tional strategies such as isotopic labeling.

In triplet excited states in frozen solution, the aza-aromatic systems demonstrate how the characteristics of the ground- and excited-state electronic structures may be compared by probing electric field gradients at the positions of quadrupolar nuclei. The practical limit for the complexity of the molecules studied is determined by the number of nuclei having significant first-order nuclear quadrupole and second-order dipolar hyperfine interactions, balanced against those which are not resolved and contribute only to the inhomogeneous line widths. Highfield ODENDOR can extend this limit but requires the stronger limitation of finding suitable single crystal hosts in which the guests are oriented.

In conclusion, it may be fairly stated that ENDOR/ TRIPLE and ODNQR methods presented in this article rightly take their place in the larger family of recognizably successful multiple resonance experiments developed in the past 3 decades.

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ARTICLES

Photooxidation of Formaldehyde in Solid Oxygen and Argon/Oxygen Matrices at 12 K

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Matrix-isolated formaldehyde in solid O_2 , Ar/O_2 , and Ar matrices at 12 K has been photolyzed by ultraviolet light in the 220-400-nm range. The photoproducts were identified by infrared spectroscopy. Stable oxidation products were CO, CO₂, H₂O, H₂O₂, O₃, and HCOOH, whereas relatively unstable products were HO₂, its hydrogen-bonded dimer (HO₂)₂, formylperoxy radical HC(O)OO, and performic acid. The observed photoproduct distribution is rationalized by the stoichiometry of chemical reactions involving one C atom, two H atoms, and odd numbers of O atoms in the cage. Photolysis of the $Ar/O_2/H_2CO$ sample (10% O₂ in solid Ar) gave poor yields of radical species. Under the experimental conditions employed, the photochemical oxidation process is not driven to completion, and therefore it is possible to trap reactive intermediates for spectroscopic and kinetic studies. Photodissociation thresholds of H₂CO and (H₂CO)₂ in solid Ar have been measured with tunable, pulsed UV laser photolysis to show that (H₂CO)₂ has a lower threshold than H₂CO.

Introduction

Photolysis of the H_2CO/O_2 mixture in the gas phase is known to involve a set of complex free-radical chain reactions,¹⁻⁶ and the kinetics of these radical reactions are of considerable interest to atmospheric chemistry and combustion of simple hydrocarbons. In an attempt to gain spectroscopic, structural, and kinetic information on the reaction intermediates involved in the oxidation processes, we have initiated a study of the low-temperature photolysis of H_2CO in solid Ar and O_2 matrices, and we present here the results of some exploratory experiments. As a sequel to the earlier H_2CO studies on the proposed photolysis intermediate HCOH (hydroxymethylene)⁷ and the photolysis of H_2CO dimer⁸ in an Ar matrix, we have measured the threshold wavelengths for photolysis of H_2CO monomers and dimers in Ar at 12 K and have carried out the photooxidation of H_2CO in solid O_2 and an Ar/O_2 matrix at 12 K. Although the solid O_2 matrix is a strongly oxidizing environment, the chain propagation prevalent in the gas-phase reactions is prevented in solid O_2 and it is possible to examine the stabilized reaction intermediates trapped in the cage, if a high matrix reactant ratio (M/R) is maintained. This condition corresponds to "extremely lean fuel" combustion.

Gas-phase studies have established the threshold wavelengths for each of the H_2CO dissociation pathways

$$H_2CO + h\nu \rightarrow H_2 + CO \tag{1}$$

$$H_2CO + h\nu \rightarrow H + HCO$$
 (2)

J. R. Sodeau and E. K. C. Lee, Rev. Chem. Intermed., 4, 259 (1980).
 E. C. A. Horner, D. W. G. Style, and D. Summers, Trans. Faraday Soc., 50, 1201 (1954).

⁽³⁾ J. J. Bufalini, B. W. Gay, Jr., and K. L. Brubaker, Environ. Sci. Technol., 6, 816 (1972).

