(b) The preparation of a *specific* mode depends crucially on the properties of the light source such as the pulse width, coherence width, Rabi frequency, and the experimental time scale.

(c) Excitation of spectrally *congested* systems undoubtedly creates incoherent excitation in the system which "washes out" the desired selective excitation.

With the above considerations in mind, we would like to emphasize the following:

(a) Reactions that depend on preparation by collisions will, in general, be statistical since collisions lead to ergodicity in the ensemble of isolated molecules.

(b) Collisionless unimolecular selective chemistry can be enhanced considerably if ultrashort pulses are used to ensure incomplete randomization of energy among modes and localization of excitation in certain parts of the vibrational phase space, or ultimately in a bond mode.

(c) Coherence and, hence, selective coupling in isolated molecules can be unraveled if the problem of states congestion, especially at higher energies, is *reduced*. Such suppression of congestion can currently be achieved by using ultracold gases.

( $\overline{d}$ ) High power lasers can be used to excite a very large fraction of molecules into higher energy states provided the phases of the

source are controlled. Such phase controls of optical pulses are now possible.<sup>21</sup>

(e) Bimolecular reactions (even in the condensed phases) are also good candidates for inducing such selective reactions on the very short time scale.

We hope that our perspective on this problem is attractive enough to enhance research activity in this new direction. It is possible that the lack of experimental proof for laser selective chemistry (in a general way) until now is due to the problems we raised here.

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# ARTICLES

# Mechanism of Photooxidation of Glyoxal and Formaldehyde in Solid $O_2$ at 12–18 K

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The UV photooxidation of solid  $O_2/trans-H_2C_2O_2$  samples at 12–18 K gives diformylperoxyl,  $[HC(O)OO]_2$ , as the most important *primary* product (via facile intermediacy of HCO radicals) and  $[HO_2]_2\cdot 2CO$  as an important *secondary* photolysis product. Degradation of these products gives HC(O)OO·CO, HCOOH·CO<sub>x</sub>, H<sub>2</sub>O<sub>2</sub>·2CO, H<sub>2</sub>O·CO<sub>2</sub>, CO, and CO<sub>3</sub>. A 30 K warm-up generates H<sub>2</sub>O<sub>2</sub>·2CO from  $[HO_2]_2\cdot 2CO$  by thermal decomposition. The photooxidation of the solid  $O_2/H_2C_2O_2$  system is driven less to completion than the photooxidation of the solid  $O_2/H_2CO$  system; because the latter system has more free radical species through the H atom recoil in the H<sub>2</sub>CO photolysis, the H atoms escape from the photolysis cage and hence a significant change in the photolysis cage stoichiometry occurs.

#### I. Introduction

The mechanisms of the UV photooxidation of glyoxal  $(H_2C_2O_2)$ and formaldehyde  $(H_2CO)$  in  $O_2$  should be similar in that both molecules involve the intermediacy of the formyl (HCO) radical generated from the primary photodecomposition processes

On the other hand, the chief dissimilarity between the two, if any, could be attributed to the *direct* generation of the H atom in the  $H_2CO$  photodecomposition and the escape of some H atoms by photochemical recoil<sup>2</sup> from the cage. Since the gas-phase oxidation of  $H_2CO$  and HCO in the presence of  $O_2$  is of importance to atmospheric chemistry and combustion chemistry of simple hydrocarbons, we have extended our recent studies<sup>1</sup> of  $H_2CO$  pho-

tooxidation in solid  $O_2$  at 12 K to  $H_2C_2O_2$ . It was shown in the previous study that the stoichiometry within the photochemical cage controls, to a large extent, the photooxidation product distribution in the solid  $H_2CO/O_2$  system; several of the product sets and the escape of some H atoms by photochemical recoil<sup>2</sup> from the cage are shown by the following reactions.

$$H_2CO + O_2 + h\nu \rightarrow HO_2 + HCO$$
(3)

 $\rightarrow$  H<sub>2</sub>O<sub>2</sub> + CO (4)

 $\rightarrow$  H<sub>2</sub>O + CO<sub>2</sub> (5)

 $\rightarrow$  HC(0)OOH (6)

<sup>(21)</sup> Warren, W. S.; Zewail, A. H. J. Chem. Phys. 1981, 75, 5956. Warren, W. S.; Zewail, A. H. J. Chem. Phys. 1983, 78, 2279. Warren, W. S.; Zewail, A. H. J. Chem. Phys. 1983, 78, 2298. Warren, W. S.; Zewail, A. H. J. Chem. Phys. 1983, 78, 3583.

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<sup>(2)</sup> Ho, P.; Bamford, D. J.; Buss, R. J.; Lee, Y. T.; Moore, C. B. J. Chem. *Phys.* **1982**, 76, 3630. The 283.8-nm photolysis of  $H_2CO$  in a molecular beam showed that the photofragments in reaction 2, H and HCO, carried away a small fraction of the available energy (15 kcal/mol) in translation. Since an H atom is light, however, its recoil effect may be significant in the matrix study.

- $H_2CO + 2O_2 + h\nu \rightarrow 2HO_2 + CO$  (7)
  - $\rightarrow HO_2 + HC(O)OO$  (8)
  - $\rightarrow$  HCOOH + O<sub>3</sub> (9)
  - $\rightarrow H_2O + CO + O_3 \qquad (10)$

Reaction 8 completes the oxidation of the HCO radical produced in reaction 3, and HCO is not observed directly in solid  $O_2$ .

The present study of the solid  $O_2/H_2CO$  system was initiated to elucidate the mechanism of the glyoxal photooxidation and compare it *qualitatively* to that of the formaldehyde photooxidation by taking into account the wavelength dependence, the photolysis time dependence, and the warm-up/diffusion behavior. It was found that a new intermediate [HC(O)OO]<sub>2</sub> which is a dimeric form of the formylperoxy radical is initially formed prior to the generation of dihydroperoxyl, [HO<sub>2</sub>]<sub>2</sub>, by its secondary photolysis. More (HO<sub>2</sub>)<sub>2</sub> but less H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, HC(O)OH, and O<sub>3</sub> are formed as the photolysis commences in the O<sub>2</sub>/H<sub>2</sub>C<sub>2</sub>O<sub>2</sub> system than in the solid O<sub>2</sub>/H<sub>2</sub>CO system. The energetics of the photooxidation processes of H<sub>2</sub>C<sub>2</sub>O<sub>2</sub> are summarized in Figure 1 in the manner that those of H<sub>2</sub>CO were given earlier.<sup>1a</sup>

#### **II. Experimental Section**

Monomeric glyoxal  $(H_2C_2O_2)$  was prepared by thermal decomposition of solid trimer (Matheson Coleman and Bell) topped with  $P_4O_{10}$  powder under vacuum at 120 °C. It was difficult to eliminate the H<sub>2</sub>CO impurity. Monomeric formaldehyde was prepared by thermal decomposition of solid paraformaldehyde under vacuum at 110-130 °C. The solid formaldehyde was obtained from various sources: H2CO (Aldrich Chemical), HDCO (98 atom %, Merck, Sharp, and Dohme), D<sub>2</sub>CO (98 atom %, MSD),  $H_2^{13}CO$  (90 atom %, MSD), and  $H_2C^{18}O$  (~50 atom %, courtesy of Dr. Irving Herman, Lawrence Livermore National Laboratory). O2 (99.999%, Liquid Carbonic) and <sup>18</sup>O2 (99 atom %, Prochem) were used directly. The monomeric glyoxal and formaldehyde were frozen into a trap at 77 K, and they were kept at this temperature until the time for the preparation of the gaseous mixture with  $O_2$  at room temperature. The gaseous mixture with a given matrix/reactant ratio (M/R = 250-4000) was made up in a 1- or 2-L glass bulb by standard manometric techniques. The use of a concentrated sample, e.g., M/R = 320, was very useful in enhancing the signals of weak absorption peaks. A few micromoles of the gas mixture was pulse deposited onto the cold CsI sample window (inside the vacuum shroud of the cryostat) maintained within 1 °C by a closed-cycle helium refrigerator (Air Products, Displex Model 202B). For calibration, authentic samples of HCOOH, HCOOD (98 atom %, MSD), and DCOOD (97 atom %, MSD) were used in order to identify the absorption frequencies of the formic acids as photoproducts.

Photolyses were carried out with a high-pressure mercury arc lamp (Osram HBO-500 w/2) or with a frequency-doubled, dye laser (Chromatix CMX-4). The Hg light was filtered by 10 cm of H<sub>2</sub>O and a chosen UV-visible filter before being imaged onto the cold sample: Schott KV 470 (440-nm cutoff), Corning CS 3-72 (430-nm cutoff), 3-73 (410-nm cutoff), CS 0-51 (360-nm cutoff), CS 4-96 (350-nm cutoff), CS 0-52 (340-nm cutoff), CS 4-97 (330-nm cutoff), Schott WG-320 or CS 0-54 (300-nm cutoff), WG 295 (270-nm cutoff), WG 280 (260-nm cutoff), CS 9-54 (240-nm cutoff), CS 7-54 (230-420-nm band-pass), 03F1A001 (340-500-nm band-pass), an interference filter ( $\sim$ 313 nm, fwhm  $\simeq$  32 nm, 12% maximum transmission), and a small monochromator (~290 nm, fwhm ~ 10 nm). With the solid  $O_2/H_2CO$ samples, two types of experiments were carried out in order to test the possibility of the H<sub>2</sub>CO reaction initiated by the photo excited  $O_2$ : (1) a comparison of the electronic absorption spectra of the pure solid  $O_2$  and the solid  $O_2/H_2CO$  (M/R = 250 and 1200) recorded with a Cary 219 UV-visible spectrophotometer at a spectral resolution of 0.1 nm for the 220-315-nm range and 0.2 nm for the 315-500-nm range and (2) wavelength dependence of H<sub>2</sub>CO photooxidation using the above set of UV filters.

