## Photooxidation of Formaldehyde in Oxygen-Lean Atmospheres

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The photooxidation of formaldehyde in  $CH_2O-O_2$  oxygen-lean mixtures was studied at 373 K. Formation of  $H_2$  and CO and the loss of O<sub>2</sub> were determined over a wide range of CH<sub>2</sub>O pressures (11-158 torr) and in the presence of CO<sub>2</sub> (0-800 torr). The photooxidation proceeds by a chain mechanism as indicated by the product quantum yields which reach values as high as 7.07 for H<sub>2</sub> and 11.6 for CO. The results are consistent with a mechanism whereby HO + CH<sub>2</sub>O reactions lead to H atom formation via an HOCH<sub>2</sub>O short-lived adduct radical and a "hot" formyl radical HCO<sup>†</sup>. For the HO reactions, HO + CH<sub>2</sub>O  $\rightarrow$  H<sub>2</sub>O + HCO<sup>†</sup> (10), HO + CH<sub>2</sub>O  $\rightarrow$  H<sub>2</sub>O + HCO (11), and HO + CH<sub>2</sub>O  $\rightarrow$  (HOCH<sub>2</sub>)  $\rightarrow$  H + HCO<sub>2</sub>H (12), the relative efficiencies are found to be  $0.64 \pm 0.2$ ,  $0.05 \pm 0.1$ , and  $0.3 \pm 0.15$ , respectively. For the H atom scavenging reactions,  $H + O_2 + CH_2O \rightarrow HO_2 + CH_2O$  (6) and  $H + O_2 + CO_2 \rightarrow HO_2 + CO_2$  (7),  $k_6$  and  $k_7$  are estimated to be equal to  $(3.3 \pm 1.7) \times 10^{10}$  and  $(4.4 \pm 0.6) \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$ , respectively.

### Introduction

The importance of formaldehyde in atmospheric chemistry and in combustion is widely recognized. The interest in the mechanism of formaldehyde photooxidation and thermal oxidation is due to its role as a source of radicals, particularly HO<sub>2</sub>, and its role as a chain carrier in the combustion of hydrocarbons. Low- and high-temperature oxidation of formaldehyde has thus been the subject of numerous studies.<sup>1-18</sup> The formation of the following primary oxidation products has been reported: CO, CO<sub>2</sub>, H<sub>2</sub>O,  $H_2O_2$ ,  $HCO_2H$ , and possibly  $HCO_3H$ . Not in every system are all of these products formed, mainly because of the heterogeneous character of some of the reactions involved in the photooxidation of formaldehyde. As a result of these reactions the nature of products formed is sensitive to the wall properties of the reactor in which the reaction is studied.

Despite the extensive effort, the mechanism of formaldehyde oxidation and, in particular, the formation of formic acid and hydrogen are not well understood. HCO<sub>2</sub>H formation at high temperatures (>423 K) has most commonly been assigned to the condensation reaction, HCO +  $O_2 \rightarrow$  HCO<sub>3</sub>, followed by hydrogen abstraction from formaldehyde and subsequent conversion of the performic acid to formic acid.<sup>9,10,12</sup> This mechanism was also considered to be responsible for HCO<sub>2</sub>H formation at lower

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temperatures.<sup>12</sup> However, in recent photooxidation studies by Su et al.<sup>16,17</sup> and Morrison and Heicklen,<sup>15,18</sup> it has been found that formic acid is formed at room temperature even though the condensation reaction between formyl radicals and O<sub>2</sub> does not take place.

When  $CH_2O$  is present in large excess over  $O_2$ , its oxidation takes a different course than that when the concentration of  $O_2$ is high. Reactions which otherwise are screened as a result of scavenging of various radicals by  $O_2$  are revealed when the  $O_2$ concentration is lowered. Thus, in the room-temperature 3130-Å photolysis of oxygen-lean CH<sub>2</sub>O-O<sub>2</sub> mixtures, formation of hydrogen with quantum yields that markedly exceed those predicted on the basis of the occurrence of the primary dissociation processes

$$CH_2O + h\nu \rightarrow H + HCO$$
 (1)

$$\rightarrow$$
 H<sub>2</sub> + CO (2)

has recently been observed by Horowitz, Su, and Calvert.<sup>13</sup> A similar observation of chain formation of hydrogen was made by Horner et al.<sup>6,7</sup> in earlier studies conducted at higher temperatures, namely, 100-150 °C. At these low temperatures dissociation of formyl radicals, HCO + M  $\rightarrow$  H + CO + M, is very slow and therefore cannot be responsible for the chain formation of hydrogen. Horowitz, Su, and Calvert<sup>13</sup> postulated that both HO<sub>2</sub> and HO are involved in the chain formation of  $H_2$  in  $CH_2O-O_2$ mixtures at 25 °C. Recent studies by Su et al.<sup>16,17</sup> and by Morrison and Heicklen<sup>18</sup> have shown that some of the HO and HO<sub>2</sub> reactions incorporated in that mechanism of H<sub>2</sub> formation indeed take place. So far, however, the overall mechanism of the chain formation of H<sub>2</sub> and other products in the low-temperature photooxidation of CH<sub>2</sub>O is not fully understood.

The present study was undertaken in order to gain further insight into the mechanism of formaldehyde oxidation, with particular emphasis on the chain mechanism of hydrogen formation. The study was conducted at 373 K, since at this temperature CH<sub>2</sub>O does not polymerize as readily as at room temperature. Consequently, at 373 K CH<sub>2</sub>O oxidation can be studied over a wide range of pressures and  $CH_2O/O_2$  concentration ratios.

## **Experimental Procedures**

Materials. Oxygen (Hoechst, prepurified) was used as received. Carbon dioxide (Matheson, Coleman, 99.99% minimum purity) was degassed and purified by trap-to-trap distillation. Formaldehyde was prepared daily from paraformaldehyde (Merck) according to the procedure of Spence and Wild.<sup>19</sup> GC analysis showed that the  $O_2$  and  $CO_2$  used were free from detectable amounts of  $H_2$  and CO.

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TABLE I: Effect of Formaldehyde Pressure on the Quantum Yields of Products of the Photolysis of  $CH_2O-O_2$  Mixtures at 3130 Å and 373 K<sup>a</sup>

pavb		10-17/			quantum yiel		
torr	irr time, s	quanta cell <sup>-1</sup>	$-O_2$ , torr	H <sub>2</sub>	CO	-0 <sub>2</sub>	$HCO_2H^c$
11.2	660	8.93		2.26	3.80		
11.7	600	8.41		2.34	3.74	N	
14.7	1800	28.8	0.492	2.47	3.92	1.91	2.37
14.9	600	9.47		2.51	4.14		
15.4	1800	28.2	0.547	2.56	3.90	1.94	2.54
15.8	420	7.13		2.50	3.95		
19.7	1500	31.3	0.761	2.92	4.58	2.43	3.20
21.7	1200	24.8	0.613	2.95	4.57	2.47	3.32
24.8	600	15.2	0.391	3.39	4.87	2.57	3.66
34.9	240	8.23		3.61	6.59		
41.2	720	24.5	0.855	4.33	6.55	3.49	4.76
49.9	180	7.06		4.61	7.55		
57.5	360	17.1	0.613	4.66	8.92	3.58	2.90
70.5	120	5.88		5.40	8.43		
74.9	90	4.86		5.53	8.56		
89.5	360	21.8	1.030	5.91	9.47	4.72	5.88
99.7	210	12.2	0.594	5.90	10.4	5.62	6.74
104.2	210	12.4	0.686	6.21	10.0	5.15	6.51
121.2	210	14.6	0.823	6.71	10.1	5.64	7.89
136.3	180	12.7	0.759	6.88	11.4	5.98	7.44
149.7	150	11.3	0.730	7.08	11.6	6.46	8.40
158.7	120	9.17	0.621	7.07	11.6	6.77	9.01

 $^{a}P^{o}O_{2} = 1.252$  torr.  $^{b}$  Calculated average pressure.  $^{c}$  Maximum quantum yield estimated by mass balance.