 ^{(4) (}a) T. L. Osif and J. Heicklen, J. Phys. Chem., 80, 1526 (1976); (b)
 B. M. Morrison, Jr., and J. Heicklen, J. Photochem., 11, 183 (1979).
 (5) A. Horowitz, F. Su, and J. G. Calvert, Int. J. Chem. Kinet., 10, 1099

 ⁽¹⁾ A. Horowitz, F. Su, and S. G. Calvert, *Int. 5. Chem. Kinet.*, 10, 1055
 (1) F. Su, G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage,

⁽d) F. Su, G. Calveri, J. H. Shaw, H. Niki, F. D. Maker, C. M. Savage, and L. D. Breitenbach, Chem. Phys. Lett., 65, 221 (1979).

⁽⁷⁾ J. R. Sodeau and E. K. C. Lee, Chem. Phys. Lett., 57, 71 (1978).
(8) M. Diem and E. K. C. Lee, Chem. Phys., 41, 373 (1979).

The threshold for molecular dissociation (reaction 1) occurs at the S_1 origin, ~355 nm, and for radical dissociation (reaction 2) in the region 336-328 nm.⁹⁻¹² Moreover, reaction 2 increases in importance as the exciting wavelength decreases.¹³⁻¹⁶

Photolysis of H₂CO in an Ar matrix at 8 K using radiation from Hg, Br₂, and H₂ lamps has shown a similar energy dependence of reactions 1 and 2.17 At wavelengths between 300 and 178 nm, only reaction 1 was seen to occur (using IR detection of CO as the criterion). At a wavelength of 163.4 nm (Br_2 discharge lamp) HCO radical was detected in the IR spectra, indicating that reaction 2 was also occurring.

Experimental Section

Monomeric H₂CO and D₂CO were prepared by thermal decomposition of solid paraformaldehyde (Aldrich Chemical) at 120 °C by the method of Spence and Wilde.¹⁸ The gases Ar and O_2 were obtained from Liquid Carbonic and had stated purities of 99.9995% and 99.999%, respectively. These were used without further purification. Isotopically labeled oxygen, ¹⁸O₂, was obtained from Prochem and had a stated purity of 99 at. %.

Samples were cooled by an Air Products Displex Model 202B closed-cycle cryostat which maintained temperatures of 12-13 K. The matrix gas and formaldehyde were mixed in a vacuum line, and samples were pulse deposited onto the cold sample window by using a system of solenoid valves. The windows on the cryostat were either CsI or KBr to allow for transmission of IR and UV radiation.

Sample systems were monitored by using two infrared spectrometers, a Perkin-Elmer 281 spectrometer and a Nicolet 7199 FT IR spectrometer. The FT IR instrument parameters were set to give a resolution of 0.3 cm⁻¹ using 500 scans. The FT IR spectrometer was purged with N_{2} , and measured accuracy was ± 0.14 cm⁻¹.

Samples of H_2CO in solid O_2 and O_2/Ar matrices were photolyzed with radiation from a 1000-W super pressure short arc Hg lamp (USHIO 1000D). In all of the experiments a 10-cm water filter and a Corning CS 7-54 filter were used to restrict the incident photolysis radiation to 220-400 nm.

The Ar/H₂CO samples were photolyzed with light from a Nd:YAG-pumped dye laser (Quanta-Ray Model DCR 1A/PDL-1). The doubled UV outputs of exciton 640, rhodamine 590, and cresyl violet perchlorate dyes were used to cover a wavelength range of 330-277 nm. The energy per pulse (10 pulses/s) in each photolysis was 0.5–0.8 mJ, and the bandwidth was 0.3 cm^{-1} at 300 nm.

Ultraviolet absorption spectra were taken at a spectral resolution of 0.1 nm by using a Cary 219 spectrophotometer with samples containing H_2CO (M/R = 5000 and 1000 in Ar). The vibrational structures were observed between 350 and 280 nm. The light scattering by Ar increased at shorter wavelengths, and therefore the base line became

(16) G. K. Moortgat and P. Warneck, J. Chem. Phys., 77, 3639 (1979).

very noisy and thus too high below 280 nm for making a useful measurement.

