

Study of the Pyrolysis of H_2O_2 in the Presence of H_2 and CO by Use of UV Absorption of HO_2

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Abstract

In dissociation experiments of H_2O_2 under shock wave conditions, the spectra of H_2O_2 and HO_2 have been observed in the UV at $2200 \leq \lambda \leq 2800 \text{ \AA}$. By the use of these spectra the H_2O_2 decomposition in the presence of H_2 and CO at $870 \leq T \leq 1000^\circ\text{K}$ has been analyzed. It was found that in this temperature range, in contrast to low temperature behavior, reactions of H atoms with H_2O_2 and with HO_2 are equally important. The rate of the reaction $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2$ was estimated in comparison with the rate of the reaction between H and HO_2 . Good agreement between calculated and measured concentration profiles of HO_2 and H_2O_2 was obtained.

1. Introduction

Reactions of the HO_2 radical are important intermediate steps in the oxidation of hydrogen and of hydrocarbons. Extensive reviews have been published [1-8]. Whereas mass-spectrometric detection of the radical in gas phase reaction systems has been used, e.g., by Foner and Hudson [8] and Albers and coworkers [9], the absorption spectrum of the radical in the UV has been utilized recently in studies of the H_2O_2 decomposition in shock waves [10]. The identification of the spectrum could be given by investigation of the spectrum under different reaction conditions [11]. Also an absolute calibration of the absorption was possible. Thus, one can follow reactions of HO_2 directly by monitoring its UV absorption.

This technique was utilized in the following study of HO_2 reactions in the H_2O_2 decomposition in the presence of H_2 . Higher temperatures were applied than in earlier flow system studies [18] of this reaction. This provided us with new information on HO_2 reactions which is unobtainable under flow system conditions. The experimental quantities used for these investigations were the time profiles of the H_2O_2 and HO_2 concentrations, both followed by means of their UV absorption spectra.

In addition to the study of the kinetics, the described experiments have been performed as a check on our identification of the HO_2 spectrum.

2. Experimental

HO₂ was produced in early subsequent reactions during the thermal decomposition of H₂O₂ behind reflected shock waves. Details of the shock wave apparatus have been given [10–12].

Reaction mixtures with relative concentrations of H₂O₂ between 0.4×10^{-3} and 2×10^{-3} were prepared by flowing Ar as carrier gas without additives (H₂ or CO) through a saturator containing about 95% aqueous H₂O₂ solution. Part of the vaporized H₂O₂ was lost during the introduction of this mixture into the shock tube, either by wall absorption or decomposition at the wall of the Al shock tube. Therefore, the reaction mixtures contained also water and oxygen.

From experiments with pure water instead of H₂O₂, the water concentration of the mixtures under our conditions was determined, as described in [12], to be 0.2×10^{-2} – 0.5×10^{-2} relative to the carrier gas Ar. This water concentration was believed to influence somewhat the shock wave data (calculated temperatures), but not the mechanism. A more serious problem arises in the H₂O–H₂ experiments from the presence of O₂ (see below). In order to account for this, the percentage of O₂ was determined by heating reaction mixtures in shock waves to temperatures above 2000°K, where O₂ absorption can be detected at 2300 Å. From these experiments, the O₂ concentration was found to be normally about 3 to 5 times that of the decomposing H₂O₂, i.e., always less than 0.5×10^{-2} relative to Ar.

In order to determine the real initial H₂O₂ content of the mixtures in the individual experiments, the H₂O₂ light absorption behind incident and reflected shocks was measured. For this calibration the temperature coefficient of the decadic absorption coefficient $\epsilon_{\text{H}_2\text{O}_2}$ was determined by Troe [11] and used together with room temperature data on $\epsilon_{\text{H}_2\text{O}_2}$. In the present work a value of $\epsilon_{\text{H}_2\text{O}_2} \approx 6.4 \times 10^4 \text{ cm}^2/\text{mole}$ was used at $\lambda = 2300 \text{ Å}$ and T around 1100°K. $\epsilon_{\text{H}_2\text{O}_2} \approx 1.9 \times 10^4 \text{ cm}^2/\text{mole}$ was used at $\lambda = 2800 \text{ Å}$.

During the decomposition of H₂O₂ behind reflected shock waves, the concentrations of H₂O₂ were followed by the light absorption of H₂O₂ at $\lambda \approx 2800 \text{ Å}$. Here, only the continuous absorption of H₂O₂ can be detected. At shorter wavelengths, the HO₂ continuum is superimposed on the H₂O₂ continuum. Behind the incident and directly behind the reflected shock, only H₂O₂ absorbs. Then, the total absorption increases with time owing to the formation of HO₂ and finally decreases owing to the consumption of H₂O₂ and HO₂.

