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THE PHOTOLYSIS OF HYDROGEN PEROXIDE IN THE PRESENCE OF CARBON MONOXIDE

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Summary

The photolysis of H_2O_2 at 2537 Å and 298 K has been studied in the presence of CO. The photodecomposition of H_2O_2 leads to a chain reaction initiated by the reaction:

$$OH + CO \rightarrow CO_2 + H \tag{4}$$

propagation proceeding by:

$$H + H_2O_2 \rightarrow OH + H_2O \tag{5a}$$

and terminated by:

$$H + H_2O_2 \rightarrow H_2 + HO_2 \tag{5b}$$

The chain reaction can be inhibited by addition of oxygen, which scavenges the H atoms. At 298 K, $k_{5a}/k_{5b} = 1.3$ and $k_2/k_4 = 4.1$ where:
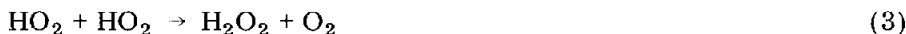
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \tag{2}$$

Introduction

Several important reactions cited in the chemistry of the upper atmosphere and in photochemical smog production involve the hydroxyl radical [1, 2]. This radical is also known to play an integral role in combustion processes [3]. In view of the recent interest in obtaining a better understanding of these systems, it becomes important to understand the chemistry of species necessary to these processes. In an attempt to obtain mechanistic information as well as rate data for reactions involving hydroxyl radicals, we decided to study the steady-state photolysis of hydrogen peroxide in the presence of added gases.

The gas-phase photolysis of hydrogen peroxide at 2537 Å has been studied in some detail [4 - 6]. Each energetically feasible primary photophysical process has been considered and the available evidence supports the mechanism.

$$H_2O_2 + h\nu \rightarrow 2OH\,(^2\Pi) \tag{1}$$

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

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{3}$$

The OH radicals are produced in the ground vibrational state with equal amounts of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. The only products are water and oxygen and the observed quantum yield is 1.7 ± 0.4. Thus this system promises a clean source of OH radicals in the absence of other reactive intermediates without complications from excited electronic or vibrational states.

In this paper we report the photolysis of H_2O_2 in the presence of carbon monoxide. Since we hope to use the reaction:

$$OH + CO \rightarrow CO_2 + H \tag{4}$$

as an actinometer for OH production in future studies, we initiated a study of this system prior to the addition of other gases whose interaction with OH radicals are less well understood.

Such a study is judged particularly critical in the light of the discrepancies existing in the literature [7, 8] concerning the reaction between hydrogen atoms and hydrogen peroxide near room temperature. Two possible channels exist for this reaction:

$$H + H_2O_2 \rightarrow OH + H_2O \tag{5a}$$

$$\rightarrow H_2 + HO_2 \tag{5b}$$

It has been fairly well established that reaction (5a) dominates, by a factor of 4 to 8, at elevated temperatures [9 - 11] but the situation is less clear at room temperature. The work of Albers $et\ al.$ [7] at 421 K gives $k_{5a}/k_{5b} = 0.23$, predicting an even lower value at 298 K. This value is to be contrasted with that obtained from the work of Gorse and Volman [8] who determined $k_{5a}/k_{5b} = 3 \pm 1$ at 298 K.

The importance of this ratio becomes evident upon recognition of reaction (5a) as a propagating step in a chain mechanism. Such a chain could manifest itself in any H_2O_2 decomposition in which hydrogen atoms are also found. In our particular instance we intend, in further studies, to use the conversion of CO to CO_2 as an indication of the rate of photochemical production of OH radicals. Thus we must assure ourselves either that no such chain process exists or that we can conveniently inhibit it should it exist. We have also used the competition between CO and H_2O_2 to determine a room temperature rate constant for reaction (2).