Results and Discussion

 Ar/H_2CO . Dissociation of H_2CO was monitored by detection of CO (at 2138.4 cm⁻¹) in the IR spectrum of the sample after irradiation for 2-3 h. In a dilute matrix (M/R = 5000) where H_2CO was present almost totally as the monomer,⁸ dissociation to CO (plus H₂) was seen to occur at 305 nm, but not at wavelengths of 313 nm and above. In this dilute matrix UV absorption peaks are blue shifted by ~ 3 nm from the gas-phase absorption peaks, and a similar UV absorption spectrum was obtained with the concentrated matrix with the dimers, placing the S_1 origin in Ar near 351 nm. No HCO was detected (at 1863 cm⁻¹) at these photolysis wavelengths, indicating that dissociation had occurred primarily via reaction 1.

To determine the dissociation threshold for the dimer, we prepared a concentrated sample (M/R = 1000) which displayed a large dimer peak in the C=O stretch region at 1738 cm⁻¹, next to the monomer peak at 1742 cm^{-1} . $\overline{8}, 19, 20$ Irradiation of the sample at 320 nm resulted in CO production, but irradiation at 323 nm and longer wavelengths gave no products. After irradiation at 320 nm the IR spectrum showed that the H₂CO dimer absorption intensity had decreased but that the monomer absorption intensity was essentially unchanged. As in the photolysis of the dilute sample, no HCO was observed.

That no HCO is present after photolysis may be the result of a cage effect in the matrix. Any photochemically generated H and HCO pairs could be trapped by the matrix cage and eventually give H_2CO (or $H_2 + CO$). Those H atoms which did escape from the cage could diffuse until meeting HCO as well as other H atoms and then recombine to give H_2CO or H_2 . Thomas and Guillory¹⁷ argue against the formation of HCO at wavelengths between 300 and 178 nm, stating that the predissociative state of H_2CO may be efficiently quenched by the matrix. However, our experiments with H_2CO in an O_2 matrix show that H_2CO is destroyed more rapidly in O_2 than in Ar, and this is likely to be due to the reaction of O_2 with the photofragments H and HCO to give HO_2 and CO, both of which are observed in solid O_2 after irradiation. At this point it is suggested that radical dissociation of H₂CO is important at excitation wavelengths of 313-178 nm, although the possibility that an H_2CO/O_2 complex photolysis or O_2 -sensitized decomposition of H_2CO contributes to some product formation cannot be ruled out in the solid O_2 system.

The fact that the dissociation threshold occurs at a shorter wavelength in Ar than in the gas phase indicates a vibrational deactivation effect by the matrix, and hence reduced efficiencies of reactions 1 and 2. Apparently the matrix quenches $H_2CO(S_1)$ before it can predissociate, so that at low excitation energies H_2CO remains intact. The radiative quantum yields of H_2CO in solid Xe^{21} and of D_2CO in solid Ne, Xe, and N_2^{22} decrease with increasing excitation frequency, indicating that nonradiative processes become more important at higher energies.

The cause for the higher dissociation threshold energy for the monomer than the dimer by a minimum of 2 kcal/mol (313 vs. 320 nm) is yet to be explained, but it cannot be due to the differences in UV absorption coef-

- Chem., 82, 2575 (1978)
- (22) J. Goodman and L. E. Brus, J. Chem. Phys., 67, 4858 (1978).

⁽⁹⁾ R. S. Lewis, K. Y. Tang, and E. K. C. Lee, J. Chem. Phys., 65, 2911 (1976)

 ⁽¹⁰⁾ J. Marling, J. Chem. Phys., 66, 4200 (1977).
 (11) J. H. Clark, C. B. Moore, and N. S. Nogar, J. Chem. Phys., 68, 1264 (1978).