By subtracting the H₂O₂ part of the absorption, studied at 2800 Å, the HO₂ part of the absorption can be isolated. Wavelengths around 2300 Å proved most suitable for this procedure. Therefore, in all experiments light absorption at 2800 Å and 2300 Å was measured simultaneously. Examples of oscillograms and a discussion of the problems of separating both spectra are given by Troe [11].

Under our conditions, absorption of OH could not be detected. H₂O₂- and HO₂-absorption-time profiles during the decomposition of H₂O₂ were obtained

with Ar as carrier gas without additives at $950^\circ \leq T \leq 1450^\circ\text{K}$ and at $[\text{Ar}]$ around $5 \times 10^{-3} \text{mole/cm}^3$. The influence of added H_2 was studied extensively in this work at $[\text{H}_2]/[\text{Ar}] = 2 \times 10^{-2}$, 4×10^{-2} , 7.5×10^{-2} , and 10×10^{-2} . At $[\text{H}_2] \geq 0.1 [\text{Ar}]$, the shock waves showed too large a deviation from ideal; density fluctuations due to nonidealities of the shock waves did not allow following the small absorption signals. The shock wave data were calculated with H_2 enthalpies from the JANAF Tables [13]. In experiments with added H_2 , because of the acceleration of the H_2O_2 decomposition, the accessible temperature range was $870^\circ \leq T \leq 1000^\circ\text{K}$. Further experiments have been performed with added CO at $[\text{CO}]/[\text{Ar}]$ up to 10^{-1} , again at temperatures lower than with pure Ar as carrier gas.

In the following, an absolute calibration of the HO_2 absorption profiles is also used, i.e., a value of the absorption coefficient ϵ_{HO_2} at 2300 \AA and T around 1000°K is adopted for representing the experimental results on the HO_2 absorption profiles. This value was obtained [11] by fitting the time dependence of the HO_2 absorption during the H_2O_2 decomposition under quite different experimental conditions to the simple mechanism discussed below. After determining the unknown rate constants from the mechanism, the absolute HO_2 concentrations were calculated and used for obtaining ϵ_{HO_2} . In the following, a value of $\epsilon_{\text{HO}_2} = 6.6 \times 10^5 \text{cm}^2/\text{mole}$ at 2300 \AA and $T = 1000^\circ\text{K}$ is used. (The uncertainty of this value is believed to be smaller than a factor of 2. The conclusions drawn later on do not depend on this uncertainty, because the ratio mainly of HO_2 yields in experiments with and without added H_2 was evaluated.) The wavelength dependence of ϵ_{HO_2} at $T \approx 1000^\circ\text{K}$ is shown in Figure 1.

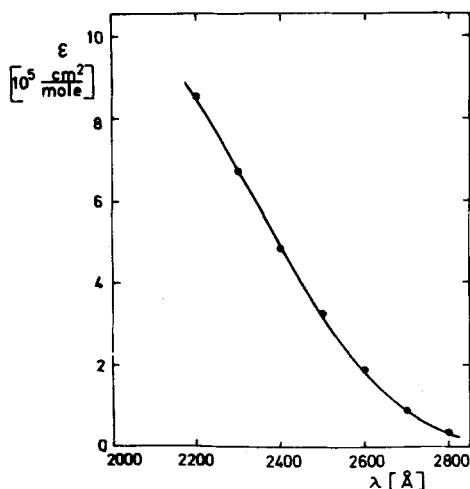


Figure 1. Decadic absorption coefficient of HO_2 at $T \approx 1000^\circ\text{K}$. From Trøe [11].

3. Results

A. Experiments with H_2O_2 -Ar mixtures

Studies on the rate of decay of H_2O_2 in Ar without additives have been described [10,11]. At temperatures between 950° and 1450°K and at $[\text{Ar}] = 10^{-4}\text{mole/cm}^3$, an effective rate constant

$$k \equiv -\frac{1}{[\text{Ar}][\text{H}_2\text{O}_2]} \frac{d[\text{H}_2\text{O}_2]}{dt} = 10^{15.8} \exp(-40,000/RT) \text{ cm}^3/\text{mole sec}$$

was obtained. As subsequent reactions could not be suppressed, this rate constant does not correspond to the unimolecular reaction alone. However, it can be used [11] to obtain the rate constant of the unimolecular reaction, which is given in the discussion (see below).

