

# Rate constants of the reaction $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ at $T \geq 1000$ K

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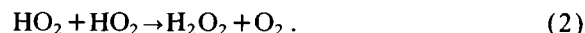
$\text{HO}_2$  profiles in the thermal decomposition of  $\text{H}_2\text{O}_2$  in shock waves over the range 1000–1250 K were analyzed with respect to the reactions  $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$  (3) and  $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  (4). Reaction (3) shows a strong up-turn of the rate constant at temperatures near 800 K. Over the range 250–1250 K,  $k_3$  can be represented as  $k_3 = [1.0 \times 10^{12} + 5.8 \times 10^{14} \exp(-4810 \text{ K}/T)] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The “anomalous” temperature dependence suggests a mechanism involving an  $\text{H}_3\text{O}_3$  intermediate complex.

## 1. Introduction

Complex-forming bimolecular reactions can have a variety of temperature coefficients (see, e.g. refs. [1–3]). On the one hand, there is the contribution from complex formation which also governs high-pressure recombination and association or capture rates. On the other hand, there is the energy- and angular momentum-dependent competition between forward and reverse unimolecular reactions of the complex. As a consequence, positive and negative temperature coefficients as well as changes between these temperature dependences are observed; likewise pressure-dependent and pressure-independent ranges are encountered. Two striking examples are the reactions



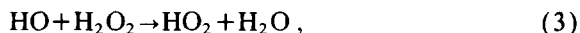
and



In the first case [4], there is a wide temperature range (250–800 K) where  $k_1$  is nearly temperature independent, before a dramatic change to a strongly positive temperature coefficient sets in (at  $T \geq 1000$  K). In the second case, recently a deep rate constant minimum of  $k_2$  (near 700 K) was found [5,6] which separates a pressure-dependent (at  $T < 700$  K) from a pressure-independent range. Because the full va-

riety of possible reaction behavior is not yet well documented, we are searching for more examples showing “anomalous” temperature (and pressure) dependences.

In the present article we report on the reaction



which shows an interesting temperature dependence if the range of observations is extended as far as possible. This reaction has been studied extensively at low [4,7–11] (250–400 K) and moderate [4,12–19] temperatures (700–800 K) where it is characterized by only a small positive temperature coefficient. At high temperatures, reactions (2), (3), and



occur in the course of the thermal decomposition of  $\text{H}_2\text{O}_2$ , following the initial dissociation



In previous work [5] we have analyzed this system for  $T \leq 1100$  K with respect to the temperature dependence of reaction (2). Also,  $k_3$  and  $k_4$  values were obtained near  $T = 1000$  K which are consistent with low-temperature extrapolations of these rate constants. The extension of this work to higher temperatures described in the present article shows that the temperature dependence of  $k_3$  dramatically changes. A strong up-turn of the rate constant sets in near 800

K which is quite analogous to that [4] of reaction (1). These observations appear consistent with the assumption that an intermediate  $\text{H}_3\text{O}_3$  complex is formed similar to the  $\text{HOCO}$  and  $\text{H}_2\text{O}_4$  complexes in reactions (1) and (2). Therefore, the interpretation of the observations waits for quantum-chemical investigations of the structural properties of  $\text{H}_3\text{O}_3$  complexes, such as was done recently [20] for the  $\text{H}_2\text{O}_3$  complex involved in reaction (4). We feel that the "anomalous" temperature dependence of reaction (3) by analogy to that of reaction (1) provides enough evidence for the participation of  $\text{H}_3\text{O}_3$  intermediate complexes in reaction (3), although this was disputed in ref. [11] on the basis of deuteration experiments.

## 2. Experimental observations

Our information on  $k_3$  and  $k_4$  in part stems from older [5,21–23], and in part from new shock tube studies in which  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$ , and  $\text{HO}$  absorption profiles in the UV were recorded during the thermal decomposition of  $\text{H}_2\text{O}_2$  (at the wavelengths 290, 230, and 308.3278 nm, respectively). Details of these experiments have been reported before and are not repeated here. So far [5] we have limited the analysis of these experiments to the contribution of reaction (2) in the temperature range 900–1100 K where  $\text{HO}_2$  profiles are sensitive to this reaction. At higher temperatures,  $k_2$  becomes practically inaccessible and  $\text{HO}_2$  consumption is mainly governed by reaction (4). In the present work, we analyzed  $\text{HO}_2$  profiles in this high-temperature range from the older and from the new experiments. Fig. 1 shows maximum  $\text{HO}_2$  yields and positions of  $\text{HO}_2$  maxima relative to the extent of  $\text{H}_2\text{O}_2$  disappearance. Apart from these quantities, full  $\text{HO}_2$  and  $\text{HO}$  absorption-time profiles were recorded. The points shown present a representative selection from about 100 older and new experiments which, within the scatter shown, are consistent with each other. The absolute calibration of fig. 1 depends on the ratio of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  absorption coefficients which has been studied earlier [22] and confirmed by consistency with more recent experiments [6]. The wavelength 230 nm was chosen because  $\text{HO}_2$  absorption here is practically independent of the temperature [22]. To a minor ex-

