

THE PHOTOOXIDATION OF CH₂O AT 3130 Å IN THE ABSENCE AND PRESENCE OF NO

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Summary

CH₂O was photolyzed at 3130 Å and 296 K in the absence and presence of O₂. With O₂ present photolyses were also done with excess N₂, CO₂ or He present. The products of the reaction were CO and H₂, both produced with a quantum yield of unity in the absence of O₂. In the presence of O₂, HCOOH was also produced with a quantum yield which increased to 2.0 as the O₂ pressure was raised above 100 Torr. The presence of O₂ first increased the CO yield, but then reduced both the CO and H₂ yields to zero as the O₂ pressure was raised above 100 Torr. The results are interpreted in terms of the primary process



The intermediate I is probably either triplet CH₂O or the H $\dot{\text{C}}$ OH biradical. The ratio k_{1a}/k_1 was found to be 0.61 ± 0.15 in satisfactory agreement with other studies and $k_4/k_{1a} = 0.43 \pm 0.03 \text{ Torr}^{-1}$.

In the presence of 50 Torr O₂ and a few millitorr NO, a long chain oxidation occurs to produce NO₂, HCOOH and CO. Thus the intermediate IO₂ must react with NO to produce radical fragments, presumably by the reaction



The oxygenated radicals (HO₂ and probably HCO₃ and HCO₂) also react with NO to give NO₂.

1. Introduction

A knowledge of the photooxidation of aldehydes is important for understanding the free radical induced formation of photochemical smog. It is believed that these photooxidations may be the primary source of free radicals in polluted urban atmospheres. However, the only simple aldehyde whose photooxidation has been well characterized is CH_3CHO [1]. Therefore we have undertaken the study of the photooxidation of the simplest aldehyde, CH_2O . Not only is this aldehyde present in polluted atmospheres, but it must also be present in the stratosphere as the result of CH_4 oxidation.

The photolysis of CH_2O in the absence of O_2 has been well studied and the results have recently been reviewed [2]. There are two primary processes with absorption into the first excited $n-\pi^*$ singlet band at about 3100 Å. One process gives $\text{H} + \text{HCO}$ and the other $\text{H}_2 + \text{CO}$. The former products correlate with the triplet state and the latter products with high vibrational levels of the ground state. The initially formed singlet state correlates with $\text{H} +$ electronically excited HCO but there is insufficient energy for this photodissociation to occur. Furthermore when the singlet is excited there is a delay in product formation which is greater than the lifetime of the singlet state [3]. Thus it can be said with certainty that products do not arise directly from the excited singlet state.

Miller and Lee [4] used triplet benzene to sensitize triplet CH_2O and found that about $\frac{1}{3}$ of the triplet CH_2O led to $\text{H}_2 + \text{CO}$ production. Thus the formation of $\text{H}_2 + \text{CO}$ when singlet CH_2O is excited may involve passage through the triplet state. In contrast, Sodeau and Lee [5] photolyzed CH_2O in a low temperature matrix and found evidence for the HCOH biradical, which they believe to be a precursor of product formation formed from the excited singlet CH_2O .

Recent work on the quantum yields of product formation has been performed by Horowitz and Calvert [6, 7] who photolyzed CH_2O in the absence and presence of various scavengers to determine the quantum efficiencies of the two primary processes. In their second paper [7] they determined the wavelength dependence of the primary processes and in their first paper [6] they carefully determined the efficiencies at 3130 Å and 25 °C. They found that, in the absence of foreign gases at 3130 Å and 25 °C, the quantum yields of H_2 and CO were both 1.0 to within the experimental uncertainty (about 10%). In the presence of isobutene or NO , $\Phi(\text{H}_2)$ was reduced to 0.32 ± 0.03 . From these results they concluded that the quantum efficiency of the free radical process $\text{H} + \text{HCO}$ was 0.68 ± 0.03 and that for the molecular process $\text{H}_2 + \text{CO}$ was 0.32 ± 0.03 . The results of Clark *et al.* [8] at 2991 Å in the presence of excess NO and those of Lewis and Lee [9] at 3035 Å in the presence of butene-1 are consistent with these values. In the presence of C_3H_6 , a slightly higher radical yield of 0.75 ± 0.02 was found by Moortgat *et al.* [10] for exciting wavelengths between 2950 and 3163 Å.