Most of the photolysis experiments were carried out using a pair of UV filters, the CS 7-54/WG 295 combination, because



Figure 1. Energetics of oxidation processes starting with  $trans-H_2C_2O_2 + nO_2$ . The standard enthalpies of the reactions at 300 K ( $\Delta H^{\circ}_{rx}$ ) giving various products are shown as in Figure 2 of ref 1a for  $H_2CO + nO_2$ . The value of  $\Delta H_f^{\circ}$  (298 K) = -50.66 kcal/mol for  $H_2C_2O_2$  (Fletcher, R. A.; Pilcher, G. Trans. Faraday Soc. 1970, 66, 794) is used.

the photolysis was very efficient with it. The photoproducts were monitored between each interval of the preset photolysis time, until most of formaldehyde was consumed. A careful temperaturecontrolled warm-up cycle (12-40 K) was followed. A thermocouple (0.07% Fe vs. chromel) attached on the CsI sample window gave a temperature reading on a digital temperature indicator.

A Fourier transform infrared spectrometer (FTIR, Nicolet 7199 Series) was used for product analysis. The following instrument parameters were used for most experiments. The frequency of a He-Ne laser served as the sampling frequency, and a germanium-coated KBr beam splitter was adequate for the frequency range of interest between 7000 and 400 cm<sup>-1</sup>. The truncated length of the travel of the moving mirror in the interfeometer set at 4.14 cm and the use of a full aperture size of IR radiation source and Hang-Genzel apodization function gave a spectral resolution of 0.37 cm<sup>-1</sup>. Higher resolution runs (0.24 cm<sup>-1</sup>) were made in an attempt to resolve some closely overlapping peaks by using the same file size but changing the sampling frequency to a half of the He-Ne laser frequency. In this case, a spectral range of 3945-400 cm<sup>-1</sup> was obtained with the truncated length set to 8.24 cm. The probable error in the FTIR spectrum was  $\sim 0.2$  cm<sup>-1</sup>. In some cases, a spectrum showing difference absorbance (the signal for the sample of interest minus the signal from the preceding sample run) is displayed in order to show the change resulting from the particular experimental step taken (photolysis or warm-up) in a series of such experimentation with the sample.

#### **III.** Results

A. Electronic Absorption Spectra. In order to evaluate the relative importance of UV absorption and hence wavelength dependence of photochemical activity of H<sub>2</sub>CO, trans-glyoxal (H<sub>2</sub>C<sub>2</sub>O<sub>2</sub>), and the solid O<sub>2</sub>, the electronic absorption spectra of these molecules were measured as shown in Figures 2 and 3. The solid O<sub>2</sub> shows two absorption peaks, Y (360.5 nm) and Z (343.5 nm), in addition to overlapping O<sub>2</sub>  $\tilde{C}^3\Delta_u \leftarrow \tilde{X}^3\Sigma_g^-$  band<sup>3</sup> and weaker O<sub>2</sub> Herzberg I band,  $\tilde{A}^3\Sigma_u^+ \leftarrow \tilde{X}^3\Sigma_g^-$ , in Figure 2c. The

<sup>(3)</sup> Goodman, J.; Brus, L. E. J. Chem. Phys. 1977, 67, 1482 and references therein.



Figure 2.  $S_1 \leftarrow S_0$  electronic absorption spectra of  $H_2CO$ : (a) absorption by 22 torr of  $H_2CO$  vapor (10-cm path length, 295 K); (b) base line of the blank sample cell (quartz window) at 12 K before sample deposition; (c) absorption by ~780  $\mu$ mol of pure O<sub>2</sub> solid at 12 K; (d) absorption by 4.8  $\mu$ mol of H<sub>2</sub>CO (O<sub>2</sub>:H<sub>2</sub>CO = 1200:1) in solid O<sub>2</sub> at 12 K. Peaks Y and Z are absorption due to solid O<sub>2</sub>.



Figure 3. Electronic absorption spectra of glyoxal: (a) base line of the evacuated gas cell at 295 K; (b) absorption by 22 torr of glyoxal vapor (10-cm path length, 295 K); (c) absorption by  $\sim 3.1 \ \mu$ mol of glyoxal (O<sub>2</sub>:H<sub>2</sub>C<sub>2</sub>O<sub>2</sub> = 250:1) in solid O<sub>2</sub> at 12 K. Peaks Y and Z are absorption due to solid O<sub>2</sub> (see Figure 2).

0-0 band expected at 284.1 nm is too weak to be observed, but the higher members of the n'-0 progression<sup>3</sup> are increasingly visible. The absorptions of the O<sub>2</sub>/H<sub>2</sub>CO solid (M/R = 1200) shown in Figure 2d indicate that peak Y is the most prominent absorber compared to all of the H<sub>2</sub>CO absorption peaks.

The electronic absorption spectrum of the solid  $O_2/H_2C_2O_2$ (M/R = 250) is shown in Figure 3c, and it indicates that the  $H_2C_2O_2$  absorption in solid  $O_2$  is qualitatively similar to that in the gas phase shown in Figure 3b. The vibrational structure of the  $S_1 \leftarrow S_0$  system of the  $H_2C_2O_2$  in solid  $O_2$  shown in Figure 3 is red-shifted from that in the gas phase by ~6 nm, whereas that of  $H_2CO$  in solid  $O_2$  in Figure 2 is blue-shifted by ~1.6 nm near the electronic origin. There is no clear indication of a new electronic transition of either  $H_2CO$  or  $H_2C_2O_2$  induced in the solid, e.g., a carbonyl- $O_2$  charge transfer band.

B. Photooxidation Products of  $H_2CO$ . Preliminary data concerning the photooxidation of  $H_2CO$  in solid  $O_2$  have been reported earlier,<sup>1</sup> and the results were indicative of high-percentage



**Figure 4.** FTIR spectra of the  $O_2/H_2CO$  sample (M/R = 2000, 2.8  $\mu$ mol of H<sub>2</sub>CO): (a) before photolysis at 12 K and the parent absorption peaks are identified by the symbol  $v_i$ ; (b) after 3.0-h photolysis at 12 K using the Hg arc lamp with the WG 295/CS 7-54 filter set (270-420-nm transition envelope).



Figure 5. FTIR spectra of the  $O_2/H_2C_2O_2$  sample (M/R = 1000, 5.1  $\mu$ mol of  $H_2C_2O_2$ ): (a) before photolysis at 12 K and the parent absorption peaks are identified by the symbol  $\nu_i$ ; (b) after 0.5-h photolysis at 12 K using the Hg arc lamp with a 313-nm (32-nm band-pass) interference filter plus a CS 7-54 filter; (c) after 7.0-h photolysis under conditions as in (b) and followed by a 30 K warm-up.

product conversion and hence undesirable complications due to secondary photolyses. In order to overcome this problem we have carried out recently photolysis experiments for a shorter time and with narrower bandwidths. An overview of the photoproduct distribution pattern for solid  $O_2/H_2CO$  and  $O_2/H_2C_2O_2$  samples is illustrated with the FTIR spectra taken in the 4000-400-cm<sup>-1</sup> range before and after photolysis in Figures 4 and 5. Varying amounts of H<sub>2</sub>O and CO<sub>2</sub> are present as atmospheric trace components due to degassing and a leak in the vacuum system, and their presence is indicated in the IR spectra. Also, the  $O_2$  absorptions induced by the matrix environment<sup>4</sup> appear as two broad features at ~1616 and ~1591 cm<sup>-1</sup> and a sharp peak at 1552 cm<sup>-1</sup>. Italics indicate the absorbing moiety of the molecular complex for a given absorption frequency. If one of the partners of the molecular complex is unknown or if there is more than one partner, it may be designated by an alphabetical character until its identity is clarified.

Photolysis of the  $O_2/H_2CO$  systems has been carried out at values of M/R = 500, 1060, and 2000 and T = 13-15 K. The