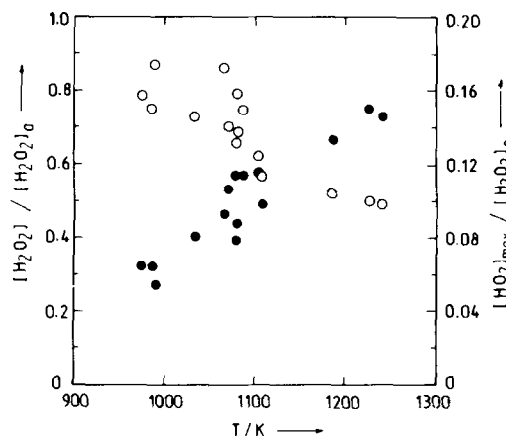


Fig. 1. Maximum  $\text{HO}_2$  yields  $[\text{HO}_2]_{\text{max}}$  (●) and  $\text{H}_2\text{O}_2$  concentrations  $[\text{H}_2\text{O}_2]$  (○) at  $\text{HO}_2$  maxima in the thermal decomposition of  $\text{H}_2\text{O}_2$  (initial concentrations of  $\text{H}_2\text{O}_2$ :  $[\text{H}_2\text{O}_2]_0$  in the range  $2.5 \times 10^{-8}$ – $2.5 \times 10^{-7}$  mol  $\text{cm}^{-3}$ ).

tent the results depend on the ratio of the absorption coefficients but this quantity is well established now. Fig. 1 indicates a considerable increase of  $\text{HO}_2$  maximum yields with increasing temperature. At the same time the position of the  $\text{HO}_2$  maxima is shifted towards larger extents of  $\text{H}_2\text{O}_2$  decomposition. In the following we show that this behavior is directly related to different temperature dependences of  $k_3$  and  $k_4$ .

## 3. Analysis of $\text{HO}_2$ yields in the decomposition of $\text{H}_2\text{O}_2$

The kinetic analysis of the dissociation mechanism of  $\text{H}_2\text{O}_2$  with the reactions (2) and (5) is straightforward. When  $\text{HO}$  and  $\text{HO}_2$  have reached quasi-stationary conditions,  $d[\text{H}_2\text{O}_2]/dt \approx -2k_5 \times [\text{M}][\text{H}_2\text{O}_2]$  is obtained.  $\text{H}_2\text{O}_2$  decay profiles in refs. [21,22] were evaluated in this way leading to [22]  $k_5 = 2.0 \times 10^{16} \exp(-21640 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $\text{M} = \text{Ar}$ . The quasi-stationary concentrations of  $\text{HO}$  and  $\text{HO}_2$  are connected by

$$[\text{HO}] \approx \frac{2k_5[\text{M}]}{k_3} \left( 1 + \frac{k_4}{k_3} \frac{[\text{HO}_2]}{[\text{H}_2\text{O}_2]} \right)^{-1} \quad (6)$$

and

$$k_2[\text{HO}_2]^2/k_5[\text{M}][\text{H}_2\text{O}_2] = f, \quad (7)$$

with

$$f = \frac{1 - k_4[\text{HO}_2]/k_3[\text{H}_2\text{O}_2]}{1 + k_4[\text{HO}_2]/k_3[\text{H}_2\text{O}_2]} \quad (8)$$

For small  $[\text{HO}_2]/[\text{H}_2\text{O}_2]$  at low temperatures,  $f$  approaches unity whereas at large temperatures it goes to zero. According to eqs. (7) and (8), measurements of  $[\text{HO}_2]$  and  $[\text{H}_2\text{O}_2]$  only lead to a relation between the ratios  $k_2/k_5$  and  $k_4/k_3$ . Unless  $f \approx 1$  or  $f \approx 0$  is approached sufficiently well, the ratios cannot be separated. Therefore, in the present work  $f$  was calculated independently using known values of the ratio  $k_2/k_5$ . For this purpose, the  $\text{H}_2\text{O}_2$  dissociation rate constants  $k_5$  such as given above (and redetermined in each individual experiment to be independent of uncertainties in  $k_2$ ,  $k_3$ , or  $k_4$ ) were employed. Furthermore, the expression  $k_2 = [4.2 \times 10^{14} \times \exp(-6030 \text{ K}/T) + 1.3 \times 10^{11} \exp(+820 \text{ K}/T)] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was used which was derived in ref. [5] by measurement of  $\text{HO}_2$  removal rates from shock-heated dimethyl peroxide/ $\text{O}_2$  mixtures. Measurements of maximum  $\text{HO}_2$  yields and  $\text{H}_2\text{O}_2$  concentrations at the positions of  $\text{HO}_2$  maxima in  $\text{H}_2\text{O}_2$  dissociation experiments were then combined with  $k_2$  and  $k_5$  to obtain the "correction factor"  $f$  of eq. (7) for each individual experiment. The expression