⁽¹²⁾ J. P. Reilly, J. H. Clark, C. B. Moore, and G. C. Pimentel, J. Chem. Phys., 69, 4381 (1978).
 (13) A. Horowitz and J. G. Calvert, Int. J. Chem. Kinet., 10, 713

^{(1978).}

 ⁽¹⁴⁾ R. S. Lewis and E. K. C. Lee, J. Phys. Chem., 82, 249 (1978).
 (15) K. Y. Tang, P. W. Fairchild, and E. K. C. Lee, J. Chem. Phys., 83, 569 (1979)

⁽¹⁹⁾ H. Khoshkoo and E. R. Nixon, Spectrochim. Acta, Part A, 29, 603 (1973)

 ⁽²⁰⁾ B. Nelander, J. Chem. Phys., 73, 1026, 1034 (1980).
 (21) L. T. Molina, K. Y. Tang, J. R. Sodeau, and E. K. C. Lee, J. Phys.

TABLE I: IR Absorption Frequencies of H₂CO in Solid Ar, O_2 , and N_2^a

mode	frequency, cm ⁻¹			
	Ar/H ₂ CO ^b	O_2/H_2CO^b	N_2/H_2CO^c	
ν ₁	2798.0 (0.40)	2810.2 (0.25)	2800.1, 2798	
ν_2	1742.2(1.00)	1740.0 (1.00)	1740.3, 1740.8	
v ₃	1498.9(0.23)	1505.5(0.37)	1499.7, 1495.9	
ν	1168.4(0.08)	1171.4(0.20)	1167.7	
vs	2864.5(0.15)	2874.2(0.20)	2865.5	
ν_6	1245.0 (0.03)	1252.7(0.02)	1250, 1239	

^a Numbers in parentheses represent intensities as measured by peak heights relative to ν_2 . ^b 12 K. ^c 11 K; ref 20.

ficients. The UV absorption spectra of both monomeric and dimeric H₂CO show that the dimer does not absorb more strongly than the monomer. The excited H₂CO dimer (excimer) must then dissociate or react more easily than the monomer, probably because of the proximity of the reactive partner in the cage, to give $CH_3OH + CO.^8$ While the monomer reaction to give $H_2 + CO$ is nearly thermoneutral, the dimer reaction is \sim 48 kcal/mol exothermic and it may involve a two-step radical mechanism to be discussed later.

 O_2/H_2CO and $Ar/O_2/H_2CO$. The IR absorption frequencies of H_2CO in solid O_2 and Ar at 12 K are given in Table I, along with the frequencies of H_2CO in N_2^{-20} The typical bandwidths in our experiments are $\leq 1 \text{ cm}^{-1}$. There was no evidence of rotation or site splitting in any of the H_2CO absorptions in solid O_2 ; each vibrational mode displayed only a single peak.

Before irradiation O_2 peaks were observed at 1615 (broad), 1591 (broad), 1549.7, and 1548.1 cm⁻¹. The absorptions were due to O₂ vibrations which were induced in the solid, as reported by Cairns and Pimentel.²³

Photolysis was carried out in O_2/H_2CO matrices (M/R = 1000, 2000) and in an $Ar/O_2/H_2CO$ matrix (1000:100:1). Photolysis of the $Ar/O_2/H_2CO$ sample gave small amounts of photooxidation products, indicating that some reactions had occurred between H2CO and O2. No HO2 was observed, although H_2O_2 , H_2O , CO, and CO_2 were detected. It should be recognized that the Ar/O_2 ratio of 10 provides on the average one molecule of O_2 as a nearest neighbor of H_2CO , and hence a limited supply of oxidant. Lower product yields in these $Ar/O_2/H_2CO$ samples made the experiment more difficult than the study of the O_2/H_2CO samples, and therefore no further experiments were done with the $Ar/O_2/H_2CO$ samples.

Photolysis was also done on isotopically labeled samples of D_2CO in O_2 . The rate of photolysis of O_2/D_2CO systems was significantly lower than that of O_2/H_2CO , reflecting the large isotope effect which has been reported in previous studies.^{7,21,24,25}

Considering the stoichiometry of H_2CO photooxidation, several sets of products can be envisioned (see eq 3-10).

