

## EVIDENCE FOR A BIPHOTONIC PROCESS IN THE MERCURY- PHOTOSENSITIZED DECOMPOSITION OF ETHYLENE OXIDE IN THE GAS PHASE\*

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### Summary

The quantum yields of CO, H<sub>2</sub> and CH<sub>4</sub> at incident resonance radiation intensities of  $I_0 = 38.6 \times 10^{15}$  and  $1.23 \times 10^{15}$  quanta s<sup>-1</sup>, used in the equations  $\Phi = kI_0^{n-1}$ , lead to values of  $n$  which are greater than unity. Considering the nature of the possible radical-radical and atom-radical reactions involved, this clearly indicates the presence of a biphotonic step or steps leading to the formation of these products in the mercury-photosensitized decomposition of ethylene oxide. The pressure dependence of the product yields at the higher intensity is thought to be the result of the deactivation of the intermediate (probably a triplet ethylene oxide molecule) before the second excitation can occur.

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### Introduction

In sharp contrast to the numerous observations of biphotonic processes in the solid and liquid phases [1], there have been relatively few reports of biphotonic processes in conventional photochemical systems in the gas phase. This is probably because of the short lifetime of many of the excited species formed and/or because of the great difficulty in identifying the products from biphotonic processes in the presence of high yields of similar products from monophotonic processes [2]. Evidence for a two-quantum process in the mercury photosensitization of acetaldehyde in the vapour phase was reported by Buchanan and McRae in 1968 [3]. This article presents evidence for a biphotonic process or processes in the gas phase mercury photosensitization of a related molecule, ethylene oxide.

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## Experimental

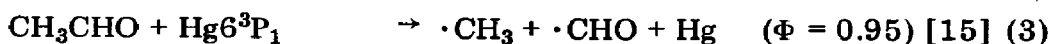
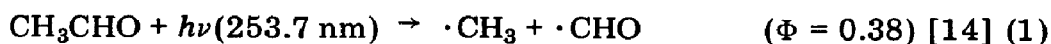
The experiments were carried out in conventional static systems similar to those used previously [4]. The light sources used were Hanovia SC 87A45 low pressure mercury lamps with Vycor envelopes to avoid mercury  $6^1P_1$  photosensitization. The reaction cells consisted of quartz cylinders 10 cm long and 5 cm in diameter fitted with plane quartz windows. The 253.7 nm resonance radiation from the lamps is entirely absorbed in these cells when the substrate pressure is greater than 15 Torr and the temperature is above 20 °C. The light intensities were determined using the mercury photosensitization of propane at 300 Torr ( $\Phi(H_2) = 0.581 \pm 0.012$ ) [2] and of *cis*-2-butene at 100 Torr ( $\Phi(\textit{trans}-2-butene) =  $0.50 \pm 0.02$ ) [6].$

Product yields were determined using classical methods and calibrated gas chromatographic peak areas.

## Results and discussion

The mercury photosensitization of ethylene oxide is a very complex reaction [7 - 9]. The major products are similar to those observed in its pyrolysis [10], its photolysis [11, 12] and in the reaction of oxygen atoms with ethylene [13]. The occurrence of as many as five distinct primary processes has been postulated to explain the photolysis at 147.0 nm and the triplet mercury photosensitization [12]. Although the sensitization products identified to date include CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH and n-C<sub>4</sub>H<sub>10</sub>, only the yields of the first three will be discussed in this paper. This is not as restrictive as it may seem since CO and H<sub>2</sub> are the major products with quantum yields  $\Phi \geq 0.3$  under most experimental conditions.

The quantum yields of CO, H<sub>2</sub> and CH<sub>4</sub>, determined as a function of the substrate pressure with  $I_0 = 1.23 \times 10^{15}$  and  $3.86 \times 10^{16}$  quanta s<sup>-1</sup>, are given in Tables 1 and 2, respectively. Comparison of the quantum yields for different reaction times at the same pressure (Table 2) shows that they are independent of the conversion. Thus these three products arise through the primary reaction(s) and not via the secondary photolysis or photosensitization of a primary reaction product such as acetaldehyde:



The ratios of the quantum yields at the two intensities were calculated using values taken from smooth curves representing the experimental points. The ratios given in Fig. 1 show that  $\Phi(\text{CO})$  and  $\Phi(\text{H}_2)$  are 20 - 40% higher at the higher intensity while  $\Phi(\text{CH}_4)$  is almost a factor of 2.5 higher.

Two explanations for the increased yields at the higher intensity have been considered.

TABLE 1

The quantum yields of CO, H<sub>2</sub> and CH<sub>4</sub> with  $I_0 = 1.23 \times 10^{15}$  quanta s<sup>-1</sup> ( $T = 28 \pm 2$  °C)

Reaction no.	Pressure (Torr)	Reaction time (s)	$\Phi(\text{CO})$	$\Phi(\text{H}_2)$	$\Phi(\text{CH}_4)$
10	22.2	1800	0.328	0.191	$\leq 0.050$
9	120.3	1800	0.277	0.239	0.044
8	440	1800	0.309	0.292	nm
7	600	1800	0.286	0.278	0.034

nm indicates not measured.