Studies of the HO_2 absorption profiles show that, after reaching the maximum, the HO_2 absorption decays half as fast as that of H_2O_2 , i. e., $k_{\text{HO}_2} \approx 0.5 k_{\text{H}_2\text{O}_2}$. Investigation of the maximum concentrations of HO_2 occurring during the dissociation of H_2O_2 leads to values which are given in Figure 2 for initial concentrations $[\text{H}_2\text{O}_2]_0/[\text{Ar}] \approx 135 \times 10^{-3}$. (The points given in all figures of this paper represent averages of several experiments.) As shown in Figure 2, $[\text{HO}_2]_{\text{max}}/[\text{H}_2\text{O}_2]_0$ increases with increasing temperature from only a few per cent at 1000°K to values of about 15 per cent at 1300°K . At higher temperatures, it decreases again; however, because of the fast reaction, a sufficiently certain separation of HO_2 and H_2O_2 spectra became too difficult.

At T around 1000°K , the $[\text{HO}_2]$ maximum is obtained at about 10% dissociation of H_2O_2 , at T around 1300°K at about 60% dissociation. This is illustrated in Figure 3. It shows that $[\text{HO}_2]$ reaches its quasi-stationary value in the early period of reaction at $T \approx 1000^\circ\text{K}$, but late at $T \approx 1300^\circ\text{K}$. Fitting the mechanism discussed later to Figures 2 and 3, it was possible [11] to determine the rate constants k_3 , k_4 (as defined in the discussion below), and the absorption coefficient ϵ_{HO_2} . It is shown later that uncertainties in k_3 mainly change ϵ_{HO_2} , and therefore the absolute values $[\text{HO}_2]_{\text{max}}/[\text{H}_2\text{O}_2]_0$, in the following way:

$$\epsilon_{\text{HO}_2} \approx (6.6 \times 10^5 \text{ cm}^2/\text{mole}) \times \sqrt{k_3/10^{12.3} \text{ cm}^3/\text{mole sec}}$$

and

$$[\text{HO}_2]_{\text{max}}/[\text{H}_2\text{O}_2]_0 \approx ([\text{HO}_2]_{\text{max}}/[\text{H}_2\text{O}_2]_0)_{\text{Fig. 1}} \times \sqrt{10^{12.3}/k_3}$$

Therefore, a small change of scale in Figure 2 may influence all points in the same way.

B. Experiments with H_2O_2 - H_2 -Ar mixtures

With added H_2 , the apparent rate constant k of the H_2O_2 decay is increased with increasing $[\text{H}_2]/[\text{Ar}]$. Whether a constant value is approached at $[\text{H}_2]/[\text{Ar}] \approx 0.1$ cannot be decided completely, as this point is the most uncertain due to

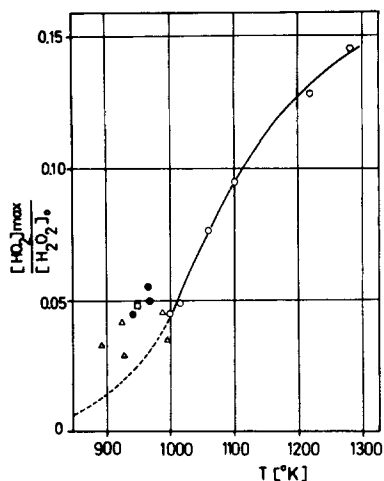


Figure 2. Maximum HO_2 yields during dissociation of H_2O_2 . (\circ) experiments with $[\text{H}_2] = 0$ and $[\text{H}_2\text{O}_2]_0/\text{Ar} \approx 1.3 \times 10^{-3}$; (---) extrapolation $\propto \sqrt{k_1}$, see text, (\square) experiments with $[\text{H}_2]/[\text{Ar}] = 2 \times 10^{-2}$ and $[\text{H}_2\text{O}_2]_0/[\text{Ar}] \approx 0.6 \times 10^{-3}$; (\triangle) $[\text{H}_2]/[\text{Ar}] = 4 \times 10^{-2}$ and $[\text{H}_2\text{O}_2]_0/[\text{Ar}] \approx 0.6 \times 10^{-3}$; (\bullet) $[\text{H}_2]/[\text{Ar}] = 7.5 \times 10^{-2}$ and $[\text{H}_2\text{O}_2]_0/[\text{Ar}] \approx 0.6 \times 10^{-3}$; (\blacktriangle) $[\text{H}_2]/[\text{Ar}] = 10 \times 10^{-2}$ and $[\text{H}_2\text{O}_2]_0/[\text{Ar}] \approx 0.6 \times 10^{-3}$.