Experimental

Experiments were performed in a 10 cm cylindrical quartz cell coupled to a modified EAI Quadrupole Model 160 mass spectrometer. Reactants and products were continuously sampled via a series of two, differentially pumped, glass leaks. The leak rate was regulated to prevent any appreciable pressure drop in the reactor during photolysis. This apparatus has been

described in detail elsewhere [12]. A Phillips mercury lamp type 93110E was used for the photolysis. A conventional mercury-free, high-vacuum line equipped with Teflon stopcocks fitted with Viton "O" rings was used. The hydrogen peroxide pressure was measured with a silicone oil manometer. Wallace and Tiernan 0 - 50 and 0 - 800 Torr pressure gauges were available for measurement of the other gases.

The $m/e = 44$ peak due to CO_2 ionization was followed as a function of time. A few Torr of argon ($m/e = 40$) was added to the reaction mixture and the ratio of the 44 to the 40 peak was plotted against time. From the slope of this plot and by knowing the pressure of argon, as well as the relative mass spectral sensitivities of CO_2 and Ar, the growth rate of CO_2 was obtained. The relative sensitivities of Ar and CO_2 were obtained using standard samples. Argon was chosen because of the proximity of its mass spectral peak to the parent peak of CO_2. This latter feature allowed us to follow the reaction by sweeping a small segment of the mass spectrum, permitting us to sample the 44/40 ratio every 20 s. This ability is important because of the curvature found in some of the CO_2 growth plots, making it necessary to use initial slopes, obtained in the first 100 s of photolysis, for our calculations.

A 90% hydrogen peroxide/water solution was obtained through the courtesy of E. 1. DuPont de Nemours & Co. The sample was carefully out-gassed prior to use and was stored in a Pyrex flask at 77 K. The N_2, O_2, Ar and CO were Matheson research purity ($\geqslant$ 99.99%). Each was passed through two, glass-wool packed, "U" traps maintained at 77 K and stored in 2 l Pyrex flasks. Mass spectrometric analysis showed no significant peaks other than the expected ones.

Early in the study it was discovered that less CO_2 was produced in the first run of each day than in an identical run immediately following. This result was attributed to heterogeneous decomposition of H_2O_2 on the walls of the vacuum line and reactor [13]. Thus the walls exposed to the hydrogen peroxide had to be conditioned by exposure to H_2O_2 before any experiments were performed. After conditioning, the CO_2 yields were very reproducible, even if the system was evacuated for 1 - 2 h between runs. If, however, the system was allowed to pump overnight the walls had to be deactivated again before any experiments were done.

The procedure used was to place the H_2O_2 storage flask in a bath at 25 °C and allow approximately 1 Torr of the vapor to fill the reactor, line and manometer. After a few minutes this peroxide sample was pumped away. A second H_2O_2/H_2O sample, at the desired pressure, was then measured into the reactor. The peroxide/water sample was frozen at 77 K into a small "U" trap incorporated into the reactor. This sample was then degassed in the trap and the argon was measured in on top of it. The much higher pressure mixture of N_2, O_2, CO was made up in the vacuum line and then expanded into the reactor and the final pressure was measured. The hydrogen peroxide was then allowed to warm up and mix with the other components. After a few minutes the stopcock to the mass spectrometer was opened and the sampling process begun. After all the flows had stabilized

(2 - 3 min) the mass scan was begun and a check was made to insure that no dark reaction was occurring. After following the $m/e = 44$ (background) to $m/e = 40$ (Ar) ratio for a few hundred seconds to insure that it was constant, the lamp cover was removed and photolysis begun. No significant amount of dark reaction was observed in any of these experiments. In several cases the lamp was turned off after several hundred seconds and the 44/40 ratio quickly became constant, indicating no extraneous sources of CO_2 other than photochemical.

The pressures of H_2O_2 tabulated in this study were calculated from the measured total H_2O/H_2O_2 pressure using the vapor phase concentration of H_2O_2. The concentration was determined by measuring the vapor pressure of the mixture at 25 °C. The liquid and vapor concentrations were then determined using standard tables [14]. Basically two separate concentrations were used during the course of this study. The early experiments were performed with the mixture as obtained from Du Pont, which was found to be 88% peroxide solution. Later this solution was vaporized at room temperature until about half of the liquid remained. The solution was then found to contain 98% peroxide. Thus during the study the pressure of H_2O_2 in the reactor varied from 0.84 to 1.45 Torr. The bulk of the variation occurred between the experiments done before and after the concentration process.