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

$$\rightarrow$$
 H₂O₂ + CO (4)

$$\rightarrow H_2O + CO_2 \tag{5}$$

$$\rightarrow \text{HC}(0)\text{OOH} \tag{6}$$

$$H_2CO + 2O_2 + h\nu \rightarrow 2HO_2 + CO \tag{7}$$

$$\rightarrow \text{HO}_2 + \text{HC}(0)00 \tag{8}$$

$$\rightarrow$$
 HCOOH + O₃ (9)

$$\rightarrow H_2O + CO + O_3 \tag{10}$$

(23) B. R. Cairns and G. C. Pimentel, J. Chem. Phys., 43, 3432 (1965). (24) R. G. Miller and E. K. C. Lee, Chem. Phys. Lett., 41, 52 (1976). (25) R. G. Miller and E. K. C. Lee, J. Chem. Phys., 68, 4448 (1978).



Figure 1. IR spectra of the O_2/H_2CO sample (M/R = 1000, ~ 12 μ mol) before (lower trace) and after (upper trace) 2-h irradiation, showing (a) CO region, (b) $CO_2(\nu_3)$ region, and (c) $CO_2(\nu_2)$ region. The lower traces show the initial impurity levels of CO and CO2 in the sample.

Most of the stable products shown in eq 3–10 have been reported in some of the numerous studies done on gas-phase photooxidation of H_2CO .^{2-6,26-28} After irradiation of H_2CO in solid O_2 all of the above products, except HCO, were observed in the infrared spectra. The photoproducts are listed in Table II, along with the observed frequencies and values reported in the literature.

Because leakage from the atmosphere was a problem with the cryostat, at times it was not certain whether the CO_2 and H_2O peaks were due to photoproducts or merely from impurities frozen onto the matrix during the course of the experiment. Photolysis of O_2/D_2CO (M/R = 1000) resulted in the appearance of peaks at 2700 and 1172 cm^{-1} , due to D_2O . To test the origin of the CO_2 peak, we prepared and irradiated an authentic sample of $Ar/^{18}O_2/$ H_2CO (1000:25:1). This sample displayed a peak at 2332.6 cm^{-1} , due to $C^{16}O^{18}O$. No $C^{18}O_2$ was observed. Thus, the photolytic origin of these two molecules was confirmed.

Table II shows that each product listed displays more than one IR absorption peak for each vibrational mode. Because matrix site splitting appears to be relatively unimportant for most of the products and H₂CO in the samples studies here, this multiplicity of peaks indicates that aggregation of the products in the cage occurs during photolysis.

- (26) R. G. W. Norrish and J. M. Thomas, Nature (London), 210, 728 (1966)
- (27) D. E. Hoare and G. S. Milne, Trans. Faraday Soc., 63, 101 (1967). (28) T. C. Purcell and J. R. Cohen, Environ. Sci. Technol., 1, 845 (1967)
- (29) B. Nelander, J. Chem. Phys., 72, 77 (1980).
- (30) G. P. Ayers and A. D. E. Pullin, Spectrochim. Acta, Part A, 32, 1629 (1976)
- (31) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies" Consolidated Vol. I, Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.), No. 39 (1972)
- (32) (a) H. Dubost and L. Abouaf-Marguin, Chem. Phys. Lett., 17, 269 (1972); (b) H. Dubost, Chem. Phys., 12, 139 (1976).
- (33) S. Pinchas and I. Laulicht, "Infrared Spectra of Labelled Compounds", Academic Press, New York, 1960.
- (34) J. L. Bruman, A. Barbe, and P. Jouve, C. R. Hebd. Seances Acad. Sci., Ser. B, 268, 549 (1969)
- (35) (a) M. E. Jacox and D. E. Milligan, J. Mol. Spectrosc., 42, 495 (1972); (b) D. E. Milligan and M. E. Jacox, J. Chem. Phys., 38, 2627 (1963)
- (36) J. A. Lannon, F. D. Verderame, and R. W. Andersen, Jr., J. Chem. Phys., 54, 2212 (1971).
 (37) P. A. Giguere and T. K. K. Srinivasan, Chem. Phys. Lett., 33, 479
- (1975)
- (38) P. D. Maker, H. Niki, C. M. Savage, and L. P. Breitenbach, Anal.

