

THE WAVELENGTH DEPENDENCE OF THE PHOTO-OXIDATION OF CH₂O

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Summary

The photo-oxidation of CH₂O in excess O₂ was studied at 253.7, 280.3, 312.8 and 326.1 nm at 25 °C. At all wavelengths except 253.7 nm, $\Phi(\text{CO}) = 1.0$. At 253.7 nm, $\Phi(\text{CO}) = 0.77$. The molecular photodecomposition is given by $\Phi(\text{H}_2)$, which is 0.28, 0.28, 0.16 and 0.40 respectively at the four wavelengths.

1. Introduction

The primary photochemical quantum yields for CH₂O are important for an understanding of atmospheric chemistry. Several groups have measured these yields over the past 10 years. In all of these experiments the quantum yields of CO and H₂, $\Phi(\text{CO})$ and $\Phi(\text{H}_2)$ respectively, have been measured in the presence of some additive that scavenges hydrogen atoms and converts HCO to CO. Thus $\Phi(\text{H}_2)$ is equal to the quantum yield for photodecomposition to CO + H₂, whereas $\Phi(\text{CO})$ represents the sum of this yield and the radical yield to form H + HCO.

Clark *et al.* [1] used excess NO to scavenge the radicals. They found $\Phi(\text{CO})$ to be 1.0 between 299 and 330 nm and to fall at higher wavelengths. Their values for $\Phi(\text{H}_2)$ were 0.30, 0.31, 0.48, 0.62, 0.69 and 0.29 respectively at 299 nm, 317 nm, 326 nm, 330 nm, 339 nm and 353 nm.

Lewis and Lee [2] used 1-butene as a radical scavenger. By measuring the C₃H₆ formed from the reaction of hydrogen with 1-C₄H₈, they determined the radical yield to be 0.68 ± 0.10 , 0.64 ± 0.10 and 0.68 ± 0.05 respectively at 275 nm, 288 nm and 304 nm. Thus the respective yields for the molecular elimination should be 0.32, 0.36 and 0.32.

Horowitz and Calvert [3, 4] used isobutene as the radical scavenger. In the absence of scavenger, where $\Phi(\text{H}_2) = \Phi(\text{CO})$, $\Phi(\text{H}_2)$ was found to be 1.0 independent of wavelength from 293 to 334 nm. In the presence of isobutene, $\Phi(\text{H}_2) = 0.32$, 0.28, 0.32 and 0.56 respectively at 289 nm, 293 nm, 313 nm and 330 nm.