In order to place the data on a common basis, compensation must be made for variation in the absorbed light intensity. Assuming Beer's law to be operative we defined a working quantum yield, $\Phi\{CO_2\}$. We converted our individual CO_2 production rates, $R\{CO_2\}$, at any $[H_2O_2]$ to quantum yields using the equation:

$$\Phi\{CO_2\} = \frac{2R\{CO_2\}/[H_2O_2]}{R'\{CO_2\}/[H_2O_2]'}$$

The primed values indicate experiments in which $[CO]/[H_2O_2] \geqslant 20$ to which oxygen had been added. $R'\{CO_2\}/[H_2O_2]'$ is a reproducible parameter varying by less than 25% during the study.

Results

$H_2O_2 + CO$

Initially, a few experiments were performed using a Phillips Zn lamp, which has an intense line at 2139 Å, as a light source. The intensity of this lamp was much lower than the Hg source used for the bulk of the experiments, and the rate of production of CO_2 was lower even though the extinction coefficient of H_2O_2 is 3 - 4 times higher at 2139 Å than at 2537 Å [15]. The resulting CO_2 growth plots (Fig. 1, curve a) were reproducible, showed no induction period, and were linear throughout the photolysis.

After a change to the Hg lamp, the initial rate of CO_2 production was about ten times higher for the same pressure of H_2O_2. The growth plots still
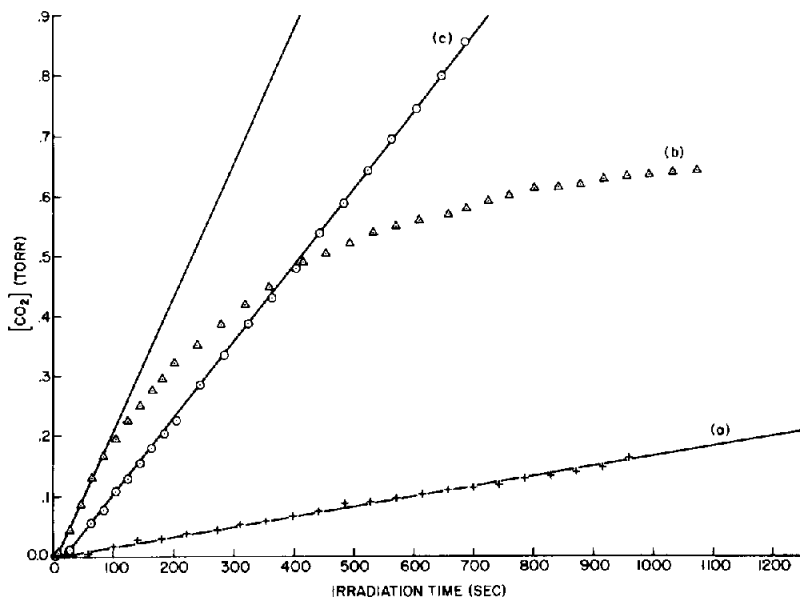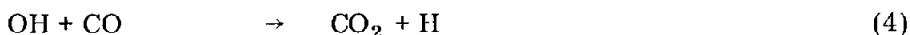
Fig. 1. Growth curves for production of CO in the photolysis of H_2O_2/CO mixtures. (a): +, $I_a \simeq 0.48 \times 10^{-4}$ Torr/s, no oxygen added; (b): $\triangle$, $I_a \simeq 5.4 \times 10^{-4}$ Torr/s, no oxygen added; (c): $\bigcirc$, $I_a \simeq 6.4 \times 10^{-4}$ Torr/s, oxygen added.