<b>CABLE I:</b> Observed IR Absorption Peaks (	cm <sup>-1</sup> )	and Assignments	from Photolysis of <i>t</i>	rans-H <sub>2</sub> C <sub>2</sub> O <sub>2</sub> in Solid (	D <sub>2</sub> (13 K)
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3633.6	$H_2O(\nu_1)$	(1761.3 (w)		
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3623.3 <sup>b</sup>	$H_2O(\nu_1) \cdot CO \cdot CO_z$	€1754.1 (w)		
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3553-40 <sup>d</sup>	$H_2O_2(\nu_1,\nu_5).2CO$	1732.5	H <sub>2</sub> C <sub>2</sub> O <sub>2</sub> ·H <sub>2</sub> CO	
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	3442.7	$H_{2}C_{2}O_{2}(2\nu_{10})$	1693	$H_2^{12}C^{13}CO_2(\nu_{10})$	
3399.4 $HO_1(y_1)$ 1616 (br) $O_2(y)$	3399.4	$HO_2(v_1)$	1616 (br)	$O_{2}(\nu)$	
$(3322.1   [HO_{3}]_{3}(\nu_{1}) \cdot 2CO   1602.1   H_{3}O(\nu_{2})$	(3322.1	$[HO_2]_2(\nu_1) \cdot 2CO$	1602.1	$H_2O(\nu_2)$	
$1591 (br) O_2(y)$	3319.7		1591 (br)	$O_{2}(\nu)$	
2877 $H_2CO(\nu_2)\cdot CO$ 1593 $H_2O(\nu_2)\cdot CO\cdot CO$	2877	$H_2CO(\nu_4)$ ·CO	1593	$H_{2}O(\nu_{2})$ ·CO·CO.	
(2853) 1588 $H_2O(\nu_2) \cdot CO \cdot CO$	(2853	2(-3)	1588	$H_2O(\nu_2) \cdot CO_2 \cdot CO$	
2848 $H_2C_2O_2(v_1,v_10)$ 1552 $O_2(v)$	2848	$H_{2}C_{2}O_{2}(\nu_{1},\nu_{10})$	1552	$O_2(\nu)$	
(1416.7  (sh)) $(140.1  (sh))$ $(140.1  (sh))$ $(140.1  (sh))$	(2812		(1416.7 (sh))	$[HO_{2}]_{2}(\nu_{2}) \cdot 2CO$	
$12807$ $H_2CO(\nu_1) \cdot CO$ $11415.2$	2807	$H_2CO(\nu_1)$ ·CO	1415.2	1	
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$2510^{d}$ ? $1314.4$ $H_2C_2O_2(\nu_1)$	2510 <sup>d</sup>	?	1314.4	$H_{2}C_{2}O_{2}(\nu_{11})$	
2345 br $CO_{2}(\nu_{3})$ ·H <sub>2</sub> O-CO 1298.5 (br) <sup>g</sup> $H_{2}O_{2}(\nu_{3},\nu_{4})$ ·2CO	2345 br	$CO_{2}(\nu_{2})\cdot H_{2}O\cdot CO$	$1298.5 (br)^{g}$	$H_2O_2(v_2,v_5)\cdot 2CO$	
2275 ${}^{13}CO_3(\mu_3)$ ·H-O-CO 1277.8 (br) <sup>g</sup> $H_2O_3(\mu_3,\mu_4)$ -CO	2275	$^{13}CO_{2}(\nu_{2}) \cdot H_{2}O \cdot CO$	1277.8 (br) <sup>g</sup>	$H_2O_2(v_2,v_6) = -$	
(2159.9) 1108.5 [HO <sub>0</sub> ] <sub>2</sub> (y)-2CO	/2159.9		1108.5	$[HO_{2}]_{2}(v_{2}) \cdot 2CO$	
2158.5 $CO(y) \cdot [HO_3] \cdot CO_4$ 1101.4 $HO_3(y_2)$	2158.5	$CO(\nu) \cdot [HO_{2}] \cdot CO_{2}$	1101.4	$HO_2(v_1)$	
1096.8 $HC(O)OH CO.$	2157.6		1096.8	HCOOH.CO.	
2155.8 ? 1091.9 <i>HC(0)00</i> -CO	2155.8	?	1091.9	<i>HC(0)00</i> •CO	
$(2149.7)$ 1066.1 (br) $CO_1(\mu_2) \cdot w(2)^{f}$	(2149.7		1066.1 (br)	$CO_2(\nu_2) \cdot W(?)^f$	
2148.5 $CO(y)$ -H-O <sub>2</sub> ·CO <sub>2</sub> 1037.8 $O_2(y_2)$	2148.5	CO(y)·H <sub>2</sub> O <sub>2</sub> ·CO <sub>2</sub>	1037.8	$O_2(v_2)$	
$(2147.2)$ $(031.0 (w)$ $O_2(w)$ complex	2147.2		1031.0 (w)	$O_2(v_2)$ complex	
21461 $CO(y)$ +H-O-CQ $c964.5$	2146 1	CO(y)·H <sub>2</sub> O·CO <sub>2</sub>	(964.5	- 3(- 3) <u>F</u>	
(2142.7 ) 958.7 [HC(0)00]	(2142.7		958.7	[HC(0)00]√	
2141 8 CO(y).H_CO 956 9	12141.8	CO(y), H, CO	956.9		
(2138.6) $(250)$ $($	(2138.6	00(1) 11200	855 (w) <sup>f,h</sup>	?	
	2137.1	$[CO]_{2}$	(807	•	
$\begin{array}{cccc} 10012 \\ 11358 \\ CO(u) \\ 804 \\ H_{1}C_{1}O(u) \\ 10012$	2135.8	CO(y)	1804	$H_{2}C_{2}O_{2}(y_{\ell})$	
$21267 (w)^{e}$ 2 (665 $CO_{(w)} + E_{OCO}$	$2126.7 (w)^{e}$	2000	(665	$CO_{2}(\nu_{2})$ ·H <sub>2</sub> O·CO	
2036 (br) $CO_2(v_2) \cdot w(2)$ [655	2036 (br)	$CO_2(\nu_1) \cdot w(?)$	1655		

<sup>a</sup> Probable accuracy of  $\pm 0.2 \text{ cm}^{-1}$ . <sup>b</sup> After a warm-up cycle these values change to "stable" values:  $3727.2 \rightarrow 3723.4$ ;  $3723.4 \rightarrow 3714.1$ ;  $3631.4 \rightarrow 3623.6$ ,  $3623.3 \rightarrow 3620.8$ . <sup>c</sup>Quartet at 3552, 3548, 3544 (s), and 3540 cm<sup>-1</sup> becomes a doublet at 3542.7 and 3538.3 cm<sup>-1</sup> after 30 K warm-up. <sup>d</sup> Behaves similar to the 2036-cm<sup>-1</sup> peak. <sup>e</sup>Appears after a warm-up cycle. <sup>f</sup>Appears with the 295-nm (laser) and 313-nm ( $\pm 16 \text{ nm}$ ) photolyses but disappears with the use of a wider band-pass light. <sup>g</sup>Shifts to lower frequencies and becomes a multiplet peak (see Figure 9) after a 35 K warm-up. <sup>h</sup> It could be the asymmetric O-O stretch of species A.

M/R = 500 sample was deposited at 13 K, thermally annealed at 20 K, and cooled back to 13 K before photolysis. This sample had an intensity ratio of 4:1 for the 1740.0-cm<sup>-1</sup> peak for the C=O stretch of the H<sub>2</sub>CO (M) vs. the 1735.8-cm<sup>-1</sup> peak of the H<sub>2</sub>CO dimer (D), and it was photolyzed with 270-420-nm light (Hg/WG 295/CS 7-54) for t = 0.5, 1.0, 2.0, 3.0, and 6.0 h. About 50% of formaldehyde was converted to photoproducts at t = 1.0 h and more than 95% at t = 6.0 h. Therefore, in this concentrated sample, it was easier to evaluate minor product yields.

The M/R = 1060 sample (with  $\sim 10\%$  dimer absorption) was used for a photolysis wavelength dependence study at 15 K, with a set of cutoff filters (360, 350, 340, 330, and 300 nm) combined with a CS 7-54 envelope filter and a typical value of t = 1.0 h.

The M/R = 2000 sample (with  $\leq 7\%$  dimer absorption) was used for a photolysis time-dependence study at 13-15 K with 270-420-nm light, using t = 6, 16, 36, 61, 90, 120, and 180 min, but only the warm-up behavior is shown in Figures 6-8. Approximately 50% of formaldehyde was converted to photoproducts at t = 90 min and  $\sim 70\%$  at t = 180 min. Glycoaldehyde and the CO-CH<sub>3</sub>OH complex which had been observed in the photolysis of the H<sub>2</sub>CO dimer in an Ar matrix<sup>5</sup> were not found in all of the above samples. The majority of the photoproduct peaks shown in Figure 4b has been identified previously<sup>1</sup> by authentic samples, isotopic substitution, and arguments justifying the observed frequency shifts from the gas-phase (or other matrix) values. The minority of the products which requires further justification of their identity includes  $H_2O(\nu_3)$ ·u,  $H_2O(\nu_1)$ ·v, and  $H_2O_2$ ·CO in the 3500-3800-cm<sup>-1</sup> region. The use of HDCO and D<sub>2</sub>CO has been also useful in the identification of the hydrogen-containing species. A detailed treatment of the spectral assignments, geometry, and stabilities of various molecular species and complexes will not be presented here, because it will be presented separately elsewhere.<sup>6</sup>

C. Photooxidation Products of  $H_2C_2O_2$ . Photolysis of the  $O_2/H_2C_2O_2$  system has been carried out using the values of M/R = 320 and 1000 and T = 12-18 K. A typical photoproduct distribution is shown in Figure 5 with the FTIR spectra of the M/R = 1000 sample taken in the 4000-400-cm<sup>-1</sup> range before and after photolysis. In the  $O_2/H_2C_2O_2$  system, the majority of the photoproduct peaks shown in Figure 5b can be identified on the basis of the identification made in the  $O_2/H_2CO$  system, with the recognition of one important difference in the cage stoichiometry that two carbonyl groups are present in glyoxal and hence one additional molecule of CO is formed by decarbonylation

<sup>(5)</sup> Diem, M.; Lee, E. K. C. Chem. Phys. 1979, 41, 373.