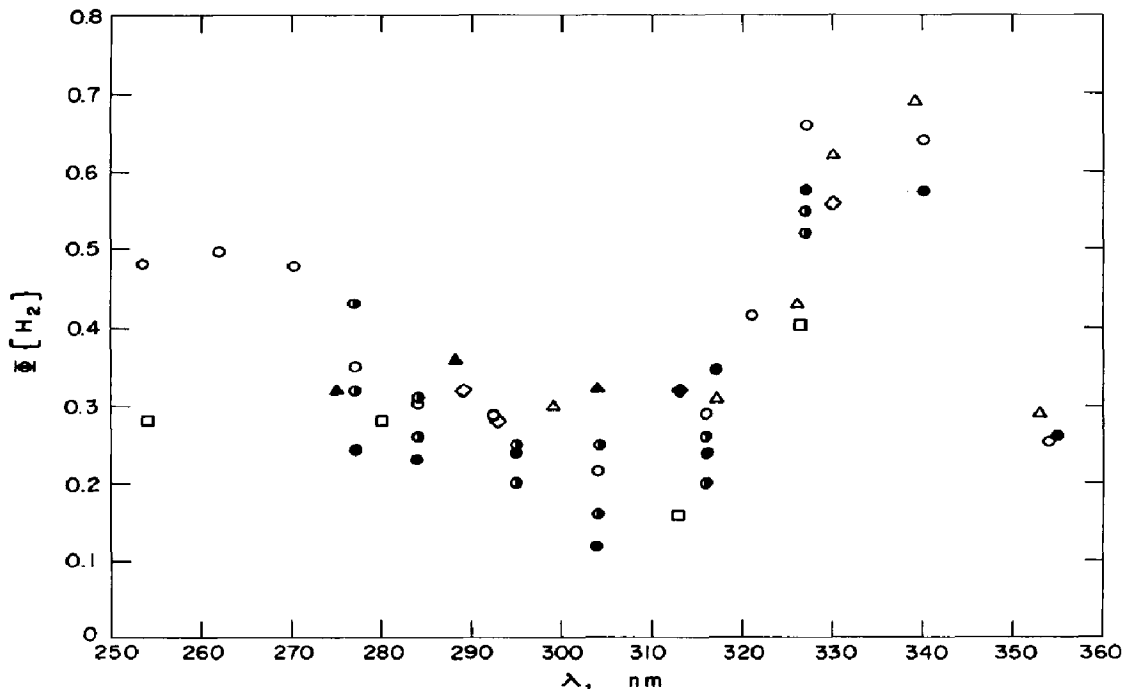


Fig. 1. Plot of $\Phi(\text{H}_2)$ in the presence of radical scavengers vs. wavelength at room temperature: Δ , Clark *et al.* [1]; \blacktriangle , Lewis and Lee [2]; \blacklozenge , Horowitz and Calvert [3]; \diamond , Horowitz and Calvert [4]; \circ , Moortgat *et al.* [5]; \bullet , Moortgat and Warneck [6]; \circ , Moortgat *et al.* [7]; \square , this work.

Experiments were done by Moortgat and coworkers [5 - 7] using C_3H_6 or 1 atm of air as a scavenger with parts per million concentrations of CH_2O . They found that $\Phi(\text{CO})$ was 1.0 from 285 to 327 nm but fell at lower and higher wavelengths. However, $\Phi(\text{H}_2)$ was about 0.50 at 253 to 262 nm, 0.65 at 327 to 340 nm and smaller at intermediate wavelengths, reaching a minimum value of about 0.21 at 304 nm. Their results for $\Phi(\text{H}_2)$, as well as those from the other studies, are given in Fig. 1.

Morrison and Heicklen [8] examined the photolysis of CH_2O at a pressure of about 2 Torr in the presence of O_2 and reported that O_2 quenched $\Phi(\text{CO})$ and $\Phi(\text{H}_2)$ to zero at 313 nm. This result is different from that reported by others. One problem encountered in their study was that excess O_2 interfered with the measurements of H_2 and CO . Therefore we have repeated their experiments and improved the resolution of the gas chromatographic separation.

2. Experimental details

The photolysis was carried out in two cylindrical Pyrex cells whose sides were fitted with quartz windows. One cell was 1170 cm^3 with 9.0 cm diameter windows and the other was 375 cm^3 with 5.0 cm diameter win-

dows. The gases were introduced into the cell from a conventional grease-free vacuum line with Teflon stopcocks. The total pressure was brought to the desired value by adding dry oxygen.

The experiments were performed at wavelengths of 253.7, 280.3, 312.8 and 326.1 nm. The light sources and the isolation of various lines have been described previously [9].

CO and H₂ were the main products of interest and were determined by gas chromatography using a thermal conductivity detector. The gases non-condensable at -196 °C were analyzed for CO on a 5 ft × $\frac{1}{4}$ in stainless steel column packed with 5A molecular sieves using helium as a carrier gas. The gases non-condensable at -125 °C were analyzed for H₂ on a 9 ft × $\frac{1}{4}$ in stainless steel column packed with 5A molecular sieves using N₂ as a carrier gas.

Formaldehyde was prepared by heating paraformaldehyde (Aldrich) at about 90 °C in vacuum and vacuum distilling the monomer from -63 °C to -131 °C. The purified formaldehyde was stored at liquid nitrogen temperature. Extra dry grade oxygen (Matheson) was passed through a trap at -196 °C before being introduced into the reaction cell. Prepurified grade hydrogen (MG Scientific) and chemically pure CO (Matheson) were used for absolute calibrations.