showed no induction period, but now there was a very pronounced curvature with the rate of CO_2 formation approaching zero after about 1000 s of photolysis (Fig. 1, curve b). Similar curvature has been reported in the thermal decomposition of hydrogen peroxide in the presence of H_2 [9] and CO [16], and in the photolysis of H_2O_2 in the presence of CO [8]. Such curvature can be accounted for by a chain mechanism:

$$H_2O_2 + (h\nu \text{ or } \Delta) \quad \rightarrow \quad 2OH \tag{1}$$

$$OH + CO \quad \rightarrow \quad CO_2 + H \tag{4}$$

or

$$OH + H_2 \quad \rightarrow \quad H_2O + H \tag{6}$$

$$H + H_2O_2 \quad \rightarrow \quad H_2O + OH \tag{5a}$$

with chain termination occurring *via* the reaction:

$$H + H_2O_2 \quad \rightarrow \quad H_2 + OH \tag{5b}$$

The results of a series of experiments undertaken to investigate the dependence of the quantum yield of CO_2 on the $[CO]/[H_2O_2]$ ratio are shown in Fig. 2. The quantum yields were calculated using initial rates, determined from the five CO_2 measurements taken in the first 100 s of photolysis. Data taken during this period were found to describe straight lines with reproducible slopes. The pressure of H_2O_2 in these experiments was 0.93 ± 0.02 Torr. Carbon monoxide was varied from 1.35 to 45.55 Torr with sufficient N_2 added to bring the total pressure to $\sim$ 49 Torr (Table 1) in each experiment.
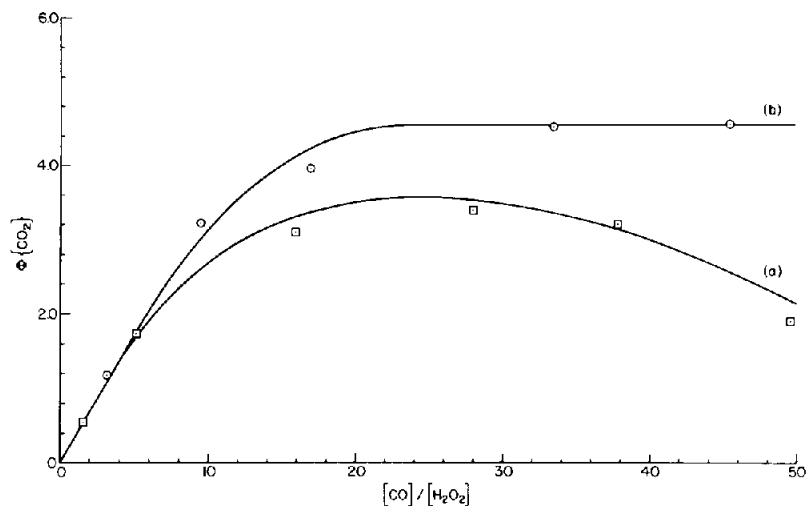
Fig. 2. Initial quantum yield of CO_2 formation as a function of the $[CO]/[H_2O_2]$ ratio for cylinder ($\square$) and purified ($\bigcirc$) CO.

TABLE 1

Photolysis of H_2O_2 at 2537 Å and 298 K in the presence of carbon monoxide[a]

[CO] (Torr)	[N$_2$] (Torr)	$\dfrac{[CO]}{[H_2O_2]}$	$\Phi\{CO_2\}$
1.35[b]	43.10	1.44	0.54
2.91[c]	42.39	3.07	1.18
4.87[b]	39.06	5.20	1.74
8.76[c]	36.26	9.42	3.22
14.55[b]	30.53	15.97	3.10
15.77[c]	28.74	16.96	3.96
26.68[b]	17.99	28.14	3.40
31.31[c]	9.94	33.45	4.54[d]
35.77[b]	8.36	37.97	3.22
42.27[c]	1.98	45.45	4.58
45.55[b]	—	49.62	1.90

[a] $[H_2O_2]$ = 0.93 ± 0.02 Torr, $[H_2O]$ = 0.62 ± 0.02 Torr, $[Ar]$ = 3.01 ± 0.43 Torr, total pressure = 49 ± 2 Torr.
[b] Carbon monoxide purified by distillation at 77 K only.
[c] Carbon monoxide distilled and passed through Oxy-Trap.
[d] $[Ar]$ = 4.07 Torr.