Apparatus and Procedures. The 3130-Å photolysis of formaldehyde was carried out in a cylindrical, 21.6 cm long, 4.6 cm i.d., quartz cell joined to a grease-free vacuum system. The cell was mounted in a heated air oven in which the temperature was regulated within ±0.3 °C. Pressure transducers (Celesco, Model P7D) were used for the measurement of pressures in the cell and of the liquid N<sub>2</sub> noncondensable product gases. The light source was an Osram HBO 200-W high-pressure mercury lamp from which the 3130-Å region was isolated with an interference filter (Oriel 6-571, 110-Å hbw). An RCA 935 photodiode mounted at the back of the cell monitored the intensity of the transmitted light. Incident light intensity was varied by use of neutral-density filters. Formaldehyde was employed for actinometry taking  $\Phi(H_2)$ =  $\Phi(CO) = 1^{14,20}$  (O<sub>2</sub> = 0). At pressures employed light absorption by formaldehyde did not follow the Beer-Lambert law and therefore the pressure dependence of  $\epsilon$  was determined and is shown in Figure 1.

Reactants were introduced into the cell in the following order: first oxygen, then formaldehyde, and finally carbon dioxide. To ensure complete mixing the mixture was then allowed to stand for 15 min. After photolysis the reactant and product gases were Toepler pumped through two traps cooled to the temperature of liquid N<sub>2</sub> and the pressure of the noncondensable fraction was determined in a precalibrated volume. Subsequently the transferred gases were separated into two samples which were analyzed on separate gas chromatographs, both of which were equipped with TC detectors. Hydrogen content was determined by using a 1/8 in.  $\times$  8 ft molecular sieve 5A column held at 25 °C with  $N_2$  as the carrier gas. A similar column with He as the carrier gas was used for the determination of  $O_2$  and CO. The accuracy of the determination of H<sub>2</sub>, CO, and O<sub>2</sub> was verified by comparison of the sum  $P_{H_2} + P_{CO} + P_{O_2}$  with the total pressure  $P_{NC}$  of the liquid N<sub>2</sub> noncondensable gases. Within the experimental error the average value of the ratio  $(P_{\rm H_2} + P_{\rm CO} + P_{\rm O_2})/P_{\rm NC}$  was found to be very close to unity  $(0.99 \pm 0.04)$ .

Carbon dioxide was determined only in a few preliminary runs. In these runs the gases from the cell were Toepler pumped through traps that were maintained at -78 °C (*n*-pentane slush) and the analysis was carried out by using a  $1/_8$  in. × 6 ft Porapak Q column held at 40 °C with He as the carrier gas.

Finally, the possibility of the occurrence of a thermal dark reaction was examined by allowing the reactant mixture to stand



Figure 1. Variation of the 3130-Å extinction coefficient of formaldehyde with its pressure (T = 373 K).

in the cell at 373 K for 30 min. Subsequent analysis of the liquid  $N_2$  noncondensable gases showed that neither  $H_2$  nor CO was formed during that period.

#### **Results and Discussion**

General Features of  $CH_2O-O_2$  Mixtures. In order to elucidate the mechanism of formaldehyde oxidation, the effects of various parameters on the formation of  $H_2$  and CO and the loss of  $O_2$ were examined. The variation of product quantum yields and  $\Phi_{-O_2}$ with formaldehyde pressure (11–158 torr) at constant initial  $P_{O_2}$ of 1.25 torr is summarized in Table I, together with estimated quantum yields of formic acid calculated by mass balance, assuming that  $H_2O$ ,  $HCO_2H$ ,  $H_2$ , and CO are the only final oxidation products. Under these conditions the following relations hold:

$$\Phi_{-CH_{2O}} = \Phi_{H_2} + 2\Phi_{-O_2}$$
$$\Phi_{CO} = \Phi_{H_2} + \Phi_{H_2O}$$
$$2\Phi_{-O_2} = \Phi_{H_2O} + \Phi_{H_2OH}$$

For obvious experimental reasons the accuracy of product (H<sub>2</sub>, CO) determination was considerably better than the accuracy with which the consumption of O<sub>2</sub> was determined. Consequently,  $\Phi_{-O_2}$  and particularly  $\Phi_{HCO,H}$  values are more scattered than the



Figure 2. Effect of irradiation time on the formation of CO (squares) and H<sub>2</sub> (triangles) and the loss of O<sub>2</sub> (hexagons).  $P^0_{CH_{2O}} = 22.0$  and  $P^0_{O_2} = 1.25$  torr.

TABLE II: Effect of Oxygen Pressure on the Quantum Yields of Products of the Photolysis of  $CH_2O-O_2$  Mixtures at 3130 Å and 373 K<sup>a</sup>

$P^0$ -	P <sup>av</sup> O <sub>2</sub> , <sup>b</sup> torr	irr time, s	10 <sup>-17</sup> I <sub>abs</sub> , quanta cell <sup>-1</sup>	product quantum yields			
torr				H <sub>2</sub>	СО	-02	
0.626	0.44	720	14.9	2.89	4.34	2.53	
1.252	0.89	1200	24.8	2.95	4.48	2.47	
1.878	1.31	2160	44.8	3.01	4.57	2.52	
2.50	2.39	450	9.01	2.92	4.43	С	
5.06	4.73	1200	22.1	2.80	4.21	С	
7.51	7.03	1800	38.2	2.74	4.11	С	

<sup>a</sup>  $P^{\circ}_{CH_2O} = 22.0$  torr. <sup>b</sup> Calculated from the experimentally determined final pressure of O<sub>2</sub>. <sup>c</sup> Loss of O<sub>2</sub> too small to allow accurate determination.

quantum yields of  $H_2$  and CO. Still, despite the considerable scatter,  $\Phi_{H_2}$ ,  $\Phi_{CO}$ ,  $\Phi_{-O_2}$ , and  $\Phi_{HCO_2H}$  reveal the same increasing trend with  $P_{O_2}$ . Worth noticing too is the fact that the increase in quantum yields slows down as  $P_{CH_2O}$  grows and that within the entire pressure range studied relative product yields remain almost constant. Finally, the chain reaction features of formaldehyde oxidation are demonstrated in the product quantum yields which throughout the entire range of CH<sub>2</sub>O pressures markedly exceed unity.

In a number of experiments the time dependence of the rate of formaldehyde oxidation was determined. Results of typical experiments at  $P^{0}_{CH_{2}O} = 22.0$  and  $P^{0}_{O_{2}} = 1.25$  torr are plotted in Figure 2, from which it can be seen that the photooxidation proceeds at a uniform rate down to 80% conversion of O<sub>2</sub>. This observation shows that CH<sub>2</sub>O photooxidation does not require an induction period and that it is not affected by the occurrence of secondary reactions, if indeed such reactions take place.