$$\frac{k_4}{k_3} = \frac{1-f}{1+f} \left( \frac{[\text{H}_2\text{O}_2]}{[\text{HO}_2]} \right)_{\text{max HO}_2} \quad (9)$$

then leads directly to  $k_4/k_3$ . For the applied conditions,  $f$  varied between about 0.2 and 0.8. An upper limit of the ratio  $k_4/k_3$  is obtained from eq. (9), if  $f$  is put equal to zero, see below.

To check the correctness of the analysis, at first numerical modelling of reactions (2)–(5) was done. Eqs. (6)–(9), based on quasi-stationary  $\text{HO}$  concentrations, were found to be valid under all conditions applied. Furthermore, the importance of secondary reactions initiated by thermal decomposition of  $\text{HO}_2$ ,



was investigated, because reactions of  $\text{H}$  atoms with  $\text{H}_2\text{O}_2$  can considerably accelerate the  $\text{H}_2\text{O}_2$  decomposition and modify the  $\text{HO}_2$  yields [23]. On the basis [4] of the reverse reaction of (10) and the equilibrium constant, one estimates  $k_{10} \approx 1.1 \times 10^{15} \times$

$\exp(-23780 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $\text{M} = \text{Ar}$ . Because of the small ratio  $k_{10}/k_5 \approx 10^{-2}$  at 1300 K, the accelerating effect of  $\text{H}$  atoms from reaction (10) does not influence the observations of this work, such as confirmed also by a detailed modelling of the complete mechanism [4] involving reactions of  $\text{H}$  and  $\text{O}$  atoms with  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$ .

Fig. 2 converts the results of fig. 1 into the representation of eq. (9) such that  $k_4/k_3$  is obtained as a function of the temperature. Obviously there is a strong temperature dependence of the ratio  $k_4/k_3$ . The scatter of the data in part is due to the uncertainties in separating  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  absorption signals, in part to the difficulties identifying the strongly temperature-dependent value of  $k_5$  which enters the correction factor  $f$ . This problem with increasing temperature becomes less serious and the points at the highest temperatures ( $T \geq 1050 \text{ K}$ ) are the most certain. It should be emphasized that a large number of similar experimental points were obtained which were consistent with the data points shown. In any case, the upper limit of  $k_4/k_3$ , such as indicated by the dashed line in fig. 2 and determined from the experimental points by putting  $f=0$ , confirms that  $k_3$  approaches  $k_4$  at high temperatures, see below.

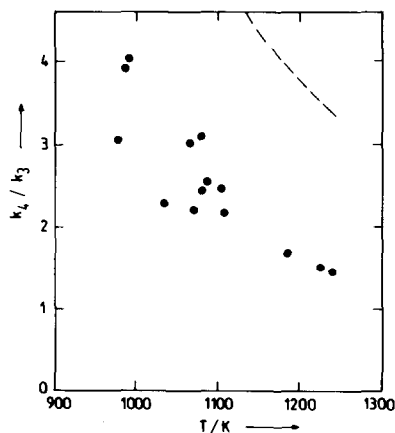


Fig. 2. Rate constant ratio  $k_4/k_3$  as a function of temperature (experiments of fig. 1 converted to  $k_4/k_3$  via eq. (9) with correction factors  $f$  from eq. (7) determined individually for each experiment, dashed line: upper limit of  $k_4/k_3$  from eq. (9) with  $f=0$ ).

#### 4. Rate constant of the reaction $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$

In the present work only ratios  $k_4/k_3$  were determined such as given in fig. 2. In order to derive absolute values of  $k_3$ , we have to refer to literature values [4] of  $k_4$ . Fig. 3 shows the most recent low-temperature data [24–26] (obtained after 1986) together with some of the few high-temperature results [5,27–31] available. The most recent low-temperature studies [24] have probably identified the sources of uncertainty of earlier work [7]. Also, the earlier suggestion of a pressure dependence of  $k_4$  was not confirmed [24]. A value of  $k_4 = 2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  near 1050 K in ref. [31] was obtained by analyzing HO profiles in the  $\text{H}_2\text{O}_2$  decomposition, such as given by eq. (6). This independent approach to  $k_3$  and  $k_4$  deserves further attention, and more measurements of this kind are underway in our laboratory. The flame studies of refs. [29,30], and [27,28] disagree with each other. The analysis here is relatively indirect and based on complex mechanisms. Because the data of refs. [29,30] appear more consistent with the more direct determination from ref. [31] and the calculation of ref. [20], they are preferred. Unfortunately, some uncertainty in  $k_4$  is left. However, with  $k_4 = (2 + 2/-1) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 950–1250 K probably a realistic estimate of this uncertainty is made.