In our original attempt to study the effect of changing the $[CO]/[H_2O_2]$ ratio on CO_2 production, we used CO, N_2 and Ar purified in the manner described above. For these studies, Fig. 2 (curve a) describes the $[CO]/[H_2O_2]$ dependence. The fall-off in the quantum yields at high values of this ratio is similar to that found by Baldwin *et al.* [9] in the pyrolysis of H_2O_2 in the

presence of H_2. This lowering of the rate at high CO pressures was found to be due to the presence of an oxygen impurity in the CO. The oxygen serves as a scavenger for hydrogen atoms, removing them through the fast reaction:

$$H + O_2 + M \rightarrow HO_2 + M \tag{7}$$

Using gas chromatographic analysis, we determined that O_2 was present as a 0.045% impurity in our CO. To remove this impurity all the gases (except the H_2O/H_2O_2 mixture) were repurified, and in addition to the original procedure, each was passed twice through an Alltech Associates indicating Oxy-Trap. Analysis now showed the O_2 to be < 0.01% of the CO. The results obtained with the gases purified in this manner are shown in Fig. 2 (curve b). The CO_2 quantum yield increases rapidly until $[CO]/[H_2O_2]$ > 20, after which it was independent of $[CO]/[H_2O_2]$.

$H_2O_2 + CO + O_2$
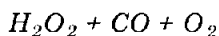
In order to establish the relative importance of the chain process on production of CO_2, oxygen was added to the photolysis mixture. All experiments included sufficient CO (Table 2) to consume all hydroxyl radicals by reaction (4). As shown in Fig. 3, small amounts of O_2 drastically inhibit CO_2 production. The quantum yield is reduced until sufficient O_2 has been added to remove all the hydrogen atoms. Once this has occurred, the rate is independent of added O_2.

These data show the CO_2 to be produced in a chain mechanism with a chain length $\simeq 2.3$. Once sufficient O_2 has been added to arrest the chain, the CO_2 growth plots become linear in the time domain studied (Fig. 1, curve c) since H_2O_2 is no longer being consumed in the chain.

A study was made in which the $[CO]/[H_2O_2]$ ratio was varied in the presence of sufficient oxygen to scavenge all hydrogen atoms. The H_2O_2 pressure was constant at ~ 1.4 Torr and N_2 was added to maintain the total pressure at ~ 50 Torr (Table 2). The result shown in Fig. 4 is a competition for the available OH radicals between CO and H_2O_2. Near the origin, hydrogen peroxide is consuming most of the OH radicals, and there is only a small amount of CO_2 formation. At the other extreme, virtually all the OH radicals are consumed by reaction (4) and CO_2 production becomes independent of the $[CO]/[H_2O_2]$ ratio. This plateau value for the rate of CO_2 production is assumed to be equal to $2I_a$ (twice the absorbed light intensity), and in this manner I_a was obtained.

Discussion

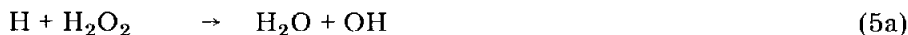The observations discussed above are interpreted in terms of the following mechanism

$$H_2O_2 + h\nu \quad \rightarrow \quad 2OH \tag{1}$$

$$OH + H_2O_2 \quad \rightarrow \quad H_2O + HO_2 \tag{2}$$

$$HO_2 + HO_2 \quad \rightarrow \quad H_2O_2 + O_2 \tag{3}$$

TABLE 2

Photolysis of H_2O_2 at 2537 Å and 298 K in the presence of CO and O_2[a]

[CO] (Torr)	[O_2] (Torr)	[N_2] (Torr)	$\Sigma[X]$ (Torr[b])	$\dfrac{[CO]}{[H_2O_2]}$	$\dfrac{[O_2]}{[H_2O_2]}$	$\Phi\{CO_2\}$
$[H_2O_2] = 0.88 \pm 0.04$ Torr[c]						
19.73	—	—	21.13	23.49	0.0106[e]	3.46
35.15	—	—	36.55	41.84	0.0188[e]	3.52
35.84	0.027	—	40.41	39.38	0.0297	2.54
34.43	0.78	—	40.25	37.84	0.857	2.12
34.71	2.68	—	42.31	38.57	2.98	1.94
34.16	5.25	—	44.56	37.96	5.83	1.94
$[H_2O_2] = 1.43 \pm 0.02$ Torr[d]						
1.29	0.86	43.83	50.23	0.89	0.597	0.34
1.89	2.30	43.09	52.70	1.31	1.61	0.54
4.67	0.59	40.36	49.91	3.22	0.407	0.88
7.03	1.80	36.98	50.13	4.87	1.25	1.28
9.21	1.62	35.87	51.26	6.38	1.13	1.56
13.81	0.37	33.22	52.23	9.57	0.255	1.86
23.78	0.63	20.57	49.49	16.80	0.444	2.04
35.15	0.94	11.07	51.66	24.39	0.653	2.08
43.98	1.17	—	49.83	32.15	0.813	2.02
51.61	1.38	—	57.27	35.78	0.958	1.92
51.02	1.36	—	56.90	36.06	0.958	1.96