In the photooxidation of CH_2O excited into the first allowed singlet absorption ($n-\pi^*$), the products were shown to be HCOOH , CO , CO_2 , H_2

and a polymer [11, 12]. Later H_2O_2 was also identified [13, 14]. Bufalini and Brubaker [14] rationalized the imbalance between peroxide formed and CH_2O consumed to be caused by radical decomposition and surface effects.

Osif [15] photooxidized CH_2O at pressures at or above 2 Torr at 3130 Å and 23 °C and obtained $\{\Phi(\text{CO}) - \Phi(\text{H}_2)\}/\Phi(\text{CO}) \approx 0.76$ independent of all conditions. However in several studies done in different vacuum lines $\Phi(\text{CO})$ was not reproducible. It varied from 0.75 to 6.7. The same high quantum yields of about 6 were reported by Horowitz and Calvert [7] and by Su *et al.* [16] in the photooxidation of CH_2O at room temperature. Clearly the high yields indicated some chain process which was not characterized and may be due to surface effects. At lower CH_2O pressures (below 0.075 Torr), however, Moortgat *et al.* [10] found $\Phi(\text{CO}) = 1.0$ and the radical yield to be about 0.80 ± 0.03 in the presence of 1 atm of air for incident wavelengths near 3130 Å. However, they did not perform photolyses with 3130 Å radiation.

We have restudied the photooxidation of CH_2O at 3130 Å and room temperature (about 23 °C) in a very large Teflon-lined cell in order to eliminate the wall reactions and to establish the effect of O_2 . The results are reported here.

2. Experimental

The gases used in these experiments were irradiated at room temperature in a long path infrared (LPIR) cell obtained from the Wilks Scientific Company. The LPIR was vertically mounted in a Beckman model 10 infrared Spectrometer. The cell was Teflon lined and had gold mirrors and a volume of 11 l. The path length for the photolysis was set at 4.0 m, and the path length for the infrared analysis was set at 40.5 m. The gases were added to the LPIR cell through a mixing tube which ran parallel to the cell axis and consisted of 10 mm o.d. Teflon tubing with 0.5 mm holes every 4 cm. The irradiations were done through a quartz window in the LPIR cell. The light source was a Hanovia 140 W medium pressure mercury lamp. The light was focused with a quartz lens before passing through an Ealing 3130 Å interference filter and into the cell. The filter was checked periodically for its transparency at 3130 Å on a Cary 14 spectrophotometer.

A conventional mercury-free high vacuum line employing Teflon stopcocks with Viton "O" rings was used in transferring the gases. Pressures were measured with a silicone oil manometer, a 0 - 800 Torr Wallace and Tiernan absolute pressure gauge and a Veeco thermocouple gauge.

The formaldehyde was prepared from paraformaldehyde (Aldrich Chemical Co.) by a procedure developed by Spence and Wild [17]. The formaldehyde was stored at -196 °C and was degassed before each experiment. The oxygen and nitrogen (Philip Wolf and Sons, Inc.) were passed through a liquid-nitrogen-cooled trap containing glass wool before entering the vacuum line to eliminate trace amounts of CO_2 . The helium (Air Products)

was used without any purification. The carbon dioxide (Philip Wolf and Sons, Inc.) contained 0.57% N₂ and 0.18% O₂. The experiments with CO₂ as an inert gas were corrected for impurities. The azomethane was prepared by the method developed by Renaud and Leitch [18]. The azomethane was stored in a darkened storage bulb to prevent light from decomposing it. Nitric oxide (Matheson) was purified by vacuum distillation from -189 °C to -196 °C. The gases condensable at -196 °C were transferred and were kept in a darkened storage bulb.

For the runs in the absence of O₂, actinometry was done by the photolysis of azomethane at 3130 Å for which $\Phi(N_2) = 1.0$. The actinometer runs were done using matched absorbances of azomethane and CH₂O, the necessary pressure ratio being determined from their respective extinction coefficients (to base 10) of 1.67×10^{-4} and 1.23×10^{-4} Torr⁻¹ cm⁻¹ at 3130 Å and 296 K. Since the quantum yield of CO from CH₂O photolysis was verified to be 1.0 in the absence of O₂, it was used as an actinometer for the photooxidation of CH₂O.