Table II summarizes the results of experiments in which the effect of  $O_2$  concentration on the rate of photooxidation was determined. It can be seen that an increase by more than 1 order of magnitude in the average pressure of  $O_2$  did not bring about a pronounced change in product quantum yields and distribution. Also at the lower end of  $O_2$  pressures the effect on the quantum yield of  $H_2$  is negligible.

The effect of absorbed light intensity on  $R_{\rm H_2}$ ,  $R_{\rm CO}$ , and  $R_{-O_2}$ was examined at two formaldehyde pressures, namely, 22 and 100 torr. The log R vs. log  $I_{\rm abs}$  plots of the results of these experiments are shown in Figures 3 and 4. The respective least-squares calculated slopes are 1.01 ± 0.02 (H<sub>2</sub>), 1.01 ± 0.02 (CO), and 1.02 ± 0.03 (O<sub>2</sub>) at  $P^0_{\rm CH_2O} = 22$  torr. At  $P^0_{\rm CH_2O} = 100$  torr the slopes were found to be 1.00 ± 0.02 (H<sub>2</sub>), 1.00 ± 0.04 (CO), and 0.96 ± 0.03 (-O<sub>2</sub>). At this pressure of formaldehyde a small increase in  $R_{-O_2}/R_{\rm H_2}$  was observed at the low light intensities. On the whole, though,  $\Phi_{\rm H_2}$ ,  $\Phi_{\rm CO}$ , and  $\Phi_{-O_2}$  appear to be insensitive to variations in absorbed light intensities, indicating that for our



Figure 3. Rate of formation of CO (triangles) and  $H_2$  (squares) and  $O_2$  consumption (circles).  $P^0_{CH_2O} = 100$  torr,  $P^0_{O_2} = 1.25$  torr.



Figure 4. Rate of formation of CO (triangles) and H<sub>2</sub> (squares) and O<sub>2</sub> consumption (circles).  $P^0_{CH_2O} = 22.0$  and  $P^0_{O_2} = 1.25$  torr.

conditions the chain termination proceeds by first-order radical reactions at the walls of the cell.

Formation of carbon dioxide was determined in several preliminary experiments and found to be very insignificant. For  $P_{O_2}^0 = 2.54$  and  $P_{CH_2O}^0 = 22$ , 100, and 150 torr,  $\Phi_{CO_2} = 0.05 \pm 0.02$ ,  $0.04 \pm 0.02$ , and  $0.06 \pm 0.03$ , respectively.

Kinetics and Mechanism. The general features of formaldehyde photooxidation in  $CH_2O-O_2$  oxygen-lean mixtures can be rationalized in terms of the following reaction scheme:

$$CH_2O + h\nu \rightarrow H + HCO$$
 (1)

$$\rightarrow$$
 H<sub>2</sub> + CO (2)

$$H + CH_2O \rightarrow H_2 + HCO$$
(3)

$$HCO + O_2 \rightarrow HO_2 + CO$$
 (4)

$$H + O_2 + O_2 \rightarrow HO_2 + O_2$$
 (5)

$$H + O_2 + CH_2O \rightarrow HO_2 + CH_2O$$
 (6)

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

 $HO_{2} + CH_{2}O \rightarrow HO_{2}CH_{2}O \qquad (8)$  $HO_{2}CH_{2}O \rightarrow HO + HCO_{2}H \qquad (9)$ 

$$HO + CH O \rightarrow HO + HCO^{\dagger}$$
(10)

$$\rightarrow H_{0} + H_{0} \qquad (10)$$

$$\rightarrow$$
  $H_2O$  + HCO (H)

$$\rightarrow \text{HOCH}_2\text{O}$$
 (12)

$$HCO^{\dagger} \rightarrow H + CO$$
 (13)

$$HOCH_2O \rightarrow HCO_2H + H$$
 (14)

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$$HO_2 + wall \rightarrow products (H_2O, O_2)$$
 (15)

$$HO_2CH_2O + wall \rightarrow products (H_2O, O_2, HCO_2H, CH_2O)$$
(16)

where HCO<sup>†</sup> represents "hot" formyl radicals. Of the two primary photodissociation reactions 1 and 2, only the former serves as the chain-initiating step. The subsequent reactions 3-14 constitute the propagation step and the chain is terminated by first-order reactions 15 and 16 at the walls of the cell. The final photo-oxidation products according to the reaction scheme proposed are H<sub>2</sub>, CO, HCO<sub>2</sub>H, and H<sub>2</sub>O.

The above-outlined mechanism is almost identical with the mechanism suggested by Horowitz, Su, and Calvert in their room-temperature study of  $CH_2O$  photooxidation.<sup>13</sup> The only difference is that the present mechanism does not include the peroxyformyl radical generating reaction

$$HCO + O_2 + M \rightarrow HCO_3 + M$$
 (4')

Arguments for the occurrence of this reaction were presented in many of the earlier studies in which the HCO<sub>3</sub> radical has been considered as the precursor of the formic acid. However, recent studies<sup>21-23</sup> have shown that the HCO-O<sub>2</sub> reaction follows second-order kinetics up to pressures of 1 atm. On the basis of this observation, it appears that under our experimental conditions reaction 4 is the sole route by which formyl radicals react with oxygen. It can also be shown that at the O<sub>2</sub> pressures and light intensities employed in the present study, the rate of reaction of formyl radicals. Hence, it is evident that, irrespective of the occurrence of reactions 5–7, the primary photodissociation step 1 can be looked upon as an indirect route by which hydroperoxy radicals are generated in the system.

One of the key assumptions in the proposed reaction scheme is the HO<sub>2</sub>-HO conversion mechanism represented by reactions 8 and 9. The idea that  $HO_2$  might add to  $CH_2O$  is not new. Horner and co-workers<sup>6,7</sup> studied the photooxidation of CH<sub>2</sub>O at 373 K. They found that their results could be rationalized only by the introduction of the  $HO_2$ -CH<sub>2</sub>O addition reaction. The HO<sub>2</sub>-HO conversion mechanism was suggested by McKellar and Norrish,<sup>8</sup> who studied the flash photolysis of CH<sub>2</sub>O-O<sub>2</sub> mixtures at 413 K. A need for such a conversion mechanism has also been expressed by Hay and Hessam,<sup>10</sup> who believed that HO<sub>2</sub> was converted into HO via the reaction with CH<sub>2</sub>O, even under their conditions of oxidation at a temperature as high as 593 K. Recent FTS-IR 25 °C studies of the direct and Cl<sub>2</sub>-sensitized photooxidation of  $CH_2O$  have been carried out by  $\tilde{Su}$  et al.<sup>16,17</sup> In these studies, under nonchain conditions, evidence was obtained for the formation of hydroperoxyhydroxymethane (HO<sub>2</sub>CH<sub>2</sub>OH) and it was suggested that reaction 7 is involved in the formation of this compound. The ability of formaldehyde to undergo addition reactions is further supported by the findings of Chang and Barker,<sup>24</sup> who studied the  $O(^{3}P) + CH_{2}O$  reaction in a discharge flow system. Their conclusion was that  $O(^{3}P)$  readily adds to CH<sub>2</sub>O and that a similar addition reaction between HO and CH<sub>2</sub>O was possible also.