Chem., 49, 1346 (1977).
(39) D. W. Smith and L. Andrews, J. Chem. Phys., 60, 81 (1974).
(40) (a) M. Diem, T.-L. Tso, and E. K. C. Lee, J. Chem. Phys., 64, 6452 (1982); (b) T.-L. Tso, M. Diem, and E. K. C. Lee, results to appear in

Chem. Phys. Lett.

(41) L. Fredin, B. Nelander, and G. Ribbegard, Chem. Scr., 7, 11 (1975).

TABLE II: IR Absorption Frequencies of Photoproducts in the O ₁ /H ₂ CO Systems at 1;

absorbing species	complexes	obsd frequencies in O_2^{a} , $a \text{ cm}^{-1}$	lit. frequencies, cm ⁻¹
$ \begin{array}{c} \mathrm{H_2O}(\nu_1) \\ \mathrm{H_2O}(\nu_2) \end{array} $	H O.CO	3635.0, 3633.0, 3631.6, 3625.7 1600.6, 1595.1, 1594.0, 1552.5 1588.7	$3634.5 (N_2), 3638.0 (Ar)^{30}$ 1597.6 $(N_2), {}^{30}$ 1589.1 (Ar)^{29} 1598.1 $(N_2)^{b}$
$H_2O(\nu_3)$		3733.7, 3723.5	$3726.9 (N_2)$, ²⁹ 3734.3 (Ar) ³⁰
$\mathrm{CO}_2(\nu_3)$	$CO_2 \cdot H_2O$ CO_2 (isolated) ^c $C^{16}O^{18}O$	2349, 2348.0, 2340.9 2345.6 (2342.4) 2339.5 (2341.8, 2344.4) 2332.6 (Ar)	2349.3 $(gas)^{33}$ 2351 $(N_2)^b$ 2332 $(gas)^{33}$
$\mathrm{CO}_2(\nu_2)$	CO_2 (isolated) ^c $CO_2 \cdot H_2O$	665.8, 662.1 (662.8) 666.9, 659.7 (654.1)	$667.3 (gas)^{ss}$ 666.3, 665.3 (N2)b
CO	$\begin{array}{c} CO \cdot (HO_2)_2 \\ CO \cdot H_2O_2 \\ CO \cdot H_2O \end{array}$	2163.7, 2153.9, 2152.9, 2137.9 2160.6 2150.8, 2149.8 2144.8	2138 (Ar) ³² 2150 (Ar) ³²
	CO (isolated)	2136.1	
${f O_{3}(\nu_{3}) \ O_{3}(\nu_{2})}$		$1038.0 \ (1031.5)^d$ 702.7	$\frac{1037 (O_2)^{34}}{708.5 (O_2)^{34}}$
$\mathrm{HO}_{2}(\nu_{1})$		3400.3 ^e 331.8 ^f	$3414 (Ar)^{35}$
$HO_2(\nu_2)$	$(HO_2)_2$ HO ₂ (isolated)	1392, 1391.5 1417 1/	$1389 (Ar)^{35}$
$HO_2(\nu_3)$	$(HO_2)_2$ HO ₂ (isolated) $(HO_2)_2$	1101.4 1108.3 ⁷	1101 $(Ar)^{35}$
$\begin{array}{c} H_{2}O_{2}(\nu_{1};\nu_{5}) \\ H_{2}O_{2}(\nu_{2};\nu_{6}) \end{array}$		3597.6, 3581, 3544.2 1279.6, 1278.1, 1276.4, 1272.6, 1268.7	3593, 3597.4 (Ar) ^{36,37} 1385, 1270.6 (Ar) ^{36,37}
$ \begin{array}{l} \text{HCOOH}(\nu_3) \\ \text{HCOOH}(\nu_4) \\ \text{HCOOH}(\nu_6) \\ \text{HCOOH}(\nu_1) \end{array} $		1762.8 641.5, 640.6 1100.3, 1099.3 3329	$\begin{array}{c} 1770 \ (gas)^{31} \\ 638 \ (gas)^{31} \\ 1105 \ (gas)^{31} \\ 3340.7 \ (gas)^{31} \end{array}$
HC(O)OOH		1734 ⁴⁰ b	1745 (gas) ³⁸
HC(O)OO		1790 ^{*0} b	
$\begin{array}{c} \mathrm{D_2O}(\nu_2)\\ \mathrm{D_2O}(\nu_3) \end{array}$		1172 [#] 2770, 2762	1178.8 (Ar) ²⁹ 2765.8 (Ar) ²⁹
$\frac{\mathrm{DO}_2(\nu_2)}{\mathrm{DO}_2(\nu_3)}$		1113? 1022	1123 (Ar) ³⁵ 1020 (Ar) ³⁵
$D_2O_2(\nu_1;\nu_5)$		2618	2632 (Ar) ³⁹ 2653 5 (Ar) 2656 (Ar) ^{36,37}
${\rm D_2O_2}(\nu_2;\!\nu_6)$		952	951 (Ar) ³⁹ 1021.5 (Ar), 950.5 (Ar) ^{36,37}