the large $[\text{H}_2]/[\text{Ar}]$ ratios applied (see above). In Figure 4 for T around 930°K , $k([\text{H}_2])/k([\text{H}_2] = 0)$ is plotted as a function of $[\text{H}_2]/[\text{H}_2\text{O}_2]_0$. The $(k[\text{H}_2])$ denotes the effective rate constant of H_2O_2 decay at the concentration $[\text{H}_2]$ of added H_2 . Due to the small absorption signals, scatter is relatively large. Therefore, no temperature dependence of the curve could be detected at $870 \leq T \leq 1000^\circ\text{K}$. In the concentration range applied, $0.4 \times 10^{-3} \leq [\text{H}_2\text{O}_2]_0/[\text{Ar}] \leq 1.0 \times 10^{-3}$, a

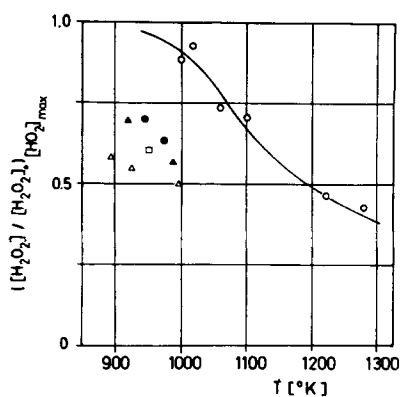


Figure 3. Undissociated H_2O_2 at the HO_2 maximum. Symbols as in Fig. 2.

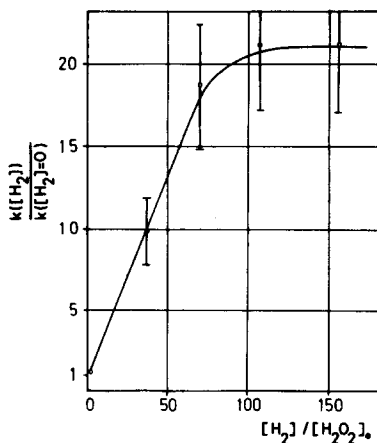


Figure 4. Acceleration of the H_2O_2 dissociation by added H_2 . $T \approx 930^\circ K$, $[H_2O_2]_0/[Ar] \approx 0.6 \times 10^{-3}$.

small additional dependence on $[H_2O_2]_0/[Ar]$ could be noticed, and low concentration points significantly fell below the curve. This effect, however, was smaller than given by the error limits in Figure 4. At small $[H_2]/[H_2O_2]_0$,

$$k([H_2])/k([H_2] = 0) \approx 1 + (0.25 \pm 0.05) \times [H_2]/[H_2O_2]_0$$

At large $[H_2]/[H_2O_2]_0$, the limiting value must be larger or equal to 21 ± 6 .

The rate constant of decay of HO_2 , k_{HO_2} , again is coupled to the corresponding value of decay of H_2O_2 , $k_{H_2O_2}$. At $[H_2]/[Ar] \approx 0.04$, a mean ratio of $k_{HO_2}/k_{H_2O_2} = 1.0 \pm 0.5$ is found. Low concentrations significantly gave low values between 0.5 and 1.0.

Maximum HO_2 yields during the dissociation are shown in Figure 2. For $[H_2]/[Ar] \geq 0.02$ with $[H_2O_2]_0/[Ar] \approx 0.06 \times 10^{-2}$ at $870 \leq T \leq 1000^\circ K$, the ratios $[HO_2]_{max}/[H_2O_2]_0$ are found to be significantly higher than in experiments with $[H_2] = 0$ where $[H_2O_2]_0/[Ar] \approx 1.35 \times 10^{-3}$. This becomes particularly pronounced if the extrapolation given for experiments with $[H_2] = 0$ is considered. (Extrapolation according to $([HO_2]_{max}/[H_2O_2]_0) \propto \sqrt{k_1}$, see below. This effect can be understood if it is taken into account that the experiments with $[H_2] = 0$ have been performed with $[H_2O_2]_0/[Ar]$ ratios about a factor of 2 higher than in the experiments with H_2 addition. Due to experimental difficulties with well decomposition of H_2O_2 , in experiments with $[H_2]/[Ar] \geq 0.02$, initial concentrations of H_2O_2 as high as in previous experiments with $[H_2] = 0$ could no longer be produced.