A complete mechanism of formaldehyde photooxidation has to account for the chain formation of hydrogen. In our mechanism this requirement is satisfied by the somewhat speculative HO-CH<sub>2</sub>O reactions 10–12. Morrison and Heicklen<sup>18</sup> studied the HO-CH<sub>2</sub>O reaction and gave convincing evidence for the occurrence of reactions 10 and 13 in their CH<sub>2</sub>O-NO<sub>2</sub> mixtures photolyzed at 3360 Å and 23 °C. On the other hand, these authors concluded that formic acid is not formed via a single-stage reaction between hydroxyl radicals and formaldehyde. This concludion, however, does not exclude the possibility that HO radicals add



**Figure 5.** Plot of the results in Table I according to expressions 18 and 19. For CO (circles), A = 1.7; for H<sub>2</sub> (squares), A = 1.

to CH<sub>2</sub>O, and HOCH<sub>2</sub>O decomposes as suggested by us. Presumably in the CH<sub>2</sub>O-NO<sub>2</sub> system the HOCH<sub>2</sub>O might have been scavenged by either NO<sub>2</sub> or NO. In any case, it can be shown that our results cannot be reconciled with reaction 10 being the only route of the chain formation of hydrogen. If this were the case, and if reactions 5-7 did not take place, the ratio of the chain-formed CO and H<sub>2</sub>,  $\Phi'_{CO}/\Phi'_{H_2}$ , would have been given by expression 17

$$\frac{\Phi'_{\rm CO}}{\Phi'_{\rm H_2}} = \frac{\Phi_{\rm CO} - (\phi_2 + 2\phi_1)}{\Phi_{\rm H_2} - (\phi_2 + \phi_1)} = 2 + \frac{R_{11}}{R_{10}}$$
(17)

At 3130 Å the sum of the quantum yields of the primary processes 1 and 2,  $\phi_1 + \phi_2$ , is unity and  $\phi_2$  is equal to 0.3.<sup>14,20</sup> Therefore, the lower limit for  $\Phi'_{CO}/\Phi'_{H_2}$  should be equal to 2. This expectation is not borne out by the experimental results presented in Table I which were obtained under conditions where H atoms scavenging by  $O_2$  is negligible.

Based on the suggested mechanism the steady-state approximation for H, HO<sub>2</sub>CH<sub>2</sub>O, HO, HO<sub>2</sub>, HCO, HCO<sup> $\dagger$ </sup>, and HOCH<sub>2</sub>O leads to the following rate laws for the formation of H<sub>2</sub> and CO:

1

$$\frac{1}{\Phi'_{H_2}} = \frac{1}{\Phi_{H_2} - (\phi_1 + \phi_2)} = \frac{k_{10} + k_{11} + k_{12}}{2\phi_1(k_{10} + k_{12})} \left[ \frac{k_{16}}{k_9} + \frac{k_{15}(k_9 + k_{16})}{k_8k_9[CH_2O]} \right] (18)$$

$$\frac{\frac{1}{\Phi'_{CO}}}{\frac{1}{\Phi_{CO} - (2\phi_1 + \phi_2)}} = \frac{1}{\frac{k_{10} + k_{11} + k_{12}}{2\phi_1(2k_{10} + k_{11} + k_{12})}} \left[\frac{k_{16}}{k_9} + \frac{k_{15}(k_9 + k_{16})}{k_8k_9[CH_2O]}\right] (19)$$

Inherent in the derivation of these two equations is the assumption that H atoms are not scavenged by oxygen. This condition is met by the results presented in Table I which were obtained in experiments in which the initial pressure of  $O_2$  was 1.25 torr. Plots of the results of Table I according to expressions 18 and 19 and taking  $\phi_1 + \phi_2 = 1$  and  $\phi_1 = 0.7$  at 3130 Å are presented in Figure 5. The respective linear least mean square expressions are 0.122  $\pm 0.015 + (7.87 \pm 0.34)/[CH_2O]$  for H<sub>2</sub> and 0.074  $\pm 0.017 \pm (5.21 \pm 0.39)/[CH_2O]$  for CO. According to relations 18 and 19 the two lines shown in Figure 4 should have the same slope/intercept ratio. For the H<sub>2</sub> line our results yield a slope/intercept value of 64.5  $\pm$  8.4, while for the CO data this ratio is equal to 70.5  $\pm$  17.1. The good agreement between these two values renders further support for the suggested mechanism.

According to expressions 18 and 19 and the ratio of the slopes of the two lines given by these expressions should be equal to the ratio of their intercepts. These ratios are given by

$$\frac{\text{slope}(H_2)}{\text{slope}(CO)} = \frac{\text{intercept}(H_2)}{\text{intercept}(CO)} = 1 + \frac{k_{10} + k_{11}}{k_{10} + k_{12}}$$
(20)

<sup>(21)</sup> N. Washida, R. I. Martinez, and K. D. Bayrs, Z. Naturforsch. A, 29, 251 (1974).

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From the individually determined parameters of the two lines the slope and intercept ratios of expression 20 are found to be 1.51  $\pm$  0.09 and 1.65  $\pm$  0.26, respectively. These two values are equal within the estimated error limits ( $2\sigma$ ). The average value of ( $k_{10} + k_{12}$ )/( $k_{10} + k_{11}$ ) is thus equal to 0.6  $\pm$  0.2. By itself, the knowledge of this value is not sufficient for the assessment of the relative importance of the three channels by which hydroxyl radicals react with formaldehyde. An additional equation connecting the three rate constants of the reactions under consideration is needed. Such an equation can be derived from the  $\Phi_{\text{HCO}_{2\text{H}}}$  values estimated by mass balance from O<sub>2</sub> loss. It can be shown that, according to the suggested reaction scheme,  $\Phi_{\text{HCO}_{2\text{H}}}$  should be given by

$$\frac{\Phi_{\rm HCO_2H} - \alpha}{\Phi_{\rm H_2} - 1} = 1 + \frac{k_{12}}{k_{10} + k_{12}}$$
(21)

where  $\alpha$  represents the quantum yield of HCO<sub>2</sub>H formed in the termination reaction. The suggested mechanism predicts that at sufficiently high CH<sub>2</sub>O pressures most of the radicals in the system are HO<sub>2</sub>CH<sub>2</sub>O radicals. If an assumption is made that the stoichiometry of reaction 16 is given by expression 22 and the rate

$$2HO_2CH_2O \rightarrow HCO_2H + CH_2O + O_2 + H_2O \quad (22)$$

of initiation  $2\phi_1 I_{abs}$  is equal to the rate of termination, then the maximum value that  $\alpha$  can reach is equal to  $\phi_1$ , i.e., 0.7. Quite obviously a clear-cut dividing line between the high and low CH<sub>2</sub>O pressures does not exist. Therefore, in somewhat arbitrary manner the ratio given in expression 21 was evaluated from the results in Table I in which  $P_{CH_2O}$  exceeded 80 torr. For those conditions, and when one takes  $\alpha = 0.7$ , the value of the ratio is found to be  $1.21 \pm 0.1$  and accordingly  $k_{12}/(k_{10} + k_{12}) = 0.21 \pm 0.1$ . It should be noted that the large error limits of the estimated value of  $k_{12}/(k_{10} + k_{12})$  reflect the inaccuracy of the determination of O<sub>2</sub> loss, the error propagation through the mass-balance estimation of HCO<sub>2</sub>H, and, particularly, the fact that the ratio in expression 21 is only slightly higher than unity.