After photolysis aliquots of sample from the LPIR cell were analyzed for CO, CO₂ and H₂ on Gow-Mac chromatographs with thermistor detectors at 0 °C. The CO was separated on a copper column 8 ft in length and with 0.25 in o.d. packed with 30/60 mesh of Molecular Sieve 13X. The CO₂ was separated on a copper column 11 ft in length and with 0.25 in o.d. with 50/80 mesh of Porapak QS packing. Helium was the carrier gas for the Porapak QS and the Molecular Sieve 13X columns. The H₂ was separated on a copper column 12 ft in length and with 0.25 in o.d. packed with 80/100 mesh of Molecular Sieve 5A. The carrier gas was argon. Formic acid was analyzed by infrared absorption at 1090 cm⁻¹. This band, which is considered to be strong [19], is in a region with little CH₂O interference. Nitrogen dioxide was determined by measuring the absorbance at 1629 cm⁻¹.

Calibration curves for CO, CO₂, H₂, HCOOH and NO₂ were determined using standard samples in the millitorr region of each compound. Formic acid exists as a mixture of a monomer and a dimer in the gas phase with an equilibrium constant *K* of 1.91 Torr at 296 K [20]. This equilibrium was taken into account when calculating formic acid pressures.

A standard sample of NO₂ was prepared by allowing a known amount of NO to react with an atmosphere of O₂ to produce a known amount of NO₂ in the LPIR cell. The absorbance of NO₂ could then be measured as a function of its pressure.

3. Results

Most irradiations were performed with 3130 Å radiation at room temperature with 2.00 Torr of CH₂O initially present. This pressure was used to minimize the percent decomposition of CH₂O needed to measure the product quantum yields and to minimize the dark polymerization of CH₂O which becomes significant at higher pressures [21]. The O₂ pressure was varied

from 0 to 162 Torr and the total pressure of the system was varied from 2.0 to 760 Torr by the addition of N₂, He or CO₂. The samples were irradiated from 2.0 to 24 h at absorbed intensities I_a of 0.58 - 1.97 mTorr h⁻¹. In the dark no products were formed but the CH₂O slowly disappeared by polymerization.

Table 1 contains the quantum yields of the measured products. The products measured were CO, H₂ and HCOOH. CO₂ was present as an 0.1% impurity in the CH₂O but there was no evidence for production of additional amounts either in the dark or during irradiation.

In the absence of O₂, HCOOH is not produced and $\Phi(\text{CO}) \approx \Phi(\text{H}_2) \approx 1.0$, in agreement with other recent measurements [6 - 10]. In the presence of even small amounts of O₂, HCOOH becomes a major product. As the O₂ pressure increases, $\Phi(\text{HCOOH})$ rises to a value of about 2. The CO yield rises with the addition of small amounts of O₂ and then decreases as the O₂ pressure is further raised, its quantum yield approaching zero at O₂ pressures exceeding 100 Torr. At O₂ pressures greater than 40 Torr, the O₂ and CO

TABLE 1

The product quantum yields from the photooxidation of formaldehyde at 3130 Å and room temperature^a

[O ₂] ₀ (Torr)	Irradiation time (h)	I_a (mTorr h ⁻¹)	$\Phi(\text{CO})$	$\Phi(\text{H}_2)$	$\Phi(\text{HCOOH})$
0.00	6.0	1.00	1.0	0.97	0.0
0.00	2.0	1.10	1.0	1.0	0.0
0.00	5.5	1.97	0.92	—	0.0
0.00	6.0	1.97	1.0	—	0.0
0.00 ^b	6.0	1.00	—	0.078	—
0.032 ^c	6.0	1.41	1.3	1.3	—
0.042 ^d	6.0	1.00	n	1.0	1.21
0.067	5.5	1.97	1.1	0.90	—
0.071	6.0	1.00	1.0	0.73	0.45
0.12	6.0	0.58	1.1	0.63	—
0.22	6.0	0.58	1.0	0.40	—
0.55 ^d	5.5	1.97	n	0.86	—
1.13	6.0	1.41	1.2	0.85	—
1.25	6.0	1.22	0.91	0.54	0.89
1.31	5.0	1.41	0.80	0.73	—
4.29	6.0	1.10	0.54	0.35	—
4.64	6.0	1.00	0.42	0.31	1.22
4.94	6.0	1.41	—	0.42	—
5.31	6.0	1.30	0.64	0.31	—
6.02	6.0	1.41	0.42	0.20	—
6.26	6.0	1.10	0.52	0.30	—
9.02	6.0	1.41	0.48	0.26	—
9.90	6.0	1.22	0.33	0.19	1.50
10.5	6.0	1.40	0.27	0.15	—
12.1	6.0	1.10	0.33	0.18	—
14.6	5.5	1.40	0.21	0.099	—