^a Frequency is assigned to the italicized molecule in the complex. Some of the frequencies are assigned neither to the isolated monomer nor to the complexes for which the assignment is confirmed in ref 40. ^b Fredin, Nelander, and Ribbegard give assignments of the frequencies of the H_2O ·CO complex in ref 41. They show shifts less than 4 cm⁻¹ in N₂ at 20 K. ^c Before photolysis, three CO₂ impurity peaks appear in the O₂/H₂CO sample. The multiplet structure may be due to site splitting or complexation. ^d Not always observed. ^e This could be the isolated monomer or the HO_2 ·CO complex. ^f It is possible that this frequency could be that of the $(HO_2)_2$ ·CO complex. ^g Probably a D_2O ·CO₂ complex.

The two molecules which best demonstrate molecular complex formation are CO_2 and CO. The IR absorption peaks of each of these products are shown in Figure 1. Here the peaks are well resolved, and the large number of complexing partners available to CO_2 and CO is evident.

In most cases, assignments can be made for individual peaks from the present work, additional results obtained in our laboratory,⁴⁰ and published results in the literature.^{41,42} Reaction 5 implies that H₂O is the most likely partner of CO₂ from the photolysis. Therefore, it is reasonable to assign the largest peak (in ν_3) and the two largest peaks (in ν_2) in each CO₂ absorption group, 2345.6 cm⁻¹ and the 659.7- and 666.9-cm⁻¹ pair, to the CO₂·H₂O complex. The splitting of the doubly degenerate vibration of CO₂ (ν_2) is very pronounced in the CO₂·H₂O complex, and it is consistent with the structure of the planar complex

in which binding occurs between the carbon atom of $\rm CO_2$ and the oxygen atom of $\rm H_2O.^{42}$ In addition, there are peaks in each $\rm CO_2$ region which are present before photolysis; the largest peak or peaks in each region (2339.5 cm⁻¹ and the 662.1- and 665.8-cm⁻¹ pair) are assigned tentatively to $\rm CO_2$ which is "isolated" in solid O₂. Other minor peaks may be from the isolated molecule due to site splitting or a complex.

In the case of the CO absorption a somewhat more detailed assignment may be made. The prephotolysis spectrum of that region shows a small peak at 2136.1 cm⁻¹ which is assigned to the isolated CO, present as a trace impurity. From the studies of Ar/H_2CO it was found that CO isolated in Ar absorbs at 2138.4 cm⁻¹. Apparently the O₂ matrix induces a red shift of a few wavenumbers in the CO frequencies. When this shift is applied to the CO·H₂O peak (2148–2149 cm⁻¹ in Ar), the large peak at 2144.8 cm⁻¹ is assigned to this complex, presumably formed by reaction 10.