Figure 6. FTIR spectra of the photolysis samples in the HOO bend region: (a)  $O_2/H_2C_2O_2 = 1000$ , 18 K, t = 1 h, Hg arc lamp with a 03F1A001 filter; (b) after a 35 K warm-up of (a); (b') after a 32 K warm-up of a sample similar to (a); (c)  $O_2/H_2CO = 2000$ , 15 K, t = 4h, Hg arc lamp with the WG 295/CS 7-54 filter set: (d) after a 30 K warm-up of (c).

reaction in the photolysis cage. Three distinctly new products are observed as shown in Figures 9, 11, and 12 and listed in Table I. The dimer of the formylperoxy radical (species A), [HC-(O)OO]<sub>2</sub>, absorbing at  $\sim$ 1820 cm<sup>-1</sup> (C=O stretch), and  $\sim$ 960 cm<sup>-1</sup> (O–O stretch), the H<sub>2</sub>CO·CO complex<sup>7</sup> absorbing at  $\sim$  2877  $cm^{-1}$  ( $\nu_5$ ), 2812/2807  $cm^{-1}$  ( $\nu_1$ ), 1739/1737.8  $cm^{-1}$  ( $\nu_2$ ), and 2141.8 cm<sup>-1</sup> (CO), and species T absorbing at  $\sim$ 2036 and  $\sim$ 1066 cm<sup>-1</sup> which could be, we believe, a molecular complex of CO<sub>3</sub>. Each of these species maintains a certain intensity ratio of its own. The absorption frequencies (and intensities) of  $CO_3(C_{2\nu})$  in the  $CO_2$ matrix are known to be  $\nu_1$  (C=O stretch) = 2045 cm<sup>-1</sup> (vs),  $\nu_2$ (O--O stretch) = 1073 cm<sup>-1</sup> (m),  $\nu_3$  (C--O, symmetric stretch) = 593 cm<sup>-1</sup> (m),  $v_5$  (C—O, antisymmetric stretch) = 972 cm<sup>-1</sup> (s) and  $v_6$  (O-C=O, bend) = 568 cm<sup>-1</sup> (m);<sup>9</sup> the absorption intensities should be very strong for  $v_1$ , medium for  $v_2$  at ~1066 cm<sup>-1</sup>, and strong for  $\nu_5$  at ~960 cm<sup>-1</sup>. [HC(O)OO]<sub>2</sub> is easily destroyed by the UV photolysis and also by a warm-up as shown in Figures 11 and 12.

The products observed in the  $O_2/H_2C_2O_2$  photolysis system are common to those observed in the  $O_2/H_2CO$  system with the exception of  $H_2CO \cdot CO$ , species A associated with the 1820-cm<sup>-1</sup> absorption, and species T associated with the 2036-cm<sup>-1</sup> absorption, which are generated in the former. The differential absorbance spectrum is Figure 5b shows the photolytic removal of  $H_2C_2O_2$ with negative peaks and the photoproduct formation with positive peaks, whereas that in Figure 5c shows the thermally induced decomposition of [HO<sub>2</sub>]<sub>2</sub>·2CO (negative peaks) and the thermal generation of  $H_2O_2 \cdot 2CO$  (positive peaks) by the warm-up cycle applied to the photolysis sample. The differential absorbance spectra of the  $CO_2$  species show both negative and positive peaks near 2340 and 660 cm<sup>-1</sup>, because one form of  $CO_2$  complex is converted to another form of  $CO_2$  complex by the warm-up.<sup>6</sup> The M/R = 320 samples showed very little dimerization of  $H_2C_2O_2$ and also no evidence of a *distinct* photolysis product attributable to the dimer of  $H_2C_2O_2$ , although the dimerization of  $H_2C_2O_2$ was observed to a somewhat greater extent and the distinct photolysis product, H2CO·H2C2O2·CO complex, was observed in the previous photolysis study<sup>7</sup> of an  $Ar/H_2C_2O_2$  sample (M/R = 500). The smaller amount of the dimer formation observed for  $H_2C_2O_2$  than for  $H_2CO$  probably reflects the predominance of the *nonpolar*, trans isomer over the *polar*, cis isomer of  $H_2C_2O_2$ at room temperature. More detailed spectra showing the effect



Figure 7. FTIR spectra of the photolysis samples in the HO stretch region: (a)  $O_2/H_2C_2O_2 = 1000$ , 18 K, t = 2 h, Hg arc lamp with a 03F1A001 filter; (b) after a 35 K warm-up of (a); (c)  $O_2/H_2CO = 2000$ , 15 K, t = 4 h, Hg arc lamp with the WG 295/CS 7-54 filter set; (d) after a 30 K warm-up of (c).



Figure 8. FTIR spectra of the photolysis samples in the CO (M) and CO-complex region: (a)  $O_2/H_2C_2O_2 = 1000$ , 18 K, t = 1 h, Hg arc lamp with a 03F1A001 filter; (b) after a 35 K warm-up; (c)  $O_2/H_2CO = 2000$ , 15 K, t = 4 h, WG 295/CS 7-54 filter set; (d) after a 30 K warm-up of (c).

of the warm-up are shown in Figures 6-8. The M/R = 320sample was photolyzed with laser light at 295 nm for t = 0.5, 1.0,and 2.0 h and also with 290-nm  $(\pm 10 \text{ nm})$  light from a Hg lamp for t = 6.0 h. This resulted in optimizing the yield of  $[HC(O)OO]_2$ (see Figures 9–11). The M/R = 1000 samples were photolyzed for a wavelength dependence study at 18 K using a set of cutoff filters (440, 430, 410, 360, 350, and 340 nm) with an envelope filter (long wavelength cutoff at 500 or 420 nm) for t = 1-2 h (see Figure 12). For a photolysis time-dependence study, M/R= 1000 samples were run at 12 K using 313-nm ( $\pm$ 16 nm) light from a Hg lamp for t = 0.5, 1.0, and 7.0 h (see Figure 10).

D. Effect of Photolysis Time. It was mentioned earlier that the primary photooxidation products appear at faster rates whereas the secondary photolysis products form at slower rates as photolysis

<sup>(7)</sup> Diem, M.; MacDonald, B. G.; Lee E. K. C. J. Phys. Chem. 1981, 85, 2227

<sup>(8)</sup> Tso, T.-L.; Lee, E. K. C., unpublished data.
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(c) Jacox, M. E.; Milligan, D. E. J. Chem. Phys. 1971, 44, 4469. 54, 919.



Figure 9. FTIR spectra of the photolysis samples in the C=O stretch, HOO bend, C—O stretch, and O—O stretch regions: (a)  $O_2/H_2C_2O_2$ = 1000, 12 K, t = 0.5 h, Hg arc lamp with a 313-nm (32-nm band-pass) interference filter: (b)  $O_2/H_2C_2O_2 = 320$ , 12 K, t = 0.5 h, dye laser output at 295 nm; (c)  $O_2/H_2CO = 1060$ , 18 K, t = 1.0 h, Hg arc lamp with the WG 320/CS 7-54 filter set.



Figure 10. FTIR spectra of the  $O_2/H_2C_2O_2$  sample (M/R = 1000) in the C=O stretch region showing the photolysis time dependence with a 313-nm (31-nm band-pass) interference filter at 13 K and the intensity was 25-30 mW: (a) before photolysis; (b) t = 0.5 h; (c) t = 1.0 h; (d) t = 7.0 h; (e) after a 29 K warm-up.

time proceeds and product conversion increases. Figure 10 shows the changes observed in product distribution in the C=O absorption region as photolysis time increased from 0.5 to 7.0 h for the  $O_2/H_2C_2O_2$  system: The primary photooxidation products  $[HC(0)OO]_2$  reached the maximum concentration already at t = 0.5 h while  $HC(O)OO \cdot CO$  continues to increase its concentration. The H<sub>2</sub>CO·CO concentration reaches the maximum value between t = 1.0 and 7.0 h due to its secondary photochemical decomposition, while HC(O)OO·CO appears to be photochemically destroyed at a rate somewhat slower than  $H_2CO$  CO. However, a better controlled kinetic study will be necessary to obtain a quantitatively significant result, and the present results on the photolysis time dependence should be considered valid for a qualitative purpose only.

In the  $O_2/H_2CO$  (M/R = 500) systems, the absorptions due to HO<sub>2</sub>, [HO<sub>2</sub>]<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HC(O)OO, HC(O)OOH, HCOOH, and  $O_3$  reach their maximum values at t = 2.0 h with 270-420-nm light. It appears that HO<sub>2</sub> is reduced a little at t = 3.0 h but not  $[HO_2]_2$  species, and this is puzzling. Clearly,  $H_2O \cdot CO_2$  continues to increase with time until the end of its photolysis at t = 6.0 h. After 6.0-h photolysis, about 1/3 of HC(O)OO and HC(O)OOH, about 1/2 of H<sub>2</sub>O<sub>2</sub>, and about 3/4 of HCOOH are present as compared to the amount present after 2.0-h photolysis. A similar photolysis time-dependent behavior was observed with the  $O_2/$  $H_2CO (M/R = 2000)$  system.

E. Isotopic Labeling. Some of the isotopic photolysis samples were<sup>6</sup> O<sub>2</sub>/H<sub>2</sub><sup>13</sup>CO (M/R = 2000, 13 K, t = 2.0, 4.0, and 6.5 h),



 $CO_3(\nu_5) \cdot w(?)$ 

(d) 6.5 hr, 290±10 nm (e) warm-up, 13 → 32 → 13K 2065 1120 1040 960 880 800 *ṽ* (cm<sup>-1</sup>) Figure 11. FTIR spectra of the C=O stretch, the C-O stretch, and the

 $CO_{3}(\nu_{2})$ 

w(?

(a)

Absorbance (0.15/div)

O-O stretch region of species A, [HC(O)OO]<sub>2</sub>, and species T, CO<sub>3</sub>.w complex: (a) before photolysis; (b) t = 0.5 h, 295 nm (laser); (c) t = 2.0h, 295 nm (laser); (d) 6.5 h, 290 nm (monochromator with a 20-nm band-pass), (e) a warm-up cycle of 13 K  $\rightarrow$  32 K  $\rightarrow$  13 K.