(continued overleaf)

TABLE 1 (continued)

[O ₂] ₀ (Torr)	Irradiation time (h)	I _a (mTorr h ⁻¹)	Φ(CO)	Φ(H ₂)	Φ(HCOOH)
17.4 ^e	6.0	1.44	0.43	0.13	—
18.9	6.0	1.40	0.19	0.067	—
20.1	6.0	1.00	0.29	0.18	1.65
21.2	6.0	1.10	0.22	0.10	—
23.2	6.0	1.41	0.34	0.12	—
29.8 ^f	5.0	1.44	0.27	0.050	—
33.8	6.0	1.40	0.16	0.098	—
39.4 ^g	5.75	1.44	0.24	0.013	—
42.0	6.0	1.10	0.098	0.073	—
44.0	6.0	1.40	0.088	0.013	—
47.9	19.0	1.10	0.080 ± 0.005 ^o	0.072 ± 0.010 ^q	—
48.0	6.0	1.22	0.040	0.040	1.80
48.0	6.0	1.41	0.055	0.0063	—
48.0	6.0	1.41	0.067	0.066	—
48.0 ^h	6.0	1.41	0.096	r	—
50.4 ⁱ	24.0	0.20	<0.10	0.09	1.84
51.3	24.0	1.00	0.09	0.06	3.7
63.0	6.0	1.10	0.10	0.091	—
73.0	6.0	1.10	0.074	0.084	—
98.0	6.0	1.22	p	0.060	1.97
98.0 ^j	6.0	1.00	0.02	0.04	—
98.0	5.0	1.97	0.020	0.028	—
148	6.0	1.10	0.024	0.0	—
155 ^k	24.0	0.088	p	0.0	—
158	6.0	1.22	p	0.0	2.12
158	6.0	1.30	0.050	0.0	—
159 ^l	6.0	1.30	n	0.0	—
162 ^m	6.0	1.30	n	0.0	—

^a Formaldehyde pressure = 2.00 Torr except for indicated runs.

^b 6.74 Torr NO present.

^c 48.0 Torr of N₂ present.

^d 98.0 Torr of N₂ present.

^e 2.7 Torr N₂ and 478 Torr CO₂ present.

^f 2.7 Torr N₂ and 468 Torr CO₂ present.

^g 2.6 Torr N₂ and 456 Torr CO₂ present.

^h 450 Torr He present.

ⁱ 0.40 Torr CH₂O.

^j 4.5 mTorr CO and 10.0 mTorr H₂ present initially. Final measured values are 4.6 and 10.2 mTorr respectively.

^k 0.202 Torr CH₂O.

^l 599 Torr N₂ present.

^m 598 Torr N₂ present.

ⁿ Not measurable. Nitrogen peak too large.

^o Average of four measurements.

^p Not measurable. Oxygen peak too large.

^q Average of six measurements.

^r Not measurable. Helium peak too large.

peaks are not resolved on the gas chromatogram, so that $\Phi(\text{CO})$ cannot be measured accurately. Also with the addition of 600 Torr of N_2 , the CO peak is completely obscured and could not be measured. With the addition of O_2 , $\Phi(\text{H}_2)$ decreases even more rapidly than $\Phi(\text{CO})$ and no H_2 was observed at O_2 pressures exceeding 100 Torr.

No performic acid was observed in the infrared spectrum. It is believed to be unstable in this system and to convert to HCOOH . Thus if performic acid were formed it would probably not be observed, but would instead appear as HCOOH (or CO_2 and H_2O).

The quenching of H_2 and CO by the addition of O_2 was surprising, so that a few additional runs were done and they are also included in Table 1. One run was done in which 6.74 Torr of NO rather than O_2 was added and the H_2 yield was markedly quenched to 0.078. No CO yield was obtained because the NO interfered with its measurement. The H_2 yield is much lower than that obtained by others [6, 8]. To check that CO or H_2 was not being lost in the analysis, one run was done with CO and H_2 added initially and very little additional was produced during irradiation. Likewise a dark run was done with CO and H_2 added (not shown in the table) and more than 90% of the CO and H_2 was recovered. In one run in Table 1, several aliquot portions of the irradiation mixture of 47.9 Torr O_2 and 2 Torr CH_2O were analyzed. Good reproducibility was found. Finally two runs were done with 0.202 and 0.40 Torr of CH_2O at high O_2 pressures to check for a CH_2O pressure effect. The inhibiting effect of O_2 was still seen.