In theory the relative magnitude of the rate constants  $k_{10}$ ,  $k_{11}$ , and  $k_{12}$  can be evaluated from the rate constant ratios derived with the use of expressions 20 and 21. It appears, however, that values obtained for these ratios lack the precision necessary for a meaningful estimation of the individual rate constants. Indeed, our results yield a  $k_{10}/k_{12}$  value of 3.3 with a close to 100% estimated error. Furthermore, this result combined with the requirement that the sum of the relative rate constants equals unity leads to values of  $k_{10}/(k_{10} + k_{11} + k_{12})$ ,  $k_{11}/(k_{10} + k_{11} + k_{12})$ , and  $k_{12}/(k_{10} + k_{11} + k_{12})$  of 0.93, -0.2 and 0.28, respectively. Obviously, a negative value of  $k_{11}$  is not acceptable and therefore an alternative method for the estimation of the rate constants is needed. Computer fitting of the relative rate constants to give the best simulation of the experimentally determined product distribution can be used for this purpose. Application of this method to our results yields  $k_{10}/(k_{10} + k_{11} + k_{12})$ ,  $k_{11}/(k_{10} + k_{11})$ +  $k_{12}$ ), and  $k_{12}/(k_{10} + k_{11} + k_{12})$  values of 0.65 ± 0.2, 0.05 ± 0.1, and 0.30  $\pm$  0.15, respectively. It appears then that within the large error limits of our estimation, reaction 10 constitutes the main route by which HO radicals react with formaldehyde. The present estimate that about 65% of these radicals are converted into "hot" formyl radicals is in good agreement with an earlier estimate of Morrison and Heicklen.<sup>18</sup> On the basis of their study of the photolysis of CH2O-NO2 mixtures, these authors estimated that about half of the HO radicals produced hot formyl radicals in their reaction with formaldehyde at room temperature.

Once the relative importance of the three channels of the HO + CH<sub>2</sub>O reaction has been assessed, additional kinetic data can be obtained from the variation of  $\Phi_{H_2}$  and  $\Phi_{CO}$  with the pressure of CH<sub>2</sub>O. The importance rate constant ratios  $k_9/k_{16}$  and  $k_8/k_{15}$  can be derived from the parameters of the lines given by expressions 18 and 19. The intercepts of the H<sub>2</sub> and CO lines coupled with the computer-assigned relative values of  $k_{10}$ ,  $k_{11}$ , and  $k_{12}$  yield  $k_9/k_{16}$  values of  $(1.44 \pm 0.21) \times 10^5$  and  $(1.36 \pm 0.36) \times 10^5$  M<sup>-1</sup>, respectively. By the substitution of these results into the expression for the respective slopes of the two lines we find



Figure 6. Effect of  $O_2$  pressure on the formation of  $H_2$  in  $CH_2O-O_2$  mixtures ( $P^0_{CH_2O} = 22.0$  torr).

that  $k_8/k_{15} = (2.59 \pm 0.39) \times 10^3$  (H<sub>2</sub> data) and  $(2.26 \pm 0.62) \times 10^3$  M<sup>-1</sup> (CO data). The estimated weighted average values of  $k_9/k_{16}$  and  $k_8/k_{15}$  thus are  $(1.42 \pm 0.18) \times 10^5$  and  $(2.50 \pm 0.33) \times 10^3$  M<sup>-1</sup>, respectively.

At low pressures of added O<sub>2</sub> the mechanism proposed predicts that, at constant CH<sub>2</sub>O pressure and when  $k_6[CH_2O] \gg k_5[O_2]$ ,  $\Phi_{\rm H}$ , should be given by

$$\frac{1}{\Phi_{\rm H_2} - \phi_2} = \frac{1}{\Phi^0_{\rm H_2} - \phi_2} \left( 1 + \frac{k_6}{k_3} [\rm O_2] \right)$$
(23)

Here  $\Phi_{H_2}^0$  is the quantum yield of H<sub>2</sub> when O<sub>2</sub> does not scavenge H atoms and  $\phi_2 = 0.3$ . As a crude first-order approximation it can be assumed that the conditions specified for eq 23 to be observed are met by the results listed in Table II. These results cover a very narrow range of O<sub>2</sub> pressures in which the effect of  $O_2$  addition on  $\Phi_{H_2}$  is quite small. The treatment of the data according to expression 23 thus serves mainly as an additional semiquantitative test of the mechanism of  $H_2$  formation, rather than an accurate method for the evaluation of  $k_6/k_3$ . A linear plot of these data according to expression 23 is shown in Figure 6. The corresponding least-squares fit gives  $1/(\Phi_{\rm H_2} - 0.3) = (0.37)$  $\pm 0.010) + \{(5.2 \pm 2.8) \times 10^{-3}\}[O_2] \text{ (torr) and a } k_6/k_3 \text{ value of} \\ (1.40 \pm 0.75) \times 10^{-2} \text{ torr}^{-1}, \text{ i.e., } (3.3 \pm 1.7) \times 10^2 \text{ M}^{-1}. \text{ The H} \\ \end{bmatrix}$ + CH<sub>2</sub>O reaction has been studied by Westenberg and deHaas<sup>25</sup> and by Ridley et al.<sup>26</sup> The average 297 K value of  $k_3$  of 2.77  $\times 10^7$  M<sup>-1</sup> s<sup>-1</sup> from these two works and an activation energy of 3.74 kcal/mol estimated by Westenberg and deHaas<sup>25</sup> yield a  $k_3$  value of 1.01 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> at 373 K. Upon substitution of the latter value into our estimated result for  $k_6/k_3$ ,  $k_6$  (373 K) is found to be equal to (3.3 ± 1.7) × 10<sup>10</sup> M<sup>-2</sup> s<sup>-1</sup>. This result compares reasonably well with the CODATA estimate<sup>27</sup> for  $M = N_2$  which gives  $k_7(373 \text{ K}) = 1.6 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$ . Wong and Davies<sup>28</sup> found that H atom scavenging by  $O_2$  for M = CH<sub>4</sub> is 7.5 times faster than when  $M = N_2$ . The present results indicate that  $CH_2O$  is more efficient than  $N_2$  as a third body and that its efficiency lies somewhere in between the efficiencies of  $N_2$  and  $CH_4$ .

Photolysis of  $CH_2O-O_2-CO_2$  Mixtures. In terms of the proposed mechanism of formaldehyde oxidation, addition of an inert gas should enhance the rate of H atom scavenging, thereby reducing the quantum yield of  $H_2$  and altering the product distribution. In order to verify this assumption a series of experiments in  $CH_2O-O_2-CO_2$  mixtures, summarized in Tables III-V, were performed. In these experiments the response of the system to one-by-one variation of its components was examined. The primary purpose of this part of the study was to establish the effect

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Figure 7. Effect of CH<sub>2</sub>O pressure on the formation of H<sub>2</sub> in CH<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> mixtures.  $P_{CO_2} = 600$ ;  $P^{av}_{O_2} = 4.7 \pm 1.5$  torr. A plot according to expression 21.

