→2HO+Ar	950–1450	$k_1=[\mathrm{Ar}]\cdot5.8\cdot10^{31}\cdot T^{-4.55}$ exp(−25580 K/T)	4, 5, This work
(2)HO+H_2O_2→H_2O+HO_2	240–1700	$k_2=1.7\cdot10^{18}$ exp(−14 800 K/T) +$2.0\cdot10^{12}$ exp (−215 K/T)	This work
(3)HO+HO_2→H_2O+O_2	1100–1600	see Fig. 7	This work
(4)HO_2+HO_2→H_2O_2+O_2	300–1100	$k_4=4.2\cdot10^{14}$ exp (−6030 K/T) +$1.3\cdot10^{1}$ exp (820 K/T)	7

in part, the observation of pressure dependences. Therefore, more experiments extending into the high pressure range, such as performed for the HO+CO reaction,[25] are desirable. Also trapping of H_3O_3, H_2O_3, and H_2O_4 species would be helpful. Nevertheless, a final proof can only be obtained by combining extensive measurements of the described type with *ab initio* calculations of the complete potential energy surface of the reaction. The HO+CO reaction serves as a model system for this purpose.

We finally summarize all rate constants of reaction (1)–(4) such as measured and combined with low temperature data in the present work (see Table II). Apart from determining k_2 and k_3, we also reevaluated k_1 from earlier experiments of Refs. 4 and 5 using the new set of rate data for reactions (2)–(4). As this led to only a minor correction of k_1 we do not discuss this reevaluation here.

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