A few runs were done with the 3130 Å interference filter removed and replaced by a Corning 0-54 filter to remove radiation below 3000 Å. In this way both the light intensity is increased and additional wavelengths (3020, 3340 and 3660 Å) are incident on the cell. The runs were done with 2.0 Torr CH_2O . In the absence of O_2 , 2.2 ± 0.2 mTorr h^{-1} of CO were produced. As O_2 was added both the H_2 and CO yield dropped to a limiting value of $18 \pm 2\%$ of that in the absence of O_2 for O_2 pressures of 39 - 100 Torr. Under these conditions the free radical process is eliminated but apparently not all of the molecular photodecomposition, which presumably comes from the higher wavelength radiation (*i.e.* 3340 Å). As before, large quantum yields of HCOOH were obtained.

One run was done with 2.0 Torr CH_2O and 48 Torr O_2 with a full arc with neither filter being used. In the absence of O_2 , CO was produced at a rate of 2.3 mTorr h^{-1} . In the presence of 48 mTorr O_2 there was a reduction in the CO and H_2 yields to below 30% and to 22%, respectively, of the yields in the absence of O_2 .

A series of runs was done at 3130 Å and room temperature with both 50 Torr O_2 and small amounts of NO present. The results are shown in Table 2. The products were NO_2 , CO and HCOOH , all formed with quantum yields in excess of unity, indicating a long chain process. Analyses for both H_2 and CO_2 indicated them to be absent. Because of the large yields, the NO is consumed rapidly. Initial quantum yields of HCOOH and NO_2 are reported because they are monitored continually by *in situ* infrared analysis. For CO,

TABLE 2

Initial product quantum yields from the photooxidation of CH₂O in the presence of NO at 3130 Å and room temperature^a

[NO] (mTorr)	Irradiation time (s)	Φ(HCOOH) ^c	Φ(NO ₂)
[CH ₂ O] = 2.00 Torr, [O ₂] = 48.5 ± 2.0 Torr, I _a = 1.1 mTorr h ⁻¹			
6	1200	41 ± 19	14
10	3000	13	11
10 ^b	1800	—	11
15	2400	7.9	7.4
26	1800	8 ± 6	8.0
[CH ₂ O] = 0.40 Torr, [O ₂] = 52.2 ± 1.2 Torr, I _a = 0.20 mTorr ⁻¹ h ⁻¹			
10	4500	<1.9	29
10	4500	<1.7	28
10 ^b	3600	<1.5	22

^a At the end of each run CO, H₂ and CO₂ were also analyzed. No H₂ or CO₂ were found, their quantum yields being below 0.2 at 2.0 Torr CH₂O and below 0.4 at 0.4 Torr CH₂O. The CO measurements were not reproducible because of the small amount of CO and the large amount of O₂ present. The integrated CO quantum yields were in the range of 1.5 - 6.

^b 700 Torr He also present.

^c The HCOOH quantum yields are quite scattered owing to the low absorption produced.

the initial quantum yield cannot be obtained since it is analyzed after termination of the irradiation. In order to get enough CO to measure, much of the NO had been consumed and the NO₂ production had been retarded. The NO₂ yield is the most reliable. At 2.0 Torr CH₂O, its quantum yield drops slightly from 14 to 8 as the NO pressure is raised from 6 to 26 mTorr. However with 0.40 Torr CH₂O, the NO₂ quantum yield is considerably higher, being about 25 with 10 mTorr NO present. Similar results (not shown) were obtained with the Corning 0-54 filter replacing the 3130 Å filter.

4. Discussion

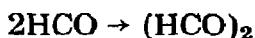
The most remarkable finding in this study is that the addition of excess O₂ quenches the CO and H₂ yields, contrary to all previous findings [7, 10, 15, 16] including those in our laboratory [15]. In previous results in the presence of O₂, Φ(CO) was found to remain near 1.0 [10, 13, 15] or to increase to a value in excess of 6 [7, 15, 16]. Φ(H₂) was typically about 0.24Φ(CO). The difficulty with the previous studies is that there was no consistent value for Φ(CO), even though the most recent study of Moorgat *et al.* [10] gave the expected value of 1.0. However different sets of experiments by Osif [15] gave values for Φ(CO) ranging from about 0.8 in one set of experiments to more than 6.0 in another set of experiments. We attribute these earlier results either to wall photolysis of the polymer or to a chain oxidation induced by either the walls or higher free radical concentrations

than those present in our study. The second finding of interest is that $\Phi(\text{HCOOH})$ is very large in the presence of O_2 , being about 2.0 at high O_2 pressures, even though CO and H_2 are completely quenched.