Figure 12. FTIR spectra of the  $O_2/H_2C_2O_2$  sample (M/R = 1000) in the HOO bend and O-O stretch regions showing the photolysis wavelength dependence at 18 K: (a) 03F1A001 filter, t = 1 h; (b) CS 0-51/0 3F1A001 filter, t = 9 h; (c) CS 4-96/CS 7-54 filter, t = 1 h; (d) WG 320/CS 7-54 filter, t = 2.5 h.

 $O_2/H_2C^{18}O$  (M/R = 2000, 13 K, t = 1.0, and 6.0 h), and  ${}^{18}\tilde{O}_2/\tilde{H}_2CO$  (M/R = 1500, 13 K, t = 1.5, 9.5, and 12.6 h). The use of HDCO and  $D_2CO$  was useful<sup>6</sup> in the identification of hydrogen-containing molecules, particularly those with D-O bonds since the isotopic frequency shift in the IR spectrum is quite large,  $\sim$ 0.29. Likewise, the IR frequency shifts observed with the use of  $H_2^{13}CO$  was helpful in distinguishing the carbonyl compounds from the  $H_xO_y$  compounds. The use of  ${}^{18}O_2$  (as the matrix gas) with  $H_2CO$  was helpful in showing that greater than 95% of the  $CO_2$  formed was  $C^{16}O^{18}O$  and all of CO formed was  $C^{16}O$ . The minor presence of  $C^{18}O_2$  (<5%) may be indicative of the decomposition involving a CO<sub>3</sub> intermediate.<sup>9b</sup> The use of H<sub>2</sub>C<sup>18</sup>O was helpful in showing the integrity of the C=18O group in HC(O)OOand HC(O)OOH as well as the lability of the O atoms in HC-(O)OH where the switching of the carbonyl oxygen atom to the acidic oxygen atom takes place as discussed elsewhere.<sup>1c</sup>

### **IV.** Discussion

A. Photooxidation Threshold Wavelength. The photolysis rate of  $H_2CO$  as measured by the appearance of the photooxidation products (HO<sub>2</sub>, [HO<sub>2</sub>]<sub>2</sub>, HC(O)OO, HC(O)OOH, CO, and O<sub>3</sub>) is an order of magnitude greater when a 330-nm cutoff filter is used than when a 340- or a 350-nm cutoff filter is used. Therefore,

the photooxidation threshold wavelength of H<sub>2</sub>CO in solid O<sub>2</sub> is at  $\leq$ 340 nm. This result and the additional data that peak Y at 360.5 nm is more intense than peak Z at 343.5 nm (see Figure 2d) clearly support the conclusion that the UV absorption by peaks Y and Z does not cause photooxidation of  $H_2CO$  and is photochemically unimportant although their identity is not known. The additional experiments in the photooxidation studies8 of acetaldehyde and acetone in our laboratory indicate that the photooxidation threshold wavelength and rate decrease substantially in order of H<sub>2</sub>CO, HDCO, and D<sub>2</sub>CO and CH<sub>3</sub>CHO, CH<sub>3</sub>CO-CH<sub>3</sub>, and HCOOH. If an electronically excited  $O_2$  species in the matrix-isolated site were a key intermediate for initiating the photooxidation, e.g., by abstraction of a hydrogen atom or addition reactions, one should expect a significantly shorter wavelength for the photooxidation threshold than that observed and also a lesser degree of sensitivity for the wavelength and rate dependence. As it will be discussed in detail later, the crucial initiation step for photooxidation of H<sub>2</sub>CO is the C-H bond rupture by photodissociation process 2.

The photooxidation threshold wavelength of  $H_2C_2O_2$  can be ascertained from the wavelength-dependence result shown in Figure 12, and it is  $\sim$ 350 nm since the HO<sub>2</sub> species begin to appear at 350 nm and shorter wavelengths but not at 360 nm and longer wavelengths. The photooxidation threshold wavelength (~350 nm) of  $H_2C_2O_2$  in solid  $O_2$  corresponds to the onset of the structureless, second electronic absorption band (referred here as the  $\tilde{B} \leftarrow \tilde{X}$  transition) shown in Figure 3c, and it is clearly longer than the previously reported photodecomposition threshold wavelength (300–288 nm) of  $H_2C_2O_2$  in solid Ar<sup>7</sup> to give  $H_2CO$ and CO. In the gas phase,  $H_2C_2O_2(S_1)$  decomposes to give molecular products, H<sub>2</sub>, CO, and H<sub>2</sub>CO,<sup>10-11</sup> but it is photochemically inactive in cryogenic matrices. Only fluorescence and phosphorescence emissions have been observed in solid Ar.<sup>7</sup> The 313-nm photolysis of  $H_2C_2O_2$  in the gas phase gave mostly  $H_2CO$ and CO as major products.<sup>12</sup> The crucial initiation step for photooxidation of  $H_2C_2O_2$  is probably the C-C bond rupture from the B state by photodissociation process 1, but we do not know how much the neighboring  $O_2$  molecules in the matrix cage influence the reaction path involved.

Under typical photolysis conditions employed in this study, the direct formation of  $O_3$  from the photolysis of solid  $O_2$  is relatively unimportant compared to the O3 formation resulting from the photodecomposition of  $H_2CO$  or  $H_2C_2O_2$  in solid  $O_2$ . The former competes effectively with the latter only at wavelengths shorter than  $\sim 250$  nm.

B. Initiation of Photooxidation. The results shown in Figures 6 and 7 indicate that the intensity ratio of monomeric  $HO_2$  to the dimeric HO<sub>2</sub> species is greater in the  $O_2/H_2CO$  system than in the  $O_2/H_2C_2O_2$ . Furthermore, the first carbonyl species appearing in the early photolysis period is HC(O)OO in the  $O_2/H_2CO$ system and species A in the  $O_2/H_2C_2O_2$  system in which the HO<sub>2</sub> species are produced in significant amounts only with the disappearance of species A. We shall show that species A is [HC-(O)OO]<sub>2</sub>. These results are consistent with the phootooxidation initiation mechanism in which the initiation step is the C-H bond rupture (process 2) for H<sub>2</sub>CO and the C-C bond rupture (process 1) for  $H_2C_2O_2$ , followed by the subsequent but rapid addition to the surrounding  $O_2$  molecules to form  $HO_2$  and HC(O)OOradicals as in process 8. Since no CH<sub>3</sub>OH, glycolaldehyde, and glyoxal are observed in the  $O_2/H_2CO$  system even with a low M/R ratio (500) and an appreciable amount of the H<sub>2</sub>CO dimer ( $\sim$ 10%), it is clear that H atoms and HCO radicals react at least an order of magnitude faster with  $O_2$  than the H<sub>2</sub>CO remaining in the cage (the dimer site). However, some subsequent reactions

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in solid  $O_2$  may occur without the aid of the second absorbed photon by  $HO_2$  and HC(O)OO, particularly if it involves a radical-radical recombination (or disproportionation) reaction with little or no activation energy. Of course, the second absorbed photon can cause the secondary photolysis to occur, and this should be important since the photoproducts from the first photon absorption are continuously in a photon bath during the photolysis period of many minutes.

C. Photooxidation Product Distribution. The stoichiometrically controlled photooxidation processes shown by reactions 3-10 for the O<sub>2</sub>/H<sub>2</sub>CO system can qualitatively account for the observed products.<sup>1</sup> Important primary oxidation product species resulting from initial photodissociation process 2 are HO<sub>2</sub>, [HO<sub>2</sub>]<sub>2</sub>, CO, HC(O)OO, and HC(O)OOH. H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, CO<sub>2</sub>, HC(O)OH, and  $O_3$  are probably secondary photolysis products. The  $H_xO_v$  species are normally complexed to CO, and the organic carbonyl products are matrix isolated,<sup>6</sup> as expected for preserving the stoichiometry of the  $H_2$ CO-containing cage. However, HO<sub>2</sub> (M) and the HO<sub>2</sub> perturbed by HC(O)OO must result from the stoichiometry in the cage containing an HCO due to the photochemical recoil of an H atom.<sup>1a,2</sup> The photooxidation kinetics are dictated largely by the escape of the recoiling H atoms from the photolysis cage, the subsequent formation of the matrix-isolated  $HO_2$  (M), and the secondary processes affecting the fate of the HC(O)OO radical in the photolysis cage. In all of the photolysis runs of the  $O_2/$  $H_2CO$  system, we have observed two  $HO_2(v_2)$  peaks: The 1392.1-cm<sup>-1</sup> peak is more intense than the 1391.5-cm<sup>-1</sup> peak at short photolysis times (see Figure 6c) whereas the latter becomes more intense than the former at long photolysis times. The former peak is associated with the 3411.7 and 1102.8  $cm^{-1}$  (1103.7- $cm^{-1}$ shoulder) peaks. After a few warm-up cycles, only the 3400.1-, 1391.5-, and 1101.4-cm<sup>-1</sup> peaks remain, and therefore we believe that these absorptions are those of the matrix-isolated monomer  $HO_2$  (M) and that the other set of absorption peaks are those of an HO<sub>2</sub> species perturbed by HC(O)OO (or HO<sub>2</sub>·CO) in the adjacent photolysis cage. This photochemically induced site migration of H atoms (in the form of HO<sub>2</sub>) is not too surprising<sup>1a</sup> and of course has important mechanistic consequences by changing the stoichiometry in the photolysis cage not only in the  $O_2/H_2CO$ system but also in the  $O_2/H_2S$  system.<sup>13</sup>