[a] [Ar] = 3.05 ± 0.3 Torr. [b] $\Sigma[X]$ = total pressure. [c] [H_2O] = 0.58 ± 0.02 Torr.
[d] [H_2O] = 0.14 ± 0.01 Torr. [e] Based on 0.045% O_2 impurity in CO, no Ar present.

$$\text{OH} + \text{CO} \quad \rightarrow \quad \text{CO}_2 + \text{H} \tag{4}$$

$$\text{H} + \text{H}_2\text{O}_2 \quad \rightarrow \quad \text{H}_2\text{O} + \text{OH} \tag{5a}$$

$$\rightarrow \quad \text{H}_2 + \text{HO}_2 \tag{5b}$$

$$\text{H} + \text{O}_2 + \text{M} \quad \rightarrow \quad \text{HO}_2 + \text{M} \tag{7}$$

where reaction (7) is important when O_2 has been deliberately added or is present as an impurity and after reaction (3) has produced enough O_2 to compete with H_2O_2 for H atoms. The radical-molecule rate constants are too large and I_a too low to allow for any significant contribution from radical–radical reactions, other than reaction (3).

In the presence of sufficient O_2, the rate of reaction (7) is much faster than that for reaction (5). Under these conditions, the CO_2 quantum yield is given by:

$$2\Phi\{CO_2\}^{-1} = (1 + k_2[H_2O_2]/k_4[CO])$$

By plotting $2\Phi\{CO_2\}^{-1}$ *versus* $[H_2O_2]/[CO]$ for the first five data points in Fig. 4, we are able to obtain the ratio k_2/k_4. The plot is shown in Fig. 5 and
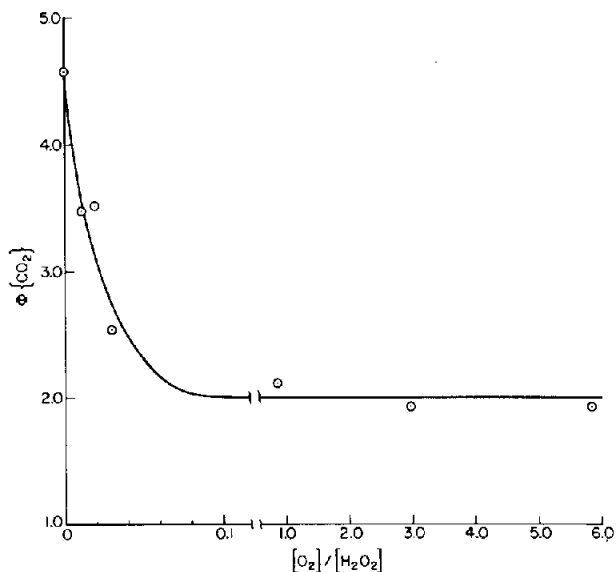
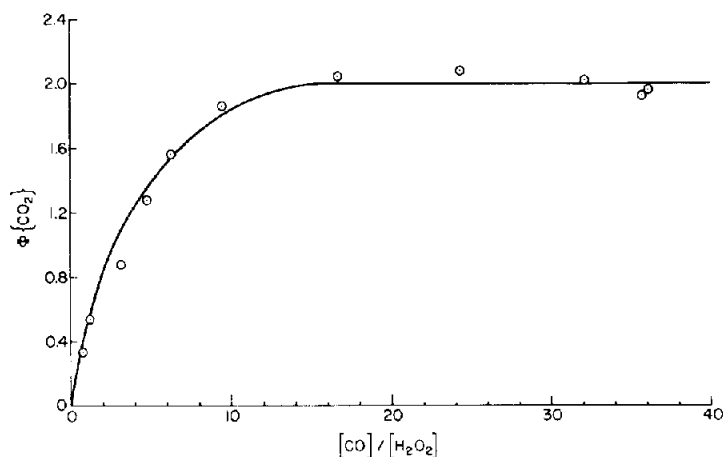Fig. 3. Quenching effect of added oxygen on the CO_2 quantum yield.