In Figure 3, the fraction of undissociated H_2O_2 at the maximum concentration of HO_2 , $([H_2O_2]/[H_2O_2]_0)_{[HO_2]_{max}}$, is compared with the corresponding data for $[H_2] = 0$. Whereas this fraction depends strongly on T for $[H_2] = 0$, being \approx

90% at $T \approx 1000^\circ\text{K}$, it is found about $60\% \pm 10\%$ for $[\text{H}_2]/[\text{H}_2\text{O}_2]_0 \approx 40$ in the temperature range $900^\circ\text{--}1000^\circ\text{K}$.

C. *Experiments with H₂O₂–CO–Ar mixtures*

CO was added to H₂O₂–Ar mixtures under about the same conditions, T , and $[\text{CO}]/[\text{Ar}]$ as H₂. Qualitatively, CO shows almost the same effect as H₂ on the rate of decay of H₂O₂ and on the maximum HO₂ yields. Quantitatively, in the temperature range applied, CO is about five times less efficient than H₂; i.e., CO experiments nearly in all details look like H₂ experiments except for $[\text{H}_2]/[\text{Ar}]$ ratios which are a factor of 5 smaller than the $[\text{CO}]/[\text{Ar}]$ ratios.

4. Discussion

A. *Experiments with H₂O₂–Ar–mixtures*

Under the conditions applied, the decomposition of H₂O₂ is probably determined by the following four reactions [10,11,14–18]:

- (1) $\text{H}_2\text{O}_2 + \text{Ar} \rightarrow 2\text{OH} + \text{Ar}$
- (2) $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$
- (3) $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
- (4) $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$

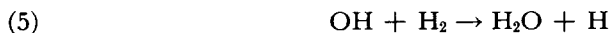
It has been shown [10,11] that quasi-stationary concentrations of OH and HO₂ are approached very early at $T \approx 1000^\circ\text{K}$. However, at $T \geq 1400^\circ\text{K}$ this assumption becomes invalid. Therefore, the effective rate constant of the decay of H₂O₂, $k_{\text{H}_2\text{O}_2}$, under our conditions changes from k_1 at $T \geq 1400^\circ\text{K}$ to $2k_1$ at $T \approx 1000^\circ\text{K}$. From the value of the effective k given above, one therefore derives for the unimolecular reaction

$$k_1 = 10^{16.2} \exp(-43000/RT) \text{ cm}^3/\text{mole sec}$$

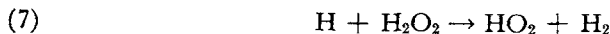
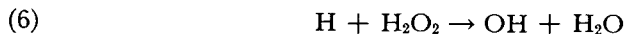
(A misprint in the preexponential factor in the summary and on page 352 ref. [10] should be corrected.) From the observed HO₂ profiles [11], the rate constants of reactions (3) and (4) were derived. Also, a comparison of literature data on k_2 , k_3 , and k_4 (based on [8,18–21]) was given.

B. *Experiments with H₂O₂–H₂–Ar mixtures*

By addition of excess H₂, the primary dissociation product OH is converted to H atoms via



Thus, reactions of H atoms with H_2O_2 , possibly via the two channels discussed by Baldwin and coworkers [18], are as follows:



And, because of our high HO_2 yields also with HO_2 , the following reactions may be initiated:



Possible reactions of H atoms with the unavoidable impurity O_2 are discussed later. The technique of introducing H atoms into the H_2O_2 decomposition has been used earlier [18] in flow system studies at 440°C . The accelerating effect of H_2 was also observed, whereas HO_2 could not be followed. Reactions (8) and (9) could be neglected at the low HO_2 yields of these experiments at low T . In order to investigate the contributions of reactions (6) to (9), at first the reaction stage at quasi-stationary values of $[\text{H}]$, $[\text{OH}]$, and $[\text{HO}_2]$ is considered. One obtains the equations

$$(10) \quad \frac{k}{k_0} = \frac{1 + \frac{k_4}{k_2} X + \frac{k_5}{k_2} Z \left\{ \frac{k_6 + k_7 + k_8 X}{k_6 + k_7 + (k_8 + k_9) X} \right\}}{1 + \frac{k_4}{k_2} X + \frac{k_5}{k_2} Z \left\{ \frac{k_7 + (k_8 - k_9) X}{k_6 + k_7 + (k_8 + k_9) X} \right\}}$$