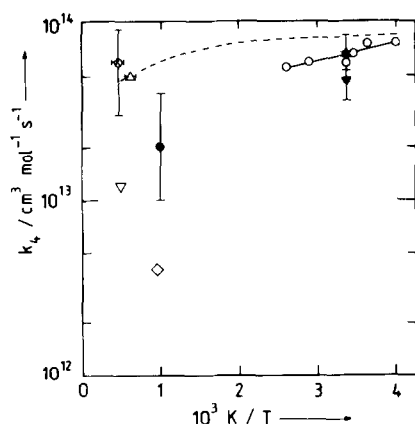


Fig. 3. Rate constant  $k_4$  of the reaction  $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ . ((○) Ref. [24]; (▲) ref. [25]; (▼) ref. [26]; (⊗) ref. [27]; (△) ref. [28]; (◇) ref. [29]; (▽) ref. [30]; (●) refs. [5,31], (---) ref. [20].)

#### 5. Rate constant of the reaction $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$

On the basis of  $k_4 = (2 + 2/-1) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  from section 4 and fig. 3, the results of fig. 2 are converted into  $k_3$ . Fig. 4 compares the results with data from earlier studies. Low-temperature experiments (data obtained after 1982 are included in fig. 4) indicated a very small positive temperature coefficient of  $k_3$  between 250 and 400 K (with  $k_3$  (300 K)  $= 1.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). Our analysis [5,31] or HO profiles in the  $\text{H}_2\text{O}_2$  decomposition near 1000 K led to a value of  $3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The present work suggests a sharp up-turn of  $k_3$  at temperatures above 800 K with  $k_3 \approx 1.9 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 1200 K. A lower limit of  $k_3 = 8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 1200 K follows from the dashed line in fig. 2, which was obtained with  $f=0$ , such that the sharp up-turn of  $k_3$  is definitely outside the experimental uncertainties.

To confirm this behavior by an independent method, further experiments analyzing HO profiles in the  $\text{H}_2\text{O}_2$  decomposition at temperatures above 1000 K are underway in our laboratory. The present conclusions on  $k_3$  would be incorrect only if  $k_4$  were very small. For example, a value of  $k_3 \approx 3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 1240 K, according to fig. 2, would require a  $k_4$  value of  $4.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at this temperature. This appears completely inconsistent

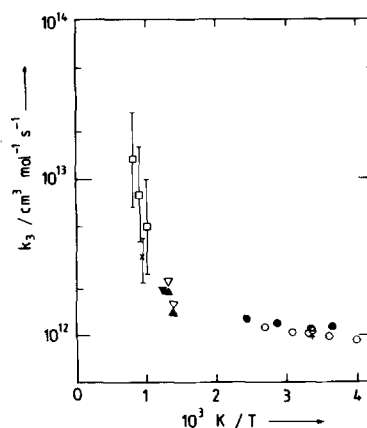


Fig. 4. Rate constant  $k_3$  of the reaction  $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ . ((□) This work, (×) ref. [31]; (▼) ref. [14]; (▽) ref. [13]; (▲) ref. [17]; (●) ref. [11]; (○) ref. [10]; (⊖) ref. [9]; (+) ref. [8].)

with the low-temperature results of  $k_4$  shown in fig. 3. Therefore, the sharp up-turn of  $k_3$  with a rise to values above  $10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $T \geq 1200 \text{ K}$  appears well established. Nevertheless, the independent confirmation as well as a reevaluation of the intermediate temperature results from ref. [19] are highly desirable.

The results of fig. 4 over the temperature range 250–1250 K can be represented as  $k_3 = [1.0 \times 10^{12} + 5.8 \times 10^{14} \exp(-4810 \text{ K}/T)] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . It should be emphasized that, in the case of a complex-forming bimolecular reaction, the preexponential factor of the Arrhenius component does not have to be of "normal" magnitude, see the corresponding expression for  $k_2$  given above.

## 6. Conclusion

After our demonstration of a deep rate constant minimum near 700 K for the reaction  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  in ref. [5], the present work manifests a similarly "anomalous" temperature dependence for the reaction  $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ . The sharp up-turn of the rate constant of this reaction near 1000 K appears quite analogous to that for the well studied reaction  $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ . This suggests intermediate complex formation during the reaction  $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ .

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