Fig. 4. Quantum yield of CO_2 as a function of $[CO]/[H_2O_2]$, with sufficient O_2 added to scavenge all hydrogen atoms.

the slope gives $k_2/k_4 = 4.1 \pm 0.6$. Of the two rate constants, k_4 has received by far the most attention. Since 1966 there have been 10 separate determinations [17 - 19 and references therein] of this rate constant. Although the data do not seem to fit simple Arrhenius behavior at higher temperatures, there is reasonably good agreement among these workers at room temperature. In fact, seven of these studies place the room temperature value between 8.0 and 9.9×10^{10} cm^3 mol^{-1} s^{-1}. This must be considered excellent agreement in view of the fact that five different techniques were employed

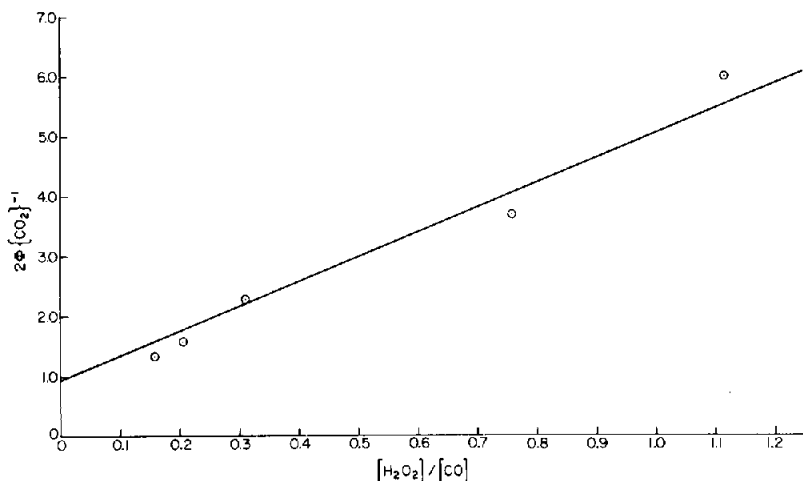Fig. 5. $2\Phi\{CO_2\}^{-1}$ vs. $[H_2O_2]/[CO]$ for runs with sufficient added O_2 to scavenge all hydrogen atoms.

to obtain these data. Taking a simple average of these seven yields a room temperature value $k_4 = 8.8 \pm 0.7 \times 10^{10}$ cm^3 mol^{-1} s^{-1}.

Combining this value for k_4 with our value for the ratio $k_2/k_4 = 4.1 \pm 0.6$, we determine $k_2 = (3.6 \pm 0.6) \times 10^{11}$ cm^3 mol^{-1} s^{-1} at 298 K. The available data on reaction (2) have been evaluated in two reviews [3, 20]. In each case the recommended Arrhenius expression predicts a room temperature rate constant, $k_2 = (4.8 \pm 2.4) \times 10^{11}$ cm^3 mol^{-1} s^{-1}. The most recent determination comes from the work of Gorse and Volman [8] who found: $k_2/k_4 = 8.13 \pm 0.56$, giving $k_2 = (7.1 \pm 0.7) \times 10^{11}$ cm^3 mol^{-1} s^{-1}. The latter number is slightly lower than the value calculated by those authors since we have used a lower value for k_4. This lower value is obtained upon inclusion of the 3 most recent determinations of k_4 [17 - 19].