In the case of the  $O_2/H_2C_2O_2$  system, the  $H_2C_2O_2$  stoichiometry is better maintained by process 1. This is an important difference between the two photooxidation systems as it will be discussed later. The CO region of IR spectra clearly supports this behavior as shown in Figure 8. For the  $O_2/H_2C_2O_2$  system, some  $H_2CO \cdot CO$ and [CO]<sub>2</sub> are observed<sup>14</sup> in addition to [HO<sub>2</sub>]<sub>2</sub>·2CO, H<sub>2</sub>O<sub>2</sub>·2CO, and presumably  $H_2O \cdot CO \cdot CO_z$  (see Figure 8a).<sup>6</sup> Only after the warm-up does CO (M) appear (see Figure 8b). Greater spectral complexities of the CO species observed in the  $O_2/H_2C_2O_2$  system are not surprising since one more molecule of CO is present in the  $H_2C_2O_2$  photolysis cage than in the  $H_2CO$  photolysis cage. Compared to the  $O_2/H_2CO$  system, a greater amount of  $(HO_2)_2$ species and lesser amounts of HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, CO<sub>2</sub>, HC-(O)OOH, and HCOOH are observed in the  $O_2/H_2C_2O_2$  system. It is interesting to note from Figure 1 that all of the latter products except HO<sub>2</sub> are formed with exothermicity greater than  $\sim 30$ kcal/mol, and HC(O)OO, [HC(O)OO]<sub>2</sub>, and (HO<sub>2</sub>)<sub>2</sub> species are formed with exothermicity less than  $\sim 20$  kcal/mol. This implies that the photooxidation of  $H_2CO$  in solid  $O_2$  is driven more to completion on a thermochemical scale than that of  $H_2C_2O_2$ (compare Figure 2 of ref 1a to Figure 1 of this paper).

D. Warm-up Reactions and Thermal Annealing. The crystal structure of  $\alpha$ -O<sub>2</sub> is monoclinic with dimensions 4.18 Å  $\times$  3.20

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 $Å \times 3.20$  Å, and a mean site diameter (nonspherical cavity site) is given as 3.64 Å, similar to that of Ar ( $\sim$  3.76 Å) and somewhat smaller than that of solid  $N_2~({\sim}4.00~\text{\AA}).^{15}~\text{It}$  is likely that  $H_2CO$ will occupy a substitution site in solid  $O_2$ , but  $H_2C_2O_2$  may require a cavity somewhat bigger. The solid oxygen undergoes a rapid, reversible phase transition from  $\alpha$  to  $\beta$  at 23.8 K and from  $\beta$  to  $\gamma$  at 43.8 K upon warming.<sup>4,15</sup> Since the melting point is 54.4 K, the matrix should become soft and allow diffusion to some extent at  $\sim 30$  K. Therefore, warm-up experiments of 3-5-min duration were seldom carried out above 35 K and the spectra were recorded at lower temperatures, 12–18 K. Because the  $\alpha \rightarrow \beta$ transition temperature is close to the uppr limit of warm-up temperature, the interpretation of the diffusion studies in solid  $O_2$  could be more complicated. Nonetheless, we have routinely run warm-up experiments with the hope of observing the disappearances of reactive chemical species.

It was shown in our preliminary study that  $[HO_2]_2$  species disappear and  $H_2O_2$  species from upon warming to  $\sim 30$  K.<sup>1b</sup> The process responsible for this warm-up behavior was attributed to the disproportionation reaction (also observed in the gas phase at room temperature)<sup>16</sup>

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{11}$$

This process is illustrated in greater detail in Figure 6 for the HOO bending region and Figure 7 for the HO stretch region. For the  $O_2/H_2C_2O_2$  samples, the 3300-3800-cm<sup>-1</sup> region of the FTIR spectrum was found to be often noisy and a good quality spectrum was obtained only with difficulty, particularly after a warm-up cycle. After a 30 K warm-up,  $H_2O_2$ ·nCO peaks not only show increased intensities but also sharpen up and show multiplet structures.<sup>6</sup> In the case of the  $O_2/H_2C_2O_2$  sample, the absorption frequencies of  $H_2O_2$ ·2CO peaks are clearly shifted to lower frequencies after a warm-up (compare spectra a and b of Figure 7). This presumably is due to thermal annealing of the matrix cage in which the cage partners find more stable geometries.

It is interesting to note in the case of the  $O_2/H_2C_2O_2$  sample that (the 1298.5-cm<sup>-1</sup> peak) the higher frequency component of  $H_2O_2(v_6)$ -2CO shows the increase in intensity rather than the lower frequency component at 1277.8 cm<sup>-1</sup>; in the HO stretch region of  $H_2O_2(v_5)$ -2CO (the ~3540-cm<sup>-1</sup> peak), the lower frequency component shows an increase in intensity. In contrast, in the case of  $O_2/H_2CO$  sample, the middle-frequency component of  $H_2O_2(\nu_6)$ ·CO at 1272.6 cm<sup>-1</sup> shows the increase in intensity rather than the higher frequency component at 1279.8-1276.5 cm<sup>-1</sup> and the lowest frequency component at  $\sim 1265 \text{ cm}^{-1}$  (very weak); in the HO stretch region of  $H_2O_2$  species, the middle-frequency component ( $\sim$ 3558 cm<sup>-1</sup>) shows an increase in intensity. If the CO absorption region is inspected in Figure 8, the 30 K warm-up decreases [HO<sub>2</sub>]<sub>2</sub>·CO peaks at 2163.5 and 2160.5 cm<sup>-1</sup> and increases intensities of the  $H_2O_2$ ·CO peak at 2149.8 cm<sup>-1</sup> (not 2150.7 cm<sup>-1</sup>) and the H<sub>2</sub>O·CO peak at 2144.8 cm<sup>-1</sup> in the  $O_2/H_2CO$ sample, whereas the 35 K warm-up increases intensities of the  $H_2O_2 \cdot 2CO$  peaks at ~2148 cm<sup>-1</sup> in the  $O_2/H_2C_2O_2$  sample. This observation is indicative of the presence of more than one kind of complex to be discussed in detail elsewhere.<sup>6</sup>

An extensive warm-up study with the  $O_2/H_2CO$  system indicates that the thermal conversion of the  $[HO_2]_2$  species to the  $H_2O_2$  species  $(+O_2)$  as in reaction 11 does not take place below 24 K. Even in a 28 K warm-up (3-5 min) the thermally induced conversion is slow. Since the  $O_2$  phase transition of  $\alpha \rightarrow \beta$  takes place at 23.8 K, the observed thermal conversion of the  $[HO_2]_2$  species to the  $H_2O_2$  species  $(+O_2)$  might be the result of a cavity change, hence allowing the geometric realignment of the complexing partners which favors the bond-breaking and bond-forming process.

With 22 and 23 K warm-ups, it was observed<sup>6</sup> that  $H_2O$ ·CO peaks at 3723.5, 3625.8, and 2144.8 cm<sup>-1</sup> do increase, accompanied by a decrease in the CO (M) peak but not  $H_2O$ ·CO<sub>2</sub> peaks. With 25, 30, and 35 K warm-ups,<sup>6,8</sup> HC(O)OO peaks at 1790.2 cm<sup>-1</sup> (1789.4-cm<sup>-1</sup> shoulder) and 1089.9 cm<sup>-1</sup> (1088.6-cm<sup>-1</sup> shoulder), strong peaks of HO<sub>2</sub> (M) at 3400.3, 1391.5, and 1101.4 cm<sup>-1</sup>, weak shoulder peaks of HO<sub>2</sub> at 3411.7, 1392.1, and 1102.8 cm<sup>-1</sup>, HC-

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(O)OH peaks at 1767.3, 1762.8, 1100.3, 641.4, and 640.6 cm<sup>-1</sup>, and HC(O)OOH peaks at 1734.8 cm<sup>-1</sup>, 1421.3 cm<sup>-1</sup> (intramolecularly H-bonded HOO bend), and 1111.8 cm<sup>-1</sup> are reduced in intensity. We assign the weak shoulder peaks of the HO<sub>2</sub> (M) to the  $HO_2$ ·HC(O)OO complex or the  $HO_2$  perturbed by HC-(O)OO in the adjacent cage. Some of the absorption peaks of stable species, e.g., HC(O)OH, may disappear due to the broadening when it forms complexes via diffusion.

In addition to the warm-up behavior described above, the disappearance of  $[HC(O)OO]_2$ , HC(O)OO Z', and  $CO_3$  (peak T) with a 30 K warm-up cycle is shown in Figures 5c and 11. The mechanism of the formation and removal of these reactive species is discussed in the next section. A thermally induced product peak appears at 987.4 cm<sup>-1</sup> in the  $O_2/H_2CO$ ,  $O_2/H_2^{13}CO$ , and  $O_2/H_2C^{18}O$  systems with a 42 K warm-up, but its identity is unknown.