and

$$(11) \quad \frac{k_3}{k_1} YX = \frac{1 - \frac{k_4}{k_2} X + \frac{k_5}{k_2} Z \left\{ \frac{k_7 - (k_8 + k_9) X}{k_6 + k_7 + (k_8 + k_9) X} \right\}}{1 + \frac{k_4}{k_2} X + \frac{k_5}{k_2} Z \left\{ \frac{k_7 + (k_8 - k_9) X}{k_6 + k_7 + (k_8 + k_9) X} \right\}}$$

where

$$(12) \quad \frac{k}{k_0} \equiv - \frac{1}{2k_1[\text{Ar}][\text{H}_2\text{O}_2]} \frac{d[\text{H}_2\text{O}_2]}{dt}$$

$$(13) \quad \frac{[\text{HO}_2]}{[\text{H}_2\text{O}_2]} = X, \quad \frac{[\text{H}_2\text{O}_2]}{[\text{Ar}]} = Y, \quad \text{and} \quad \frac{[\text{H}_2]}{[\text{H}_2\text{O}_2]} = Z$$

With $[\text{H}_2] = 0$, one obtains $k = k_0$. Further, at low temperatures with small X , and therefore $k_4X/k_2 \ll 1$, it follows that

$$(14) \quad X \equiv \frac{[\text{HO}_2]}{[\text{H}_2\text{O}_2]} \approx \sqrt{\frac{k_1[\text{Ar}]}{k_3[\text{H}_2\text{O}_2]}}$$

Equation (14) leads to the low-temperature extrapolation of $[\text{HO}_2]_{\text{max}}/[\text{H}_2\text{O}_2]_0$ chosen in Figure 2 and to the error estimates for ϵ_{HO_2} mentioned above.

With increasing $[\text{H}_2]$, at first an increase of k/k_0 is observed. In this region the denominators of the right-hand side in eqs. (10) and (11) can be put approximately at 1, if the simplification $k_4X/k_2 \ll 1$ is used at $T \leq 1000^\circ\text{K}$. Then, one obtains

$$(15) \quad \frac{k}{k_0} \approx 1 + \frac{k_5}{k_2} \left\{ \frac{1 + \frac{k_8}{k_6 + k_7} X}{1 + \frac{k_8 + k_9}{k_6 + k_7} X} \right\} Z$$

The experimentally observed accelerations k/k_0 as a function of $[\text{H}_2]/[\text{H}_2\text{O}_2]_0$, which are shown in Figure 4, are in good agreement with this equation. In order to see this, it has to be taken into account that the experiments were evaluated during 50–90% dissociation of H_2O_2 . Thus, in the experiments, $Z \equiv [\text{H}_2]/[\text{H}_2\text{O}_2] \approx (1-2)[\text{H}_2]/[\text{H}_2\text{O}_2]_0$, and from Figure 4, $(k/k_0)_{\text{exp}} \approx 1 + (0.12-0.25)Z$. From the later discussion of reactions (6)–(9) it follows that the expression within the braces in eq. (15) is not far from 1. Therefore, the experimental factor Z between 0.12 and 0.25 agrees fairly well with the earlier determination of $k_8/k_2 \approx 0.25$ at 930°K (e.g., from $k_8/k_2 \approx 0.21$ at 773°K [18] and $E_8 - E_2 \approx 3$ kcal/mole [7]).

At a very large excess of H_2 , at $Z \gg 1$, according to eq. (10) k/k_0 becomes independent of Z :

$$(16) \quad \frac{k}{k_0} \approx \frac{k_6 + k_7 + k_8 X}{k_7 + (k_8 - k_9) X}$$

HO_2 yields for constant Y at $Z \gg 1$ should fall below those given for the case $[\text{H}_2] = 0$, according to

$$(17) \quad \frac{k_3}{k_1} Y X^2 \approx \frac{1 - \frac{k_9 + k_8}{k_7} X}{1 - \frac{k_9 - k_8}{k_7} X}$$