In the absence of O_2 , the results are the same as those reported by others and the mechanism is



This mechanism gives $\Phi(\text{CO}) = \Phi(\text{H}_2) = 1.0$ in conformance with the observations. In order to fit the observations it is necessary that all the HCO radicals give $\text{CH}_2\text{O} + \text{CO}$ according to reaction (3) and that the competing reaction to give glyoxal is unimportant:

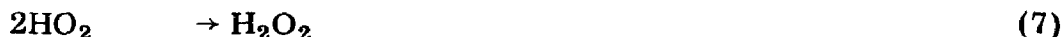


Other investigators [6 - 8] reached the same conclusion. Presumably any glyoxal that is formed has sufficient excess energy to decompose to $\text{CH}_2\text{O} + \text{CO}$ before being stabilized by collision. The intermediate I has been introduced to account for the observation that decomposition is not directly from the excited singlet state as discussed in Section 1. I might be the triplet state of CH_2O or the biradical $\text{H}\dot{\text{C}}\text{OH}$ preferred by Sodeau and Lee [5] or some other species.

In the presence of O_2 at 3130 Å, our results clearly indicate that the intermediate I is scavenged because the CO and H_2 yields are reduced to zero at high O_2 pressure. Thus we propose the steps



This mechanism also accounts for $\Phi(\text{HCOOH}) = 2.0$ at high O_2 pressures. At lower O_2 pressures reaction (1) still occurs and the fate of the H atom, in addition to reaction (2), is



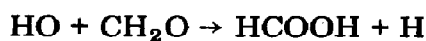
The oxidation of HCO has been a subject of much debate. Everyone agrees that CO is formed and that CO_2 is not formed. However, the debate centers around whether HCO can add O_2 in a third order reaction eventually to produce HCOOH . Work in our laboratory [15, 21] on the oxidation of CH_2O shows that HCOOH is produced and is consistent with its production through the chain oxidation of HCO . Also Niki *et al.* [22] have seen HCOOH in CH_2O oxidation and they conclude that HCO addition to O_2 must be important. However, Shibuya *et al.* [23] found no pressure dependence on

HCO oxidation and concluded that only the direct production of $\text{HO}_2 + \text{CO}$ occurs. Possibly the HCOOH seen in the oxidation studies could come not from HCO oxidation, but from the reaction of either HO_2 or H_2O_2 with CH_2O . This argument for H_2O_2 as the reactive agent can be excluded for two reasons.

(1) $\Phi(\text{HCOOH})$ was too large (about 10) in the study of Osif *et al.* [21] to be produced solely by H_2O_2 oxidation. A chain mechanism must have been involved.

(2) In the studies reported here in the presence of NO , all the HO_2 is scavenged by the NO and no H_2O_2 is produced, yet HCOOH is produced in a chain reaction.

Neither argument is conclusive against HO_2 as the chain carrier since the HO radicals generated by the $\text{HO}_2\text{-CH}_2\text{O}$ or $\text{HO}_2\text{-NO}$ reaction might react with CH_2O to produce HCOOH , as suggested by Su *et al.* [16]:



However, there is not much evidence for HCOOH formation by either HO_2 or HO reactions.

Perhaps the apparent conflict can be resolved if we discard the usually accepted formation of CO through direct transfer of an H atom from HCO to O_2 and consider the HCO oxidation to proceed as follows:



If $k_{-8} \ll k_9$, then the rate of disappearance of HCO is independent of the total pressure.

Performic acid is known to be unstable and to decompose readily on surfaces to formic acid [19]. In a glass-Teflon system similar to ours, Maker *et al.* [24] found HCO_3H decomposition to be less than 15% in 30 min. However, the experiments performed in Table 1 for which HCOOH was measured lasted at least 6 h, so that decomposition should be fairly complete. Furthermore HCO_3H has a band shifted only 20 cm^{-1} to higher frequencies than HCOOH , so that the two compounds would be difficult to distinguish from each other.

With small additions of O_2 , reactions (8) - (12) become important before reactions (4) and (6); HCOOH is formed and $\Phi(\text{CO})$ rises, while $\Phi(\text{H}_2)$ is not much affected. As more O_2 is added, the quenching reaction (4) becomes important, both $\Phi(\text{CO})$ and $\Phi(\text{H}_2)$ fall, but $\Phi(\text{HCOOH})$ continues to increase because of reaction (5). With further increases in O_2 or total pressure, reaction (6) becomes important, and $\Phi(\text{H}_2)$ falls even faster than $\Phi(\text{CO})$.