TABLE III: Effect of Oxygen Pressure on the Quantum Yields of Products in the Photolysis of  $CH_2O-O_2-CO_2$  Mixtures at 3130 A and 373 K<sup>a</sup>

P <sup>0</sup> O <sub>2</sub> , torr	pav <sub>O2</sub> , torr	irr time, s	$\begin{array}{c} 10^{-17} \times \\ I_{abs}, \\ quanta \\ cell^{-1} \end{array}$	Ф <sub>Н2</sub>	Φco	Φ-02
0.625	0.49	600	13.0	2.57	3.98	2.07
1.256	0.88	1800	38.0	2.13	3.42	1.97
2.52	2.30	1000	21.9a	1.83	3.14	b
3.77	3.24	3000	66.1	1.78	2.97	Ь
5.02	4.77	1200	24.9	1.41	2.59	Ь
7.54	7.21	1800	36.5	1.27	2.50	b

 ${}^{a}P_{CO_{2}} = 400; P^{av}_{CH_{2}O} = 21.6 \pm 0.2 \text{ torr.}$  b Consumption of O<sub>2</sub> too low to allow accurate determination.

of composition on hydrogen formation. For constant  $O_2$  and  $CO_2$  pressures and when  $k_3 \gg k_5[O_2]$ , as in the case of the results presented in Table III, the following equation should apply:

$$\frac{\Phi_{\rm H_2}^0 - \phi_2}{\Phi_{\rm H_2} - \phi_2} = 1 + \frac{k_7 [\rm O_2] [\rm CO_2]}{k_3 [\rm CH_2 O]}$$
(24)

where  $\Phi^0_{H_2}$  is the quantum yield of H<sub>2</sub> at the same CH<sub>2</sub>O and O<sub>2</sub> pressures, but in the absence of CO<sub>2</sub>. A reasonably straight line given by (1.01 ± 0.26) + (4.88 ± 8.9)[CH<sub>2</sub>O] (torr<sup>-1</sup>) is obtained when the data are treated according to expression 24 (see Figure 7). For the conditions under which these experiments were performed,  $P_{CO_2} = 600$  and  $P^{av}_{O_2} = 4.7 \pm 0.15$  torr, the slope of the line gives  $k_7/k_3 = (1.73 \pm 0.32) \times 10^{-2}$  torr<sup>-1</sup>, which is equal to (4.02 ± 0.74) × 10<sup>2</sup> M<sup>-1</sup>.

It can also be shown that according to the suggested mechanism  $\Phi_{H_2}$  and  $\Phi_{CO}$  should be equally reduced as a result of the enhanced H atom scavenging in the presence of CO<sub>2</sub>. Within the experimental error this expectation is borne out by the results in Table IV that yield an average  $\Delta[H_2]/\Delta[CO]$  value of  $1.06 \pm 0.3$ . Incidentally, a similar trend in  $\Phi_{H_2}$  and  $\Phi_{CO}$  is revealed by the 373 K photooxidation data of Horner and Style,<sup>6</sup> who studied this



Figure 8. Effect of O<sub>2</sub> pressure on the formation of H<sub>2</sub> in CH<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> mixtures.  $P_{CO_2} = 400$  and  $P_{CH_{2}O}$  21.6 ± 0.4 torr. A plot according to expression 25.  $R = (\Phi^0_{H_2} - \phi_2)/(\Phi_{H_2} - \phi_2) - 1$ .



**Figure 9.** Effect of CO<sub>2</sub> pressure on the formation of H<sub>2</sub> in CH<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> mixtures.  $P^{av}_{CH_2O} = 21.8 \pm 0.2$  and  $P^{av}_{O_2} = 1.13 \pm 0.03$  torr. A plot according to expression 26.

reaction at both higher  $CH_2O$  and  $O_2$  pressures.

For the experiments of Table IV, in which  $P_{CO_2}$  and  $P_{CH_2O}$  were kept constant, the effect of O<sub>2</sub> pressure on  $\Phi_{H_2}$  should obey the following expression:

$$\frac{1}{(\Phi^{0}_{H_{2}} - \phi_{2})/(\Phi_{H_{2}} - \phi_{2}) - 1} = \frac{k_{6}[CH_{2}O]}{k_{7}[CO_{2}]} + \frac{k_{3}[CH_{2}O]}{k_{7}[CO_{2}]} \frac{1}{[O_{2}]}$$
(25)

where, in this case,  $\Phi_{H_2}^0$  represents the quantum yield in the CH<sub>2</sub>O-O<sub>2</sub> system in which CH<sub>2</sub>O pressure was the same as in the CH<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> mixtures and  $P_{O_2}$  was sufficiently low so that formation of hydrogen was not reduced by it. The left-hand side of expression 25 should be linear with the reciprocal of O<sub>2</sub> pressure. This indeed is the case, as can be seen from the plot shown in Figure 8, which was obtained by taking  $\Phi_{H_2}^0 = 2.95$ . The least-squares-calculated slope and intercept of the line in Figure

TABLE IV: Photolysis of  $CH_2O-O_2-CO_2$  Mixtures at 3130 A and 373 K and the Effect of Formaldehyde Pressure on Product Quantum Yields

P <sup>o</sup> CH <sub>2</sub> O, torr	$P_{\rm CO_2},$ torr	$P^{0}O_{2},$ torr	irr time, s	$10^{-17}I_{abs}$ , quanta cell <sup>-1</sup>	$\Phi_{\rm H_2}$	Фсо	$\Delta[H_2]/\Delta[CO]$
20		5.08	420	7.89	2.91	4.34	
20	600	5.08	900	16.5	0.99	2.50	1.04
30		5.08	360	8.88	3.31	5.07	
30	600	5.08	900	21.7	1.44	3.01	0.91
50		5.08	240	8.47	4.47	7.41	
50	600	5.08	480	17.2	2.20	5.57	1.23
80		5.08	180	9.21	5.72	8.79	
80	600	5.08	180	9.01	3.89	7.17	1.13
100		5.08	150	10.6	6.01	9.68	1.15
100	600	5.08	180	12.3	4.28	8.17	$1.06 \pm 3$ (av)

TABLE V: Effect of Carbon Dioxide Addition on Product Quantum Yields in the Photolysis of  $CH_2O-O_2$  Mixtures at 3130 Å and 373 K<sup>a</sup>

$P_{\rm CO_2},$ torr	irr time, s	10 <sup>-17</sup> I <sub>abs</sub> , quanta cell <sup>-1</sup>	ФH2	Фсо
125	480	8.93	2.79	4.24
240	480	8.73	2.24	4.03
370	480	9.01	2.21	3.79
470	480	8.96	1.94	3.36
500	480	8.88	2.10	3.55
600	600	10.1	1.75	3.27
700	600	9.93	1.87	3.16
800	600	9.98	1.62	3.28

$${}^{a}P^{av}_{CH_{2}O} = 21.8 \pm 2; P^{av}_{O_{2}} = 1.13 \pm 0.03 \text{ torr.}$$

8 are 2.64 ± 0.64 torr and 0.14 ± 0.62, respectively. Of these two parameters only the slope has been determined with sufficient precision to allow a meaningful estimation of  $k_7/k_3$ . Taking into account that the experiments in Table IV were carried out at  $P_{CO_2}$ = 400 and  $P_{CH_2O}$  = 21.6 ± 0.4 torr, the slope of the line presented in Figure 8 gives a  $k_7/k_3$  value of (2.04 ± 0.50) × 10<sup>-2</sup> torr<sup>-1</sup>, i.e., (4.75 ± 1.16) × 10<sup>2</sup> M<sup>-1</sup>. This value is in good accord with the  $k_7/k_3$  value derived from the results in Table III.