In order to estimate with these formulas the relations between k_6 , k_7 , k_8 , and k_9 , the HO_2 maximum yields that may be attributed to the quasi-stationary period of reaction were investigated, Figure 5 shows the corresponding values of $[\text{HO}_2]/[\text{H}_2\text{O}_2] = X$ at different temperatures and for different $[\text{H}_2\text{O}_2]/[\text{Ar}] = Y$. Experiments without H_2 and with comparatively high Y values are given by curve 1. The full curves 2 and 3 have been calculated by the use of eq. (14) from curve 1 for $[\text{H}_2] = 0$ and Y values as low as those used in the H_2 -catalyzed experiments. The measured HO_2 yields at $Z \gg 1$, within the uncertainty, agree with curves 2 and 3. (The systematic deviations at the lowest concentrations probably are due to experimental errors at the smallest absorption signals.) The observation that maximum HO_2 yields in experiments with large excess of added H_2 are in agreement with, or at least not significantly lower than in, experiments without added

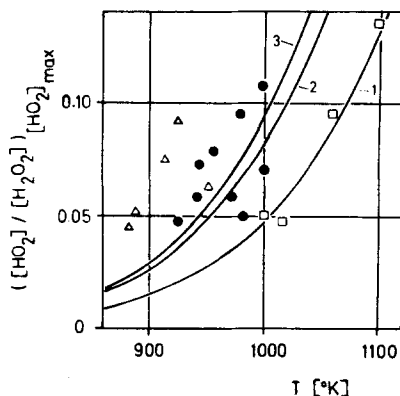


Figure 5. Comparison of $[\text{HO}_2]/[\text{H}_2\text{O}_2]$ at $[\text{HO}_2]_{\text{max}}$ for experiments with $[\text{H}_2]/[\text{H}_2\text{O}_2]_0 \geq 40$ and $[\text{H}_2] = 0$: (\square) (1) $[\text{H}_2] = 0$ and $[\text{H}_2\text{O}_2] \approx 1.2 \times 10^{-3}$ at $[\text{HO}_2]_{\text{max}}$; (2) $[\text{H}_2] = 0$ and $[\text{H}_2\text{O}_2] \approx 0.42 \times 10^{-3}$ at $[\text{HO}_2]_{\text{max}}$ (calculated from curve 1); (3) $[\text{H}_2] = 0$ and $[\text{H}_2\text{O}_2] \approx 0.34 \times 10^{-3}$ at $[\text{HO}_2]_{\text{max}}$ (calculated from curve 1); (\bullet) $[\text{H}_2]/[\text{H}_2\text{O}_2]_0 \geq 40$ and $[\text{H}_2\text{O}_2] \approx 0.42 \times 10^{-3}$ at $[\text{HO}_2]_{\text{max}}$; (Δ) $[\text{H}_2]/[\text{H}_2\text{O}_2]_0 \geq 40$ and $[\text{H}_2\text{O}_2] \approx 0.34 \times 10^{-3}$ at $[\text{HO}_2]_{\text{max}}$.

H_2 can be used for an estimate that relates the magnitude of k_7 with that of k_8 and k_9 . This observation, according to Baldwin and Brattan [17], requires that

$$(18) \quad k_7/(k_8 + k_9) \gtrsim \left(\frac{[\text{HO}_2]}{[\text{H}_2\text{O}_2]} \right)_{[\text{HO}_2]_{\text{max}}} \approx 0.08$$

at temperatures 950°–1000°K. As $k_8 + k_9 \geq 10^{13}$ cm³/mole sec (see below), k_7 also cannot be much larger than given by $0.08(k_8 + k_9)$.

Whereas the observed HO_2 yields lead to the estimate eq. (18) relating k_7 with $k_8 + k_9$, the observed limiting acceleration of the H_2O_2 dissociation at a large excess of H_2 gives another relation between the rate constants of reactions (6)–(9). At temperatures as low as used earlier in the flow system experiments [18], the terms with X in eq. (16) can be neglected, so that, from the limiting acceleration of the reaction at large concentrations of H_2 , a value of k_6/k_7 was immediately postulated. Under our conditions with large HO_2 yields, the evaluation is more complicated. Here, with the experimental values of $X \approx 0.08$ and $k/k_0 \approx 21$, one obtains from eq. (16) a relation between k_6 , k_7 , k_8 , and k_9 . If for k_6/k_7 a ratio of 5–10 is taken (as determined in the flow system studies of the H_2 -catalyzed dissociation of H_2O_2 : $k_6/k_7 = 6.2$ at 713°K [18], 8.1 at 773°K [18], or 4 at 798°K [23]) and for k_8/k_9 a ratio of 0.2 is accepted (as determined from flame studies at 1030°K [25]), then this relation leads immediately to

$$(19) \quad k_7 \approx (0.5\text{--}0.7)k_8$$

This is consistent with the estimate eq. (18) obtained from the HO_2 yields, which, with $k_8/k_9 = 0.2$, yields $k_7 \gtrsim 0.5k_8$. It must, however, be emphasized that from our experiments only information on k_7 and not on k_6 may be derived. If reaction

(6) would be completely neglected, the acceleration of the H₂O₂ decomposition by addition of H₂ under our conditions also might be explained by reactions (7), (8), and (9) alone, and one would obtain from eq. (16), instead of eq. (19) the estimate $k_7 \approx 0.4k_8$.