A steady state analysis on I and the free radicals leads to the result that

$$\{\Phi(\text{CO}) - \Phi(\text{H}_2)\}^{-1} = k_1/k_{1a} + k_4 [\text{O}_2]/k_{1a} \quad (\text{I})$$

Figure 1 is a plot of the left-hand side of eqn. (I) *versus* $[\text{O}_2]$. The plot gives a reasonable straight line. The intercept gives $k_{1a}/k_1 = 0.61 \pm 0.15$ in good agreement with the more accurate value of 0.68 obtained by Horowitz and Calvert [6]. The slope of Fig. 1 gives $k_4/k_{1a} = 0.43 \pm 0.03 \text{ Torr}^{-1}$.

The mechanism further predicts that

$$\{[\Phi(\text{H}_2) - \beta](k_1/k_{1a} + k_4[\text{O}_2]/k_{1a})\}^{-1} = 1 + k_6[\text{O}_2][\text{M}]/k_2[\text{CH}_2\text{O}] \quad (\text{II})$$

where

$$\beta \equiv k_{1b}/(k_1 + k_4[\text{O}_2])$$

The function β can be computed from the parameters k_1/k_{1a} and k_4/k_{1a} evaluated from Fig. 1, since $k_{1b} \equiv k_1 - k_{1a}$. Thus the left-hand side of eqn. (II) can be computed and it is plotted against $[\text{O}_2][\text{M}]/[\text{CH}_2\text{O}]$ in Fig. 2, where $[\text{M}]$ is taken to be $[\text{O}_2] + [\text{N}_2] + 2[\text{CO}_2] + 3[\text{CH}_2\text{O}]$. The data can be fitted by a straight line with an intercept of 1.0 and a slope of $0.033 \pm 0.010 \text{ Torr}^{-1}$. The slope is k_6/k_2 and agrees reasonably well with the value of

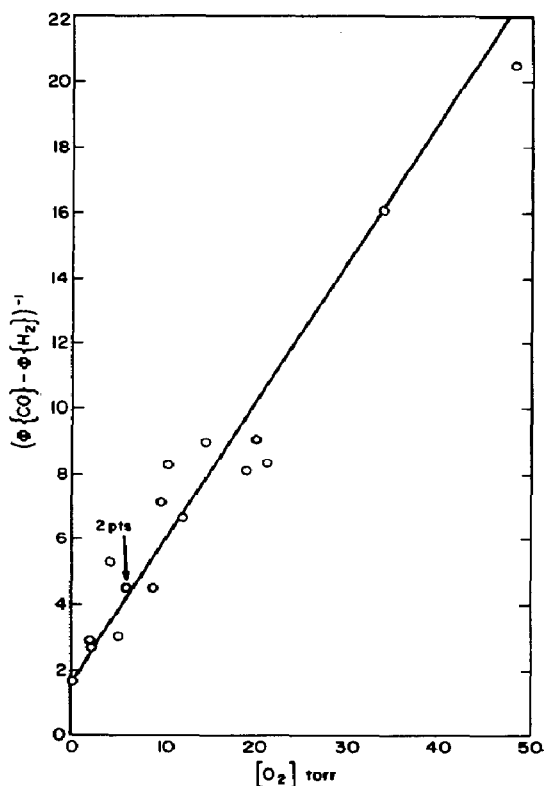


Fig. 1. Plot of $\{\Phi(\text{CO}) - \Phi(\text{H}_2)\}^{-1}$ vs. $[\text{O}_2]$ in the photooxidation of 2 Torr CH_2O at 3130 Å and room temperature.

