Rate constants of the reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$ at $T \ge 1000 \text{ K}$

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HO₂ profiles in the thermal decomposition of H₂O₂ in shock waves over the range 1000–1250 K were analyzed with respect to the reactions HO+H₂O₂ \rightarrow HO₂+H₂O (3) and HO+HO₂ \rightarrow H₂O+O₂ (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 H₃O₃ 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

$$HO + CO \rightarrow H + CO_2 \tag{1}$$

and

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
. (2)

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 $T \ge 1000$ 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

$$HO + H_2O_2 \rightarrow HO_2 + H_2O$$
, (3)

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

$$HO + HO_2 \rightarrow H_2O + O_2 \tag{4}$$

occur in the course of the thermal decomposition of H_2O_2 , following the initial dissociation

$$H_2O_2 + M \rightarrow 2HO + M. \tag{5}$$

In previous work [5] we have analyzed this system for $T \le 1100$ 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 H_3O_3 complex is formed similar to the HOCO and H_2O_4 complexes in reactions (1) and (2). Therefore, the interpretation of the observations waits for quantum-chemical investigations of the structural properties of H_3O_3 complexes, such as was done recently [20] for the H_2O_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 H_3O_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 H₂O₂, HO₂, and HO absorption profiles in the UV were recorded during the thermal decomposition of H_2O_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 HO₂ profiles are sensitive to this reaction. At higher temperatures, k2 becomes practically inaccessible and HO₂ consumption is mainly governed by reaction (4). In the present work, we analyzed HO₂ profiles in this high-temperature range from the older and from the new experiments. Fig. 1 shows maximum HO₂ yields and positions of HO₂ maxima relative to the extent of H₂O₂ disappearance. Apart from these quantities, full HO₂ and 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 HO₂ and H₂O₂ absorption coefficients which has been studied earlier [22] and confirmed by consistency with more recent experiments [6]. The wavelength 230 nm was chosen because HO₂ absorption here is practically independent of the temperature [22]. To a minor ex-

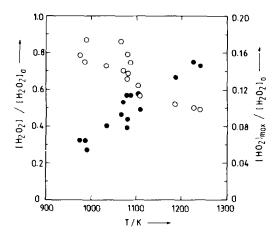


Fig. 1. Maximum HO₂ yields $[HO_2]_{max}$ (\bullet) and H₂O₂ concentrations $[H_2O_2]$ (\bigcirc) at HO₂ maxima in the thermal decomposition of H₂O₂ (initial concentrations of H₂O₂: $[H_2O_2]_0$ in the range $2.5 \times 10^{-8} - 2.5 \times 10^{-7}$ mol cm⁻³).

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 HO_2 maximum yields with increasing temperature. At the same time the position of the HO_2 maxima is shifted towards larger extents of H_2O_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 HO_2 yields in the decomposition of H_2O_2

The kinetic analysis of the dissociation mechanism of $\rm H_2O_2$ with the reactions (2) and (5) is straightforward. When HO and HO₂ have reached quasi-stationary conditions, $\rm d[H_2O_2]/dt \approx -2k_5 \times [M][H_2O_2]$ is obtained. $\rm H_2O_2$ decay profiles in refs. [21,22] were evaluated in this way leading to [22] $k_5 = 2.0 \times 10^{16} \exp(-21640 \ {\rm K/T}) \ {\rm cm}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1}$ for M=Ar. The quasi-stationary concentrations of HO and HO₂ are connected by

[HO]
$$\approx \frac{2k_5[M]}{k_3} \left(1 + \frac{k_4}{k_3} \frac{[HO_2]}{[H_2O_2]} \right)^{-1}$$
 (6)

and

$$k_2[HO_2]^2/k_5[M][H_2O_2] = f,$$
 (7)

with

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

For small $[HO_2]/[H_2O_2]$ at low temperatures, fapproaches unity whereas at large temperatures it goes to zero. According to eqs. (7) and (8), measurements of [HO₂] and [H₂O₂] 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 H₂O₂ 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 $k_2 = [4.2 \times 10^{14} \times$ $\exp(-6030 \text{ K/T}) + 1.3 \times 10^{11} \exp(+820 \text{ K/T})$ cm³ mol⁻¹ s⁻¹ was used which was derived in ref. [5] by measurement of HO₂ removal rates from shock-heated dimethyl peroxide/O₂ mixtures. Measurements of maximum HO2 yields and H2O2 concentrations at the positions of HO₂ maxima in H₂O₂ 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

$$\frac{k_4}{k_3} = \frac{1 - f}{1 + f} \left(\frac{[H_2 O_2]}{[HO_2]} \right)_{\text{max HO}_2}$$
 (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 HO concentrations, were found to be valid under all conditions applied. Furthermore, the importance of secondary reactions initiated by thermal decomposition of HO_2 ,

$$HO_2 + M \rightarrow H + O_2 + M$$
, (10)

was investigated, because reactions of H atoms with H_2O_2 can considerably accelerate the H_2O_2 decomposition and modify the HO_2 yields [23]. On the basis [4] of the reverse reaction of (10) and the equilibrium constant, one estimates $k_{10} \approx 1.1 \times 10^{15} \times$