Finally, for the experiments at fixed  $P^{av}_{O_2}$  of 1.13  $\pm$  0.03 and  $P^{av}_{CH_2O} = 21.8 \pm 0.2$  torr summarized in Table V, the formation of H<sub>2</sub> as a function of CO<sub>2</sub> pressure is given by expression 26 A

$$\frac{1}{\Phi_{\rm H_2} - \phi_2} = \frac{1}{\Phi^0_{\rm H_2} - \phi_2} \left( 1 + \frac{k_7 [\rm O_2]}{k_3 [\rm CH_2 O]} [\rm CO_2] \right) \quad (26)$$

plot of the experimental data according to this relation is presented in Figure 9 and the respective least-squares expression for the line shown there is  $1/(\Phi_{H_2} - 0.3) = 0.37 \pm 0.07 + \{(4.6 \pm 1.4) \times 10^{-4}\}[CO_2]$  (torr). The  $k_7/k_3$  value computed from the slope/ intercept ratio is equal to  $(2.42 \pm 0.89) \times 10^{-2}$  torr<sup>-1</sup>, i.e.,  $(5.6 \pm 2.1) \times 10^2$  M<sup>-1</sup>. Although the last result is not as accurate as the other two estimates of  $k_7/k_3$ , it is still in fair agreement with them. It appears, therefore, that on the whole the experimental findings in the CH<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> system are consistent with the suggested mechanism and render further support for its validity. In addition, the experiment in this system provides new kinetic data on the H + O<sub>2</sub> + CO<sub>2</sub> reaction.

Scope and Limits of the Mechanism. It has been demonstrated that the experimental findings in the present study can be satisfactorily explained in terms of the suggested mechanism of formaldehyde oxidation. On the basis of this mechanism new rate constant data summarized in Table VI have been evaluated. To some extent the apparent success of the mechanism proposed in creating a self-consistent picture of the routes by which the main products are formed is misleading. The mechanism is based on a number of assumptions of somewhat speculative nature, which still require experimental verification. Critical examination of these assumptions and their effect on the meaning and accuracy of the kinetic data thus seems to be in order.

The reaction path for hydrogen formation, i.e., HO<sub>2</sub>-HO conversion followed by reactions 10 and 12, appears to be one of the most questionable aspects of the present mechanism. As has been shown in an earlier study, these two reactions of hydroxyl radicals have quite a favorable overall thermochemistry.<sup>13</sup> From this point of view the formation of hot formyl radicals via reaction 10 seems to be a feasible postulate. Less acceptable though is the assumption that these hot radicals are not thermalized at high pressures attained in the present work by the addition of 800 torr of  $CO_2$ , or in the study of Morrison and Heicklen<sup>18</sup> by the addition of 750 torr of He. It has been pointed out already that the observed product distribution requires two different HO + CH<sub>2</sub>O reactions. At the present time it is hard to foresee any alternative  $HO + CH_2O$  reaction that would ultimately lead to the chain formation of hydrogen. Hence, at this stage and in spite of all the reservations, instantaneous decomposition of hot formyl radicals appears to be the only explanation for the absence of a

TABLE VI: Summary of Estimated Rate Constants at 373 K

no.	reaction	k	com- ments
10	$OH + CH_2O \rightarrow H_2O + HCO$	$(5.1 \pm 1.6) \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	а
11	$\rightarrow$ H <sub>2</sub> O + HCO	$(3.9 \pm 7.8) \times 10^8$ M <sup>-1</sup> s <sup>-1</sup>	а
12	$HO_2 + CH_2O \rightarrow HOCH_2O$	$(2.3 \pm 0.8) \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	а
8	$HO_2 + CH_2O \rightarrow HO_2CH_2O$	$(2.4 \pm 0.5) \times 10^3$ M <sup>-1</sup>	b
9	$HO_2CH_2O \rightarrow HO + HCO_2H$	$(1.4 \pm 0.3) \times 10^{5}$ M <sup>-1</sup>	С
15 16	$HO_2 + wall \rightarrow products$ $HO_2CH_2O + wall \rightarrow products$		
3	$H + CH_2O \rightarrow H_2 + HCO$	$1.01 \times 10^{8}$ M <sup>-1</sup> s <sup>-1</sup>	d
6	$H + O_2 + CH_2O \rightarrow HO_2 + CH_2O$	$\begin{array}{c} (3.3 \pm 1.7) \times 10^{10} \\ M^{-2} \ s^{-1} \end{array}$	е
7	$H + O_2 + CO_2 \rightarrow HO_2 + CO_2$	$(4.0 \pm 0.7) \times 10^{10}$ M <sup>-2</sup> s <sup>-1</sup>	e, f
		$\begin{array}{c} (4.7 \pm 1.2) \times 10^{10} \\ M^{-2} \ s^{-1} \end{array}$	e, g
		$(5.6 \pm 2.1) \times 10^{10}$ M <sup>-2</sup> s <sup>-1</sup>	h
		$(4.8 \pm 1.3) \times 10^{10}$ M <sup>-2</sup> s <sup>-1</sup> (av)	

<sup>a</sup> Based on  $k_{10} + k_{11} + k_{12} = 7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>b</sup>  $k_8/k_{15}$ average vaue from H<sub>2</sub> and CO data in Table I. <sup>c</sup>  $k_9/k_{16}$  average value from H<sub>2</sub> and CO data in Table I. <sup>d</sup>  $k_3$  value based on ref 25 and 26; see text. <sup>e</sup> Based on above  $k_3$  value. <sup>f</sup> Data in Table III. <sup>g</sup> Data in Table IV. <sup>h</sup> Data in Table V.

significant pressure effect on product distribution.

Another aspect of our mechanism that needs a more detailed inspection is the  $HO_2$ -CH<sub>2</sub>O addition reaction and the subsequent reactions of the hydroperoxyhydroxymethyl radicals (HO<sub>2</sub>CH<sub>2</sub>O). Su et al.<sup>17</sup> found that by internal H transfer the HO<sub>2</sub>CH<sub>2</sub>O rearranges to O<sub>2</sub>CH<sub>2</sub>OH and that this reaction sequence is reversible

$$O_2CH_2OH \approx HO_2CH_2O \approx HO_2 + CH_2O$$
 (27)

In the present system in which the lowest  $CH_2O$  pressure was about 100 times higher than in the direct and  $Cl_2$ -sensitized study by Su et al. there is, however, no evidence for the reversibility of the  $HO_2$ - $CH_2O$  reaction. In any case, if reaction 8 is indeed reversible, then the present results indicate that at 373 K and in the  $CH_2O$  pressure range of 10–160 torr the equilibrium of this reaction is completely shifted to the right.