Phosgene was used as an actinometer for the experiments performed at 253.7 and 280.3 nm. It was obtained from Air Products (chemically pure grade) and was distilled from -90 °C to -127 °C before use. For the experiments performed at 312.8 and 326.1 nm, formaldehyde itself was used as an actinometer. The quantum yield of CO in the absence of oxygen was taken as unity [1, 3, 4].

3. Results and discussion

Photolyses were performed with 2.55 Torr CH₂O in the absence and presence of O₂ at 253.7, 280.3, 312.8 and 326.1 nm at 23 °C. The quantum yields of CO and H₂ formation are reported in Tables 1 and 2 respectively. Preliminary experiments at 312.8 nm showed that $\Phi(\text{CO})$ was independent of conversion for CO from 1.2% to 3.7% in the presence of 22.5 Torr O₂ or for H₂ from 0.5% to 2.1% in the presence of 8 Torr O₂.

In the absence of O₂, $\Phi(\text{CO})$ is taken to be 1.0 at 312.8 and 326.1 nm in agreement with other studies [1, 3, 4]. Likewise, $\Phi(\text{CO})$ was found to be 1.0 in the absence of O₂ at 253.7 and 280.3 nm as obtained from actinometry by COCl₂.

As O₂ is added, $\Phi(\text{CO})$ first increases at all wavelengths and then decreases as the O₂ pressure is raised. The initial increase in yield is due to the HO₂-induced chain oxidation of H₂CO [8, 10], which is suppressed at high O₂ pressure. At high pressures $\Phi(\text{CO})$ is the sum of the primary photodecomposition processes, which is 1.0 at 280.3, 312.8 and 326.1 nm in agreement with the findings of Clark *et al.* [1], Horowitz and Calvert [3, 4]

TABLE 1

Effect of O₂ pressure on the CO quantum yield in the photolysis of formaldehyde ([CH₂O] = 2.55 ± 0.1 Torr; temperature, 298 K)

[O ₂] + [CH ₂ O] (Torr)	Irradiation time (min)	Φ(CO)
$\lambda = 253.7 \text{ nm}; I_a = 6.1 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	325	1.06
2.6 ^a	410	1.00
6.3	321	1.39
21	360	0.93
430	855	0.77
505	815	0.80
550	646	0.77
550	815	0.71
$\lambda = 280.3 \text{ nm}; I_a = 6.9 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
4.5	302	3.85
9.2	300	2.26
25	360	1.44
27	306	1.41
65	520	1.21
110	664	1.41
165	700	1.31
331	695	1.28
430	720	1.18
600	690	1.18
$\lambda = 280.3 \text{ nm}; I_a = 5.7 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
6.9	310	2.47
15.4	511	1.57
21	530	1.41
137	760	1.34
220	700	1.26
$\lambda = 312.8 \text{ nm}; I_a = 1.58 \times 10^{-4} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	125	1.00 ^b
3.7	35	5.53
4.1	110	4.47
7.5	91	2.86
7.5	30	2.70
10.9	90	2.01
23.8	100	1.42
35	145	1.29
70	163	1.17
110	141	1.12
192	210	1.08
225	140	1.14
330	180	1.11
432	200	1.14
595	180	1.16
$\lambda = 326.1 \text{ nm}; I_a = 1.65 \times 10^{-4} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	125	1.00 ^b
4.7	70	3.10

(continued)

TABLE 1 (continued)

[O ₂] + [CH ₂ O] (Torr)	Irradiation time (min)	Φ(CO)
5.1	115	2.79
7.5	75	2.04
7.8	100	2.23
12.1	106	1.66
48	120	1.40
85	125	1.22
175	124	1.12
305	170	1.02
410	90	0.99
485	145	1.04
615	160	0.91

^a O₂ absent.

^b Φ(CO) assumed equal to 1.0.