 $\exp(-23780 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ for M=Ar. Because of the small ratio } k_{10}/k_5 \approx 10^{-2} \text{ at } 1300 \text{ K, the accelerating effect of H atoms from reaction (10) does not influence the observations of this work, such as confirmed also by a detailed modelling of the complete mechanism [4] involving reactions of H and O atoms with <math>H_2O_2$ and 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 HO₂ and H₂O₂ 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 ($T \ge 1050 \text{ K}$) 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.

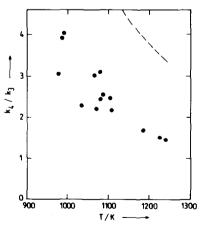


Fig. 2. Rate constant ratio k_4/k_3 as a function of temperature (experiments of fig. 1 converted to k_4/k_3 via eq. (9) with correction factors f from eq. (7) determined individually for each experiment, dashed line: upper limit of k_4/k_3 from eq. (9) with f=0).

4. Rate constant of the reaction $HO+HO_2 \rightarrow H_2O+O_2$

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 lowtemperature 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 $k_4=2\times10^{13}$ cm³ $\text{mol}^{-1} \text{ s}^{-1} \text{ near } 1050 \text{ K in ref. } [31] \text{ was obtained by}$ analyzing HO profiles in the H₂O₂ 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 $k_4 = (2+2/-1) \times 10^{13}$ cm³ mol⁻¹ s⁻¹ at 950-1250 K probably a realistic estimate of this uncertainty is made.

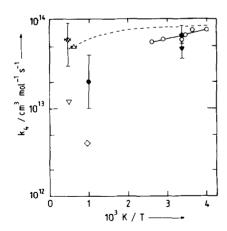


Fig. 3. Rate constant k_4 of the reaction $HO + HO_2 \rightarrow H_2O + O_2$. ((\bigcirc) Ref. [24]; (\triangle) ref. [25]; (∇) ref. [26]; (\bigotimes) ref. [27]; (\triangle) ref. [28]; (\bigotimes) ref. [29]; (∇) ref. [30]; (\bullet) refs. [5,31], (---) ref. [20].)

5. Rate constant of the reaction $HO+H_2O_2 \rightarrow HO_2+H_2O$

On the basis of $k_4 = (2+2/-1) \times 10^{13}$ cm³ mol⁻¹ 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 H₂O₂ decomposition near 1000 K led to a value of 3×10^{12} cm³ mol⁻¹ s⁻¹. The present work suggests a sharp up-turn of k_3 at temperatures above 800 K with $k_3 \approx 1.9 \times 10^{13}$ cm³ mol⁻¹ s^{-1} at 1200 K. A lower limit of $k_3 = 8 \times 10^{12}$ cm³ mol⁻¹ s⁻¹ at 1200 K follows form 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 $\rm H_2O_2$ 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 $k_3 \approx 3 \times 10^{12} \, \rm cm^3$ mol⁻¹ s⁻¹ at 1240 K, according to fig. 2, would require a k_4 value of $4.5 \times 10^{12} \, \rm cm^3$ mol⁻¹ s⁻¹ at this temperature. This appears completely inconsistent

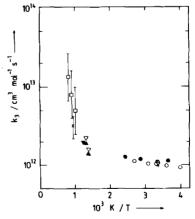


Fig. 4. Rate constant k_3 of the reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$. ((\square) This work, (\times) ref. [31]; (∇) ref. [14]; (∇) ref. [13]; (\triangle) ref. [17]; (\bigcirc) ref. [11]; (\bigcirc) ref. [10]; (\ominus) ref. [9]; (+) ref. [8].)

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} cm³ mol⁻¹ s⁻¹ at $T \ge 1200$ 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 $HO_2+HO_2\rightarrow H_2O_2+O_2$ in ref. [5], the present work manifests a similarly "anomalous" temperature dependence for the reaction $HO+H_2O_2\rightarrow HO_2+H_2O$. The sharp up-turn of the rate constant of this reaction near 1000 K appears quite analogous to that for the well studied reaction $HO+CO\rightarrow H+CO_2$. This suggests intermediate complex formation during the reaction $HO+H_2O_2\rightarrow HO_2+H_2O$.

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