E. Effect of Photolysis Wavelength on Product Distribution. A narrow-bandwidth photolysis of glyoxal using the doubled dye laser output at 295 nm ( $\pm 0.1$  nm) gives more [HC(O)OO]<sub>2</sub> and less HC(O)OO, CO<sub>3</sub>, and O<sub>3</sub>, relative to HO<sub>2</sub> and [HO<sub>2</sub>]<sub>2</sub> species, than medium-bandwidth photolyses using either the Hg/monochromator output at 290 nm ( $\pm 10$  nm) or the Hg/interference filter output at 313 nm ( $\pm 16$  nm). If a wider bandwidth and a longer wavelength, e.g., 340-500 nm, are used in the photolysis of  $H_2C_2O_2$ , the [HC(O)OO]<sub>2</sub> peaks are substantially reduced, and the [HO<sub>2</sub>]<sub>2</sub>·2CO, H<sub>2</sub>O<sub>2</sub>·2CO, CO<sub>3</sub>, and HCOOH peaks become more intense. Some of these photolysis wavelength effects are illustrated in Figures 9 and 12. The laser photolysis gives the highest ratio of the dimeric  $[HC(O)O_2]_2$  to the monomeric HC-(O)OO, 10-20 (see Figure 9a), whereas the medium-bandwidth (32 nm) photolysis gives a smaller ratio of 3-5 (see Figure 9b) and the wide-bandwidth photolyses (of the samples in Figure 12a,c,d but not shown) give even smaller ratio,  $\leq 0.1$ .

The above observation demonstrates the photodecomposition of the diformylperoxyl at a near-UV-visible wavelength

$$\bigcup_{\substack{||\\ (HCOO)_2 + \lambda_v}}^{O} (UV-vis) \longrightarrow [HO_2]_2 + 2CO \qquad (12)$$

Similarly, we have found that the secondary photolysis in the UV-visible wavelengths destroys the formylperoxy radical in the  $O_2/H_2CO$  system

Probably reaction 12 will become more and more important with the progress of photolysis in the  $O_2/H_2C_2O_2$  system.

It was also found that in the  $O_2/H_2C_2O_2$  system the  $[HO_2]_2$  species are present in amounts 5–10 times greater than the monomeric HO<sub>2</sub> species, whereas the amounts of each species are comparable in the  $O_2/H_2CO$  system (see Figure 9). This probably reflects the greater importance of reaction 12 over reaction 13 in the  $O_2/H_2C_2O_2$  system where the  $H_2C_2O_2$  cage stoichiometry is more strictly maintained.

The effect of variation of photolytic wavelength was studied in a sequence of spectra a-d as shown in Figure 12 with the  $O_2/H_2C_2O_2$  system: spectrum b indicates that 360-500-nm light converts  $[HO_2]_2$ ·2CO to HO<sub>2</sub> species and  $H_2O_2$ ·2CO; spectrum c indicates that 350-420-nm light produces a small amount of  $[HO_2]_2$ ·2CO but removes HO<sub>2</sub> species; spectra a indicates that 340-500-nm light gives substantial yields of  $[HO_2]_2$ ·2CO,  $H_2$ - $O_2$ ·2CO, and HO<sub>2</sub> species but a small yield of O<sub>3</sub>; and spectrum d indicates that 300-420-nm light gives high yields of  $[HO_2]_2$ ·2CO and O<sub>3</sub> and a small yield of HO<sub>2</sub> species but reduces  $H_2O_2$ ·2CO.

On the basis of the above observation, it can be stated that (i) light of the wavelength shorter than 340 nm certainly removes  $H_2O_2$ , HC(O)OO,  $[HC(O)OO]_2$ , HC(O)OOH, and HCOOH species in the system, (ii)  $HO_2$  and  $[HO_2]_2$  species are removed more effectively at shorter wavelengths, and (iii) light of wavelength in the 340-500-nm region is effective in removing species such as HC(O)OO and  $[HC(O)OO]_2$ . The photolysis of the solid  $O_2/HCOOH$  system is not effected at wavelengths longer than ~250 nm,<sup>6,8</sup> and therefore HCOOH formed in the photolysis of

the  $O_2/H_2CO$  system must be removed by some secondary processes involving the secondary photolysis of either HO<sub>2</sub> or  $O_3$ .

F. CO<sub>3</sub> Formation Mechanism. Earlier, peak T has been assigned to CO<sub>3</sub>, a secondary photolysis product, in the  $O_2/H_2C_2O_2$  system, but neither CO<sub>3</sub> nor [HC(O)OO]<sub>2</sub> was observed in the  $O_2/H_2CO$  system. Therefore, it is likely that diformylperoxyl is the precursor

$$\begin{array}{c} 0 \\ || \\ (HCOO]_2 + 2O_2 + h_{\nu} (UV-vis) \longrightarrow [HO_2]_2 + 2CO_3 (14) \end{array}$$

Since  $CO_3$  was not observed in the  $O_2/H_2CO$  system, it is likely that a reaction such as (15) is not able to compete with reaction 16

$$\begin{array}{c} 0 \\ || \\ HCOO \cdot + O_2 + h_{\nu} (UV-vis) \longrightarrow HO_2 + CO_3 \quad (15) \\ 0 \end{array}$$

$$\frac{||}{HCOO} + h_{\nu}(UV - vis) \longrightarrow HO_2 + CO$$
(16)

A further reaction of HO<sub>2</sub> and CO may result in the formation of HO + CO<sub>2</sub> (with an exothermicity of ~61 kcal/mol) which can subsequently react with the second HO<sub>2</sub> molecule from an adjacent site to give the most thermochemically favored products, H<sub>2</sub>O + CO<sub>2</sub>. No absorption attributable to OH was found however in either photooxidation system.<sup>6</sup> Benson<sup>17</sup> gives an estimate of  $\Delta H_f^{\circ}$  (300 K) of -45 kcal/mol for CO<sub>3</sub>, and we estimate  $\Delta H_f^{\circ}$  (300 K) of -32 kcal/mol for HC(O)OO by the Benson's group additivity rule. Hence, we can further estimate that reaction 15 is ~10 kcal/mol exothermic and reaction 14 is ~20 kcal/mol exothermic, if the dimerization enthalpies of [HO<sub>2</sub>]<sub>2</sub> and [HC(O)OO]<sub>2</sub> are about the same, -10 kcal/mol. Therefore, the absence of CO<sub>3</sub> in the O<sub>2</sub>/H<sub>2</sub>CO system cannot be explained on the basis of thermochemical values for reactions 14 and 15.

G.  $O_3$  and HC(O)OH Formation Mechanism. An additional reaction which can compete with reaction 15 may give formic acid and ozone

as reported earlier from the <sup>18</sup>O<sub>2</sub> isotopic labeling study.<sup>2</sup> Since HC(O)OO radicals are slowly generated as a minor product (probably as a secondary photolysis product) in the  $O_2/H_2C_2O_2$ system, the virtual absence of HC(O)OH and  $O_3$  at early photolysis periods is consistent with this mechanism. Again, a more efficient formation of HC(O)OH and  $O_3$  in the  $O_2/H_2CO$  system can be attributed to the H atom recoil and the escape of an H atom from the photolysis cage. The results of the lower rate of  $HO_2$  formation and the higher rate of  $O_3$  formation shown in Figure 12d are consistent with reaction 17. Short UV wavelength photolysis is effective in giving the 1037.8-cm<sup>-1</sup> peak of  $O_3$  (M) as well as the weaker but sharp 1031.0-cm<sup>-1</sup> peak which is more rapidly reduced in amounts than the 1037.8-cm<sup>-1</sup> peak by 340-500-nm light. We assign the 1031.0-cm<sup>-1</sup> peak to the  $O_3(\nu_3)$ complexed probably to  $O_3$ . The disappearance of this peak proceeds by an O-O bond migration in the solid O<sub>2</sub> by the secondary photolysis of  $O_3$ .

H.  $[HC(O)OO]_2$  Formation Mechanism. One expected the photooxidation product of interest that was not observed is diformyl peroxide

This process is estimated to be  $\sim 52$  kcal/mol exothermic by the additivity rule.<sup>17</sup> The secondary photolysis of this peroxide with near-UV-visible light should give  $2HO_2 + 2CO_2$  via an inter-

mediacy of HC(O)O, formyloxy radical, or HC(O)OH +  $CO_2$ .<sup>18</sup> Since extremely small amounts of HC(O)OH and CO<sub>2</sub> (0.2–0.5 times CO) are observed even in wide-band photolyses, it is suggested that the primary photooxidation process which gives diformylperoxyl is

This process must be more dominant than the other primary photooxidation process 18.

H

I. Molecular Complexes. Most of the IR absorption frequencies of the photooxidation products resulting from the  $O_2/$  $H_2C_2O_2$  system have been assigned with the assumption that the elemental composition in the photolysis cage is two carbons, two hydrogens, and even numbers of oxygen. Since photochemically induced "site migration" can occur with an H atom by photochemical recoil and an O atom by O<sub>3</sub> photodecomposition,<sup>1a</sup> this stoichiometric restriction can be slightly relaxed for the oxygen composition and to a lesser degree for the hydrogen composition in the  $O_2/H_2C_2O_2$  system. A comprehensive treatment of the frequency assignments will be given separately elsewhere,<sup>6</sup> but the assignments pertinent to this paper are tabulated in Table I. In the case of the  $O_2/H_2CO$  system, however, this stoichiometric restriction is even more relaxaed because of the prevalence of H atom recoil.<sup>1a</sup> Since CO is an important primary photooxidation product in the  $O_2/H_2CO$  system and it is an important secondary photooxidation product in the  $O_2/H_2C_2O_2$  system, its molecular complexes have been studied in some detail and reported elsewhere.<sup>1a,6,16,19</sup> The cyclic hydrogen-bonded dimer of  $HO_2^{1b}$  and some of  $H_2O$  complexes<sup>6,15,16</sup> have been studied previously. The full account of the molecular complexes formed in the  $O_2/H_2CO$ system will be reported separately,<sup>6</sup> but some results relevant to the  $H_2C_2O_2$  photooxidation mechanism will now be discussed.