TABLE 2

Effect of O₂ pressure on the H₂ quantum yield in the photolysis of formaldehyde ([CH₂O] = 2.55 ± 0.1 Torr; temperature, 298 K)

[O ₂] + [CH ₂ O] (Torr)	Irradiation time (min)	Φ(H ₂)
$\lambda = 253.7 \text{ nm}; I_a = 4.8 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
5.4	360	1.29
9.1	325	0.84
13.7	320	0.61
15.9	305	0.57
37.3	395	0.37
68	485	0.30
108	470	0.24
152	780	0.27
$\lambda = 253.7 \text{ nm}; I_a = 6.1 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	150	0.97
5.3	185	0.96
18.9	390	0.41
122	805	0.28
180	840	0.30
180	896	0.30
$\lambda = 280.3 \text{ nm}; I_a = 2.01 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	290	0.99
5.3	360	2.75
9.6	305	1.03
12.4	650	0.72
21	460	0.49
25	835	0.42
30	485	0.41
34	780	0.36

(continued)

TABLE 2 (continued)

[O ₂] + [CH ₂ O] (Torr)	Irradiation time (min)	Φ(H ₂)
42	810	0.28 ^b
45	866	0.30
47	875	0.28
47	700	0.30
50	775	0.25
50	780	0.29
85	860	0.30 ^b
145	810	0.27 ^b
$\lambda = 312.8 \text{ nm}; I_a = 1.58 \times 10^{-4} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	82	0.91
4.4	70	2.48
4.5	65	2.61
5.8	75	1.95
11.6	92	0.77
21.8	130	0.37
25	120	0.33
50	90	0.18
57	315	0.21
$\lambda = 312.8 \text{ nm}; I_a = 1.29 \times 10^{-4} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	85	1.00 ^c
30	240	0.27
52	390	0.20
90	870	0.16
145	840	0.16
170	805	0.15
$\lambda = 326.1 \text{ nm}; I_a = 1.65 \times 10^{-4} \text{ photons min}^{-1} \text{ molecule}^{-1} \text{ of CH}_2\text{O}$		
2.6 ^a	85	1.10
4.2	120	1.75
10.0	155	0.89
20.5	150	0.55
28	235	0.42
40	125	0.34
70	170	0.39
122	255	0.42

^a O₂ absent.

^b $I_a = 2.13 \times 10^{-5} \text{ photons min}^{-1} \text{ molecule}^{-1}$ of CH₂O based on Φ(CO) in the absence of O₂ equal to 1.00.

^c Φ(H₂) assumed equal to 1.00.

and Moortgat and coworkers [5 - 7] at wavelengths from 285 to 330 nm. At 253.7 nm Moortgat *et al.* [7] reported Φ(CO) = 0.72, in good agreement with our value of 0.77.

The quantum yields of H₂ formation are given in Table 2. In the absence of O₂, Φ(H₂) ≈ 1.0 at all wavelengths. As with Φ(CO), Φ(H₂) first increases as O₂ is added but then decreases to a limiting value as O₂ is in-

creased. Large amounts of O₂ interfere with the H₂ analysis, both obscuring and broadening the H₂ peak. Thus it was not possible to go to very large O₂ pressures. Nevertheless, $\Phi(\text{H}_2)$ seems to have reached a lower limiting value at the highest pressures used. The values are 0.28, 0.28, 0.16 and 0.40 at 253.7 nm, 280.3 nm, 312.8 nm and 326.1 nm respectively. These values are plotted in Fig. 1 along with those of other workers. Our data at the three highest wavelengths are in satisfactory agreement with those of other workers. However, at 253.7 nm, the one other determination that exists gives $\Phi(\text{H}_2) = 0.48$ [7], considerably higher than our value of 0.28.

In conclusion, we find that O₂ does not quench either of the primary photodecomposition processes in CH₂O, contrary to the earlier report from our laboratory [8]. The error in the earlier report was caused by the interference of O₂ in the gas chromatographic analysis for CO and H₂. The O₂ both obscured and broadened the CO and H₂ peaks, so that it appeared that they were quenched. The better resolution in this study gives results in agreement with other workers at 280.3, 312.8 and 326.1 nm. Our result for $\Phi(\text{H}_2)$ at 253.7 nm is somewhat lower than that of Moortgat *et al.* [7].

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