TABLE 2

The quantum yields of CO, H<sub>2</sub> and CH<sub>4</sub> with  $I_0 = 3.82 \times 10^{16}$  quanta s<sup>-1</sup> ( $T = 25 \pm 1$  °C)

Reaction no.	Pressure (Torr)	Reaction time (s)	$\Phi(\text{CO})$	$\Phi(\text{H}_2)$	$\Phi(\text{CH}_4)$
15	49.6	180	0.44	0.31	0.10 <sub>5</sub>
19	49.4	180	0.43	0.28	0.095
16	49.6	360	0.43	0.30	0.094
11	200.6	30	0.42	0.36	0.10 <sub>9</sub>
12	198.0	150	0.39	0.36	0.094
17	200.6	360	0.39	0.28	0.086
14	700.0	255	0.39	0.34	0.075
18	700.0	360	0.35	0.32	0.084

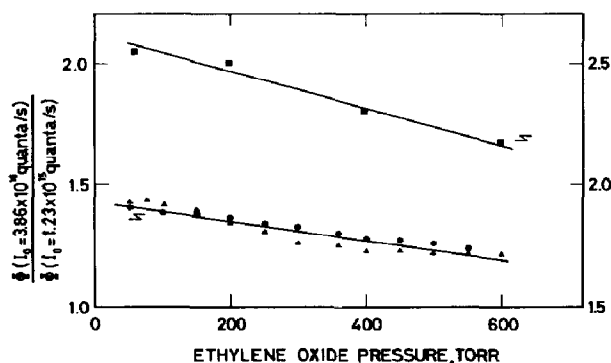
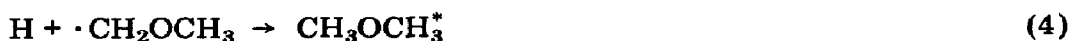


Fig. 1. The ratio of the quantum yields of CO (●), H<sub>2</sub> (▲) and CH<sub>4</sub> (■) at the intensities  $38.6 \times 10^{15}$  and  $1.23 \times 10^{15}$  quanta s<sup>-1</sup>, as a function of ethylene oxide pressure.

### (1) Atom-radical or radical-radical processes

These yield excited molecules which can undergo fragmentation. An example of such processes was reported by Payette *et al.* [16] in the mercury photosensitization of dimethyl ether. Extra methane is formed at high

intensities via the reactions



In the present study it is expected that  $\Phi(\text{CO})$  and  $\Phi(\text{H}_2)$  would actually be decreased at higher light intensities by the competition of the reactions



and



with the decomposition of  $\text{H}\dot{\text{C}}\text{O}$  to H and CO ( $E_a \approx 18 \text{ kcal mol}^{-1}$ ) [17].

## (2) Biphotonic processes

Using the quantum yields taken at 400 Torr ethylene oxide pressure from smooth curves representing the experimental points and from the simple equation

$$\Phi \propto I_0^{n-1} \quad (10)$$

values of  $n = 1.07, 1.06$  and  $1.24$  were calculated for CO,  $\text{H}_2$  and  $\text{CH}_4$ , respectively. These values are lower than those ( $n = 1.3 - 1.6$ ) obtained by Pailthorpe and Nicholls [18] for the UV induced ionization of heratin but they are similar to those found by Buchanan and McRae [3] ( $n = 1.15$  at  $69^\circ\text{C}$  and  $1.06$  at  $150^\circ\text{C}$ ) for the rate of  $\text{C}_2\text{H}_6$  production in the mercury photosensitization of acetaldehyde.

Moan [2] has shown that the data of Pailthorpe and Nicholls could be fitted to the equation

$$\text{rate} = \text{const.} \times I^2 / (k + aI) \quad (11)$$

which gives the rate for a purely biphotonic process. It is clear that at least one biphotonic process is operative in the mercury photosensitization of ethylene oxide.

Although the exact nature of the biphotonic process cannot be ascertained, it is interesting to speculate on the species involved. Since  $\Phi(\text{CO})$  at  $I_0 = 1.23 \times 10^{15} \text{ quanta s}^{-1}$  is independent of substrate pressure (within the limits of experimental error) any excited molecules formed in the monophotonic primary steps must have very short lifetimes. This is typical of many electronically excited singlet states. Paraffinic-type quenching would also be expected to be independent of substrate pressure although the subsequent ratio of radical-radical to radical-molecule interactions should be pressure

dependent. The excited molecules which participate in the biphotonic process(es) have longer lifetimes since they are usually deactivated collisionally at the lower light intensity. Collisional deactivation, in competition with the biphotonic process(es), would explain the decreases in  $\Phi(\text{CO})$  and  $\Phi(\text{CH}_4)$  with increasing ethylene oxide pressure. If the biphotonic process involves a second triplet mercury atom, normal quenching, increasing with increasing ethylene oxide pressure, would also lead to lower yields for the biphotonic process at higher pressures. The most probable biphotonic process is thus the excitation of a triplet ethylene oxide molecule, either by direct absorption of light or by a second triplet mercury atom.

## Conclusions

While it is not possible, from the limited results available, to determine the relative importance of the monophotonic and biphotonic processes occurring in the mercury photosensitization of ethylene oxide, it is clear that at least one biphotonic process is occurring with a total quantum yield of CO production greater than 0.12 at 50 Torr. Other instances of probable biphotonic processes in mercury photosensitization are known to the author and they may be much more common than the literature indicates. It is important that light intensity dependences of the product yields be determined over large intensity ranges in mercury photosensitization studies.

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