In the  $H_2CO$  photooxidation HC(O)OO is formed as a primary product, and its IR absorption frequency assignments at 1790.2 cm<sup>-1</sup> (C==O) and 1089.9 cm<sup>-1</sup> (C==O) have been established earlier.<sup>2,6</sup> In the  $H_2C_2O_2$  photooxidation,  $HC(O)OO \cdot CO$  is formed as a minor product, and its IR absorption frequencies have been assigned at 1788.4/1787.1 cm<sup>-1</sup> (C=O) and 1091.1 cm<sup>-1</sup> (C-O) in Table I. In both systems, it is possible that  $HO_2$  may be complexed to these species, and a question arises as to whether any one of the 1421.4/1417.2/1413.1-cm<sup>-1</sup> peaks in the O<sub>2</sub>/H<sub>2</sub>CO system and the 1416.7/1415.2-cm<sup>-1</sup> peaks in the  $O_2/H_2C_2O_2$ system might be assigned to the  $HO_2$ ·HC(O)OO complex. Since the intensity ratios of the HC(O)OO peaks at 1790-1787 cm<sup>-1</sup> to the 1421-1415-cm<sup>-1</sup> peaks shown in spectra a (or b) and c of Figure 9 are observed to be far from being equal, to a first approximation, the 1790-1417-cm<sup>-1</sup> groups cannot be assigned to a "common" species, HO2.HC(O)OO complexes. Therefore, the earlier assignment<sup>1</sup> of the 1420-cm<sup>-1</sup> group to the HOO bend  $(\nu_2)$ in  $[HO_2]_2$ ·CO is firmly confirmed, and the earlier assignment<sup>1c</sup> of the 1790-cm<sup>-1</sup> group to the C=O stretch in HC(O)OO is also confirmed. However, it is difficult to rule out the possibility of the latter assignment for the  $HC(O)OO \cdot HO_2$  complex or for the HC(O)OO perturbed by  $HO_2$  in the adjacent site.

The assignment of the 1820-cm<sup>-1</sup> quartet peak to  $[HC(O)OO]_2$ is justified by an additional high-frequency shift from the 1790cm<sup>-1</sup> doublet peak of the monomeric HC(O)OO whose assignment was previously justified for the presence of a peroxide group<sup>2,8</sup> and the fact that the C=O stretching ( $\nu_3$ ) and HCO bending ( $\nu_2$ ) frequencies of the HCO radical are 1863 and 1087 cm<sup>-1</sup>, respectively, in solid Ar.<sup>20</sup> The possibility of assigning the 1820and 960-cm<sup>-1</sup> absorptions (each with three to four peaks) to the

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<sup>(20) (</sup>a) Milligan, D. E.; Jacox, M. E. J. Chem. Phys. 1969, 51, 277 and references therein. (b) Ewing, G. E.; Thompson, W. E.; Pimentel, G. C. J. Chem. Phys. 1960, 32, 927. The IR frequencies in solid CO are 1861 and 1090 cm<sup>-1</sup>, respectively, for  $\nu_3$  and  $\nu_2$ .

HO<sub>2</sub>·HC(O)OO complex is ruled out, since the intensity ratios of the 1820-cm<sup>-1</sup> peak to the 1416-cm<sup>-1</sup> peak (the HOO bend) are again far from being equal in Figure 9a, b. The possibility of them being due to HC(O)OO(O)CH has also been ruled out in the preceding discussion (section IV.H) because of a low molar ratio of CO<sub>2</sub>/CO observed in the O<sub>2</sub>/H<sub>2</sub>C<sub>2</sub>O<sub>2</sub> photolysis. Therfore, we are left with the possibility of their assignment to the dimeric [HC(O)OO]<sub>2</sub>. The structure of the dimeric species should involve either the presence of a -OOOO- group, with the linkage of the radical positions, or the presence of a cyclic, head-to-tail linkage. An additional isotopic study will be useful for more definitive structural determination.

As mentioned earlier, the assignments of various complexes of CO, CO<sub>2</sub>,  $H_2O_2$ , and  $H_2O$  are treated elsewhere,<sup>6</sup> and therefore it is unnecessary to provide the details. It suffices to use the results.

#### V. Summary

The mechanism of UV photooxidation of glyoxal and formaldehyde in solid O<sub>2</sub> has been examined in this paper. The spectral assignment of diformperoxyl,  $[HC(O)OO]_2$ , is given here, but those of other radicals and molecular complexes will be presented in detail separately.<sup>6</sup> Several findings will be summarized below in regards to the photooxidation mechanism:

1. Stoichiometry in the photolysis cage is maintained in a rigid  $O_2$  matrix when photochemical recoil and photochemically induced "migration" are absent; the photooxidation stoichiometry is two hydrogens, one carbon and an *odd* number of oxygen atoms for formaldehyde and two hydrogens, two carbons, and an *even* number of oxygen atoms for glyoxal.

2. H atoms can recoil out of the photolysis cage, and the dislodging of the H atom as an HO<sub>2</sub> monomer in a neighboring cage is observed in a significant amount in the  $O_2/H_2CO$  system and in a much lesser amount in the  $O_2/H_2C_2O_2$  system.

3. O atoms can "migrate" out of the photolysis via the  $O_3$  photodecomposition and the subsequent oxygen-oxygen bond migration in the  $O_2$  matrix. Hence, a significant fraction of the  $O_3$  species is matrix isolated as a monomer.

4. As a result of (3) and (4), the absorptions by the perturbed  $HO_2$  and  $O_3$  species are observed near the absorption peaks of the monomeric species.

5. When an  $\dot{H}$  atom recoils out of the cage, the trapping of free radical species with an *odd* number of electrons is favored in the original photolysis cage, e.g., HO<sub>2</sub> and formylperoxy radical HC(O)OO from the O<sub>2</sub>/H<sub>2</sub>CO system.

6. When two radical species are immobilized in the original photolysis cage, recombination/disproportionation products are formed; e.g.,  $[HO_2]_2$ ·CO and  $H_2O_2$ ·CO in the  $O_2/H_2$ CO system

and  $[HC(0)OO]_2$  and  $H_2O_2 \cdot 2CO$  in the  $O_2/H_2C_2O_2$  system. 7. All of the species formed in (5) and (6) are also degraded

by secondary photolysis, e.g.,  $[HO_2]_2$  to  $H_2O_2 + O_2$ ,  $[HC(\breve{O})OO]_2$  to  $[HO_2]_2 + 2CO$ , and  $H_2O_2 \cdot CO$  to probably  $H_2O \cdot CO_2$ .

8. HC(O)OOH, HC(O)OH, and  $O_3$  are probably formed by a secondary photolysis step involving HC(O)OO and HO<sub>2</sub>.

9. A 25-30 K warm-up allows an efficient diffusion between adjacent cages. The radical species are destroyed by thermally induced recombination/disproportionation processes, e.g.,  $[HO_2]_2 \rightarrow H_2O_2 + O_2$ , whereas stable species form molecular complexes.

10. No OH and HOCO species have been observed, although they should be formed by the secondary photolysis  $H_2O_2$  species. This may be due to the high reactivity of OH toward CO and the further reaction of the HOCO to give  $CO_2 + H_2O$  (or  $HO_2$ ).

11. The C-C bond rupture in the  $O_2/H_2C_2O_2$  system is responsible for observing more  $[HO_2]_2$  and less HC(O)OO,  $H_2O_2$ , H<sub>2</sub>O, CO<sub>2</sub>, HC(O)OOH, HC(O)OH, and O<sub>3</sub> than in the O<sub>2</sub>/H<sub>2</sub>CO system.

12. The  $O_2/H_2C_2O_2$  system, not the  $O_2/H_2CO$  system, gave species A, [HC(O)OO]<sub>2</sub>, and species T (CO<sub>3</sub>); species A is the precursor of CO<sub>3</sub>. Further work is necessary to explain how CO<sub>3</sub> is formed in the  $O_2/H_2C_2O_2$  system.

13. A variety of *molecular complexes* of  $H_xO_y$  and  $CO_z$  has been made by photooxidation, and their IR spectra and geometry will be presented in detail elsewhere.<sup>6</sup> The present experimental method of preparation is unique and simple, free of the complications encountered in the conventional preparation of the molecular complexes using premixed gas samples or double sprays.

14. Many of the complexes formed in (13) have hydrogen bonding of the types O-H-O as well as O-H-C, and further studies will be in order.<sup>6</sup>

15. There is a great deal of similarility between the  $O_2/H_2CO$  and  $O_2/H_2S$  systems, because of the photochemical recoil of H atoms.

16. The product distribution controlled by the stoichiometry of the photolysis cage in a solid reactive matrix can be used to optimize the conditions for generating and trapping of interesting radical species and molecular complexes at cryogenic temperature.

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**Registry No.**  $H_2CO$ , 50-00-0;  $H_2C_2O_2$ , 107-22-2;  $O_2$ , 7782-44-7;  $HO_2$ , 3170-83-0;  $[HO_2]_2$ , 29683-94-1; HC(O)OO, 56240-83-6; HC(O)OOH, 107-32-4; CO, 630-08-0;  $O_3$ , 10028-15-6;  $CO_2$ , 124-38-9;  $H_2O$ , 7732-18-5;  $H_2O_2$ , 7722-84-1; HCOOH, 64-18-6;  $[HC(O)OO]_2$ , 92270-13-8;  $H_2^{13}CO$ , 3228-27-1;  $H_2C^{18}O$ , 3228-24-8;  $^{18}O_2$ , 32767-18-3;  $C^{16}O^{18}O$ , 18983-82-9.