According to the reaction scheme proposed unimolecular decomposition reaction 9 and wall termination (reaction 16) are the only reactions of the HO<sub>2</sub>CH<sub>2</sub>O radical. In other studies<sup>6,7,16</sup> the occurrence of other reactions of HO<sub>2</sub>CH<sub>2</sub>O or its isomer HOC-H<sub>2</sub>O<sub>2</sub> was considered. These reactions are

$$HO_2CH_2O + HO_2 \rightarrow HO_2CH_2OH + O_2$$
 (28)

$$HO_2CH_2O + CH_2O \rightarrow HO_2CH_2OH + HCO$$
 (29)

$$2HO_2CH_2O \rightarrow 2HOCH_2O + O_2 \tag{30}$$

A mechanism of formic acid formation via reaction 28 followed by decomposition of  $HO_2CH_2OH$  (reaction 31) has been proposed

$$HO_2CH_2OH \rightarrow HCO_2H + H_2O$$
 (31)

by Su et al.<sup>17</sup> Reaction 28 is a biradical termination reaction that should follow second-order kinetics. Therefore, the occurrence of this reaction in the present system cannot be reconciled with the observed first-order termination kinetics. It is well established now that formaldehyde oxidation kinetics depends very strongly on wall properties and cell geometry. The transition from first-order termination in the present system to the second-order termination kinetics observed by Su et al.<sup>17</sup> presumably reflects differences of this kind. It should also be noted that reaction 28 is somewhat similar to the disproportionation reaction of HO<sub>2</sub> radicals which is pressure dependent and has a negative activation energy.<sup>29</sup> The occurrence of reaction 28 at 373 K and at low pressures is therefore less likely than at room temperature and high pressures.

The possibility that at 373 K HO<sub>2</sub>CH<sub>2</sub>O or HOCH<sub>2</sub>O<sub>2</sub> might abstract H atoms from CH<sub>2</sub>O has been raised by Horner and co-workers,<sup>6,7</sup> while Su et al.<sup>17</sup> concluded that this reaction is not important at room temperature. A large variation of  $\Phi_{\rm H_2}/\Phi_{\rm CO}$ and  $\Phi_{-O_2}/\Phi_{H_2}$  with CH<sub>2</sub>O pressure can be expected if the Htransfer reaction is important. In the present system significant change of product distribution with CH<sub>2</sub>O pressure was not observed; hence, it appears that reaction 29 does not take place. This H-transfer reaction presumably requires a considerable activation energy and at 373 K is still too slow to compete with wall termination and unimolecular decomposition. We tend to believe that under our experimental conditions the latter two reactions are also much faster than reaction 30.

In the derivation of the rate constants listed in Table VI the variation of the termination rate constants with pressure was ignored. This approximation bears no effect on those of the rate constants that were derived from product distribution, namely, the relative values of  $k_{10}$ ,  $k_{11}$ , and  $k_{12}$ . The rate constants determined from experiments carried out over a narrow pressure range, as those listed in Tables II-IV, should also be quite accurate. On the other hand, a considerable error might have been introduced into the rate constants that are based on the experiments in Tables I and V in which the total pressure was increased by more than 1 order of magnitude. The potential consequences of neglecting pressure effects in the latter case could be quite serious and therefore warrant a more detailed inspection.

Diffusion of radicals to the walls of the cell is slowed down as the pressure in the cell increases. Pressure growth thus results in lower termination rates that, in the absence of other effects, should cause an increase in the chain length, i.e., product quantum yields. Hence, upon addition of large amounts of  $CO_2$  to a

 $CH_2O-O_2$  mixture, this effect should, at least to some extent, offset the reduction in  $\Phi_{\rm H}$ , as a result of enhanced H atom scavenging via reaction 7. Consequently, the value of  $k_7$  determined from the results in Table V should be considerably lower than the value obtained from the results in Tables III and IV. Inspection of the  $k_7$  values listed in Table VI shows that this is not the case. It appears therefore that in the CH2O-O2-CO2 system the variation of the termination rate constants with pressure is small. The situation is not that clear in the case of the experiments in Table I in which the CH<sub>2</sub>O pressure was increased from 11 to 159 torr. Here the main effect should be on the ratio  $k_8/k_{15}$  derived from the slopes of the lines plotted according to expressions 18 and 19. The intercept values of these lines were used for the estimation of  $k_9/k_{16}$ . This procedure which in principle can be considered as equivalent to linear extrapolation of the pressure effects seems to be quite accurate. Undoubtedly though, pressure effects are at least to some extent superimposed on the results in Table I and are strongly reflected in the estimated values of  $k_8/k_{15}$ .

In conclusion, the present study despite it limitations clearly establishes the fact that a complete mechanism of formaldehyde oxidation has to account for the chain formation of hydrogen. This aspect of CH<sub>2</sub>O oxidation has been overlooked in most of the studies carried out so far. This work also shows that the addition of HO<sub>2</sub> to CH<sub>2</sub>O must be a key step in CH<sub>2</sub>O oxidation, even at quite high temperatures.

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# One- and Two-Electron Reduction of Aluminum and Tin Pyridylporphyrins. A Kinetic Spectrophotometric Study<sup>1</sup>

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Al<sup>III</sup>TPyP (TPyP = tetra-4-pyridylporphyrin), Al<sup>III</sup>TMPyP (TMPyP = tetrakis(*N*-methyl-4-pyridyl)porphyrin), Sn<sup>IV</sup>TMPyP,  $Sn^{IV}TPP$  (TPP = tetraphenylporphyrin),  $Sn^{IV}TPMMPyP$  (TPMMPyP = triphenylmono(*N*-methyl-4-pyridyl)porphyrin), and  $Sn^{IV}TPMPyP$  (TPMPyP = triphenylmono-4-pyridylporphyrin) were studied by steady-state and pulse radiolysis spectrophotometric techniques in neutral and alkaline aqueous and methanolic solutions. Both aluminum porphyrins (Al<sup>III</sup>P), in neutral and basic methanol, undergo one-electron reduction to form transient species which exhibit absorption maxima at 700 and 740 nm, respectively, and are thus characterized as ligand radicals (Al<sup>III</sup>P). These species decay by disproportionation with second-order rate constants of  $\sim 10^8 - 10^9$ . The final products depend on the nature of the porphyrin and the medium but are mainly phlorins (Al<sup>III</sup>PH<sub>2</sub> or Al<sup>III</sup>PH<sup>-</sup>). Factors which influence the formation of final products are discussed. The tin(IV) pyridylporphyrins form one-electron-reduced species  $(Sn^{IV}\dot{P})$  which are stable in alkaline aqueous and methanolic solutions. These products can be further reduced to give the phlorin. In neutral or acidic solutions the 1e-reduction products disproportionate rapidly into phlorin and porphyrin. Sn<sup>IV</sup>TPP exhibits a different behavior in that the 1e-reduced species is not very long-lived and the 2e-reduction product is mainly a chlorin rather than a phlorin.

## Introduction

One-electron reduction of tetraphenylporphyrins (TPP) and tetrakis(N-methylpyridyl)porphyrins (TMPyP) leads to the formation of radical ions which exhibit absorption maxima around 700-750 nm.<sup>2,3</sup> However, disproportionation of these radicals in protic solvents was found to lead to different products. Radiolytic experiments in methanol showed that all the TMPyP metallo complexes and free bases are reduced predominantly to phlorins.<sup>3</sup> On the other hand, the TPP complexes form mainly

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