According to the analysis given above, our observations on the accelerating effect of H₂ in the H₂O₂ pyrolysis and on the magnitude of the HO₂ yields do not lead to any argument against our earlier identification of the HO₂ spectrum.

Up to now, only the reaction period with quasi-stationary [HO₂] was used. In order to get also a complete analysis of the initial period of reaction, before [HO₂] becomes quasi-stationary, the rate equations were integrated numerically. The rate constants of reactions (1)–(5) given above and in ref. [11] were used together with the discussed estimates $k_6/k_7 \approx 10$, $k_8/k_9 \approx 0.2$, and $k_7/k_8 \approx 0.5$. Within experimental error, good agreement was found between measured and calculated concentration profiles of HO₂ and H₂O₂ as long as k_7 was chosen larger than 10¹¹ cm³/mole sec at T around 900°K. As long as this condition is fulfilled, our experiments lead to relations (18) and (19) between k_7 and $k_8 + k_9$.

For comparison, some literature data on rate constants of reactions (6)–(9) are given below:

$$k_6 \approx 10^{11.5} \text{ at } 713^\circ\text{K} [18,26,27]; k_6 \approx 10^{12.0} \text{ at } 773^\circ\text{K} [18,20,26]$$

$$k_7 \approx (7 \pm 4) \times 10^{12} \exp(-4200/RT) \text{ at } 294^\circ\text{--}464^\circ\text{K} [9]$$

$$k_9 \approx 6 \times 10^{12} \text{ at } 300^\circ\text{K} [7], k_9 \approx 6.6 \times 10^{13} \text{ at } 773^\circ\text{K} [6,20]$$

$$k_8 + k_9 \approx 2 \times 10^{13} \text{ at } 300^\circ\text{K} [28]$$

All values are in cm³/mole sec. Reaction rate constants are summarized by Baulch and coworkers [26]. Our results on the relation between k_7 and k_8 are in reasonable agreement with these data. Low temperature values of k_6/k_7 have been found significantly lower, 0.1–0.2 at 420°K [9], than the high temperature values mentioned above. This would lead to somewhat improbable preexponential factors of k_6 and $k_7 > k_6$ at low T and $k_6 > k_7$ at high T . No information on this problem is given in our experiments. For k_8/k_9 , a low temperature value of 0.33 at 300°K has been reported [24], not too different from the high temperature value used above.

One possible complication with our experiments has to be discussed briefly. During the reaction, O₂ is produced. Also, O₂ as impurity in the reaction mixtures could not be avoided. This oxygen in the experiments with excess H₂ might react with the H atoms being formed via the reaction



Then, oxygen atoms would react with H₂O₂ probably [9,28] via



and with HO₂ via



Taking into account these reactions adds a term $-k_{20}[\text{O}_2]/[\text{H}_2\text{O}_2]$ in the denominator of eq. (16), which at $T \lesssim 1000^\circ\text{K}$ in our experiments always was smaller than $5 \times 10^{11} \text{ cm}^3/\text{mole sec}$ [26]. Therefore, this term probably always could be neglected against k_9X . At most, some scatter might be due to this effect. Finally, it should be mentioned that the possibility of bringing oxygen atoms into the reaction via the primary dissociation of H₂O₂ also has not yet been completely ruled out.

C. Experiments with H₂O₂-CO-Ar mixtures

By addition of CO instead of H₂, the H atom-producing reaction (5) is replaced by reaction (5a):



No significance for other reactions of CO or CO₂ in the mechanism was found. However, it cannot be excluded that other reactions might be of importance in this system (see, for example, Schofield [6]). Experimentally we observed that CO shows the same effects on the H₂O₂ decomposition as H₂, but with an effectiveness about a factor of 5 times smaller. This indicates that our experiments correspond to the region with intermediate Z values, as discussed above. The smaller effectiveness of CO by a factor of 5, which in this region directly corresponds to the ratio k_5/k_{5a} , is in very good agreement with earlier conclusions on this ratio as summarized by Schofield [6].

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