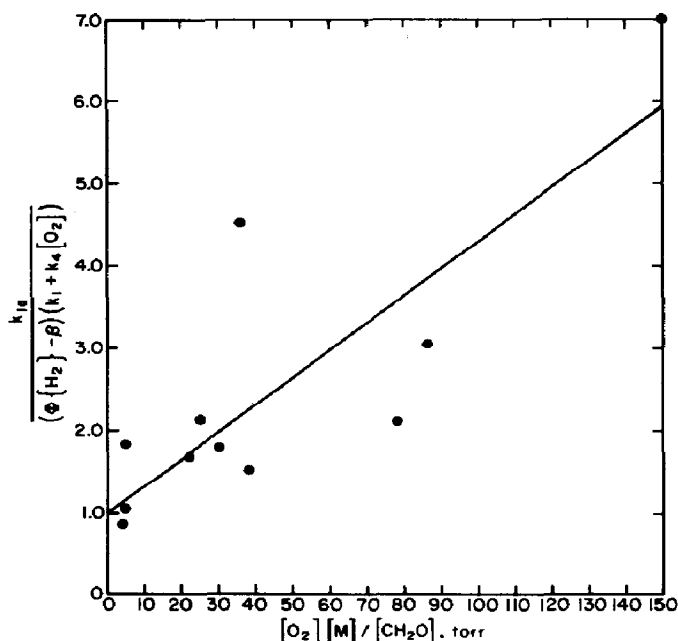


Fig. 2. Plot of $\{[\Phi(\text{H}_2) - \beta] (k_1/k_{1a} + k_4[\text{O}_4]/k_{1a})^{-1}$ vs. $[\text{O}_2][\text{M}]/[\text{CH}_2\text{O}]$ in the photooxidation of 2 Torr CH_2O at 3130 Å and room temperature. The values used for k_1/k_{1a} and k_4/k_{1a} were 1.65 and 0.43 Torr⁻¹ respectively. $[\text{M}]$ was computed as $[\text{O}_2] + [\text{N}_2] + 2[\text{CO}_2] + 3[\text{CH}_2\text{O}]$.

0.046 Torr⁻¹ computed from the rate coefficients listed in Hampson and Garvin [25]. The rate coefficient data are summarized in Table 3.

Now we comment on the fact that at low CH_2O pressures Moortgat *et al.* [10] found that $\Phi(\text{CO}) = 1.0$ and that $\Phi(\text{H}_2) = 0.20$ in the photolysis of CH_2O in air at incident wavelengths near 3130 Å. It should be noted that $\Phi(\text{H}_2)$ is different from the value found by others [6, 8] (and by us) of 0.32 in the absence of O_2 and is slightly lower than their own value of 0.25 in the presence of C_3H_6 . Perhaps at low CH_2O pressure other processes such as

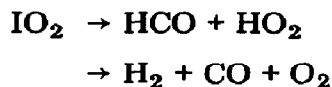


TABLE 3

Rate coefficient ratios

Ratio	Value	Units	Source
k_{1a}/k_1	0.68	None	Horowitz and Calvert [6]
k_{1a}/k_1	0.75	None	Moortgat <i>et al.</i> [10]
k_{1a}/k_1	0.61	None	This work
k_4/k_{1a}	0.43	Torr ⁻¹	This work
k_6/k_2	0.033	Torr ⁻¹	This work
k_6/k_2	0.046	Torr ⁻¹	Hampson and Garvin [25]

can compete with reaction (5). Alternatively, the formation of the intermediate I may be very wavelength specific and may appear only with incident radiation at 3130 Å.

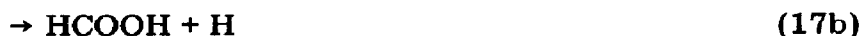
In the presence of NO, a long chain process occurs. This means that the IO₂ complex must react with NO to produce free radicals:



The free radicals also react with NO



and the HO radical can react with CH₂O or NO



Reaction (18) is the termination step which is needed. However $k_{17} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_{18} = (7.8 \pm 1.2) \times 10^{-31} \text{ cm}^3 \text{ s}^{-1}$ [25]. Thus with 2 Torr CH₂O, 50 Torr O₂ and 10 mTorr NO, the relative importance of reaction (17) to reaction (18) is 2200. This would lead to much longer chain lengths than observed. Furthermore the chain length should increase with the [CH₂O]/[NO] ratio, contrary to observation. Thus reaction (18) is not an important terminating step and some other termination must be involved. One possibility is that some of the HCO₂-NO reactions lead to formyl nitrite:



although there is no positive evidence for this reaction. Also the reaction of HCO₂ (if it is present) with CH₂O may also occur. Furthermore since CO₂ is not produced, HCO₂ (if it is present) apparently does not react with O₂ to produce CO₂.

The data show that an increase in CH₂O pressure reduces the chain length of NO₂ formation. Thus some species must react with CH₂O to terminate chains. This cannot be an odd electron species and leaves only IO₂ as the species which terminates via reaction (5). Thus further evidence is provided for the existence of IO₂.

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