Our result is in good agreement with the rate constant recommended by the two reviews. The agreement with Gorse and Volman's work is less satisfactory. This is particularly surprising considering the similarity of the techniques used.

In the absence of O_2 and with sufficient CO to consume all OH radicals, the mechanism simplifies to include reactions (1), (3), (4), (5a) and (5b). Under these conditions, the rate of CO_2 production is simply:

$$R\{CO_2\} = 2I_a(1 + k_{5a}/k_{5b})$$

When there is an excess of CO and sufficient O_2 to scavenge all hydrogen atoms the rate becomes:

$$R\{CO_2\} = 2I_a = R'\{CO_2\}$$

Thus the quantum yield obtained at high [CO] in the absence of O_2 is:

$$\Phi\{CO_2\} = 2(1 + k_{5a}/k_{5b})$$

$$= 2(\text{chain length}) = 4.6$$

and $k_{5a}/k_{5b} = 1.3$.

Several workers have measured this ratio at elevated temperatures and reported values of 6 at 713 K [10], 4 at 798 K [11], and 8 in the range 713 - 773 K [9]. Albers *et al.* [7] have determined the ratio by studying the equivalent reactions using deuterium atoms:

$$D + H_2O_2 \quad \rightarrow \quad OH + HDO \qquad\qquad (5a)(D)$$

$$\rightarrow \quad HD + HO_2 \qquad\qquad (5b)(D)$$

and by measuring HD and HDO mass spectrometrically. They determined $[HD]/[HDO] \simeq 10$ at 421 K which, when corrected for an isotope effect $k_{5a}(D)/k_{5a} = 0.43$, gives $k_{5a}/k_{5b} = 0.23$. This value indicates abstraction to be the dominant channel at this temperature and predicts an even lower value for k_{5a}/k_{5b} at room temperature (possibly as low as 0.01). This result is in direct conflict with that reported by Gorse and Volma [8] who found $k_{5a}/k_{5b} = 3.0 \pm 1.0$ at room temperature, indicating the production of hydroxyl radicals to be the important channel and finding a chain mechanism to be operative. Our results are consistent with the findings of the latter workers. It is difficult for us to place meaningful error limits upon our determination of k_{5a}/k_{5b} but in view of the problem of maintaining an oxygen free environment in the presence of H_2O_2 we feel that the only proper adjustment would make our value larger.

There are several features of the experiment of Albers *et al.* which may explain the large discrepancy between their results and those of Gorse and Volman and this work. Aside from the inherent complexity of their experiments, and the difficulty in accurately determining labelled water due to rapid isotopic exchange reactions with the walls, Albers *et al.* did not consider the possibility of:

$$D + H_2O_2 \quad \rightarrow \quad OD + H_2O \qquad\qquad (8)$$

which under their conditions of high O atom concentrations would be followed by

$$OD + O \quad \rightarrow \quad O_2 + D \qquad\qquad (9)$$

These authors and others [7, 20] have cited the work of Stief and DeCarlo [6] on the photolysis of H_2O_2 at 1236 Å as evidence that $k_{5a}/k_{5b} < 1$ at room temperature. Because of the nature of these experiments, it is impossible to conclude anything about the value of this ratio from their data, and in fact Stief and DeCarlo did not do so.

As a final point, it should be noted that in contrast to the study of Baldwin *et al.* [16] at 713 K, the rate of formation of CO_2 is independent of added CO once enough is present to eliminate reaction (2). This is further evidence in support of the conclusion [21] that although the reaction:

$$HO_2 + CO \rightarrow CO_2 + OH \qquad\qquad (10)$$

is fairly rapid at elevated temperatures, it proceeds very slowly at room temperature.

Acknowledgement

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Note added in proof (December 27, 1974)

Volman has informed us that the value for k_{5a}/k_{5b} reported by him and Gorse [8] as 3.0 ± 1.0 should have been 2.0 ± 1.0. In a more recent paper (R. A. Gorse and D. H. Volman, *J. Photochem.*, *3*, 115 (1974) they re-evaluated the data and obtained 1.86 ± 0.14 for k_{5a}/k_{5b} in good agreement with our value of 1.3, which may be slightly low as discussed above.