⁽⁴²⁾ B. Jonsson, G. Karlstrom, and H. Wennestrom, Chem. Phys. Lett., 30, 58 (1975).

Reactions 4, 7, and 10 indicate that H_2O_2 , HO_2 , $(HO_2)_2$, and H_2O should be partners of CO. Thus, the peak at 2160.3 cm⁻¹ is assigned to $CO \cdot HO_2$ and (or) $CO \cdot (HO_2)_2$, the peaks at 2150.8 and 2149.8 cm⁻¹ to $CO \cdot H_2O_2$, and the peak at 2144.8 cm⁻¹ to $CO \cdot H_2O$. Support for this assignment comes from warming experiments,⁴⁰ which show the disappearance of peaks due to the self-reaction of $(HO_2)_2$, and an increase in intensity of peaks due to the formation of H_2O_2 . Along with these changes we observe a disappearance of the 2160.3-cm⁻¹ peak and a growth of the peaks at 2150.8 and 2149.8 cm⁻¹. If H atom escapes from the photolysis cage, as will be discussed later, then the CO-HO₂ complex is formed. Similarly, if O₃ "escapes" from the photolysis cage, then the CO·H₂O complex is formed.

In a study of CO-X complexes by Dubost and Abouaf-Marguin^{32a} it was reported that the CO frequency increases with increasing polarity of the partner for $X = N_2$, CO, NH_3 , and H_2O . According to this trend, $CO \cdot H_2O_2$ and $CO \cdot HO_2$ (and $CO \cdot (HO_2)_2$) should absorb at frequencies higher than that for $CO \cdot H_2 CO$. This trend is approximately followed by the CO complexes in the O_2/H_2CO system.

Another parameter which follows the CO-X frequencies is the gas-phase acidity of the partner. The acidity values for these same molecules show a correspondence to the IR frequency shifts for the CO complexes with those molecules. Thus, gas-phase acidities of HA-type molecules appear also to be useful parameters with which to correlate the shifts in the observed CO peaks.

The absorptions attributable to HO₂ show evidence of a hydrogen-bonded complex.^{40,43} The peaks at 3400.3, 1392, and 1101.4 cm^{-1} are accompanied by peaks at 3318, 1417.1, and 1108.3 cm⁻¹. The peaks at 1392 and 1101.4 cm^{-1} are assigned to the HO₂ monomer, but the peak at 3400.3 cm⁻¹ is shifted from the frequency in an Ar matrix by an unexpectedly large amount (-14 cm^{-1}) and may be due to HO_2 ·CO or some other HO_2 complex. The latter three peaks show respectively a large red shift in the O-H stretch, a blue shift in the H-O-O bend, and a small blue shift in the O-O stretch. Because HCO is not observed after photolysis, it must quickly react with O₂ to give HO₂ and CO (reaction 7).40 Reactions 3 and 7 indicate that the two HO₂ radicals should be in very close proximity and therefore the hydrogen-bonded complex of HO₂ described above is believed to be the HO₂·HO₂ dimer as described in a recent paper.^{40a} This dimer is further complexed to CO.

The production of O_3 appears to be mainly a result of O_2 photolysis at 220-400 nm. Irradiation of solid O_2 under the same conditions used in O_2/H_2CO photolysis resulted in the appearance of the O_3 peaks, with about the same intensities observed in O_2/H_2CO photolysis. But, O_3 is mainly formed by photooxidation of H₂CO, if a longerwavelength UV cutoff (290-400 nm) is employed.^{40b}

Because O_3 should be more easily photolyzed than O_2 , the ratio of O_3/O_2 could reach a photostationary state. We do not reach this limit under our experimental conditions. Once a molecule of O_3 is generated, it is surrounded by O_2 molecules. If photodissociation of O_3 then occurs, the O atom produced will probably combine with another O2 and regenerate O_3 . Thus, there is no net destruction of O_3 , unless it is photolyzed in the presence of H₂CO or its photoproducts, including O_3 . The repetition of this regeneration process would in effect cause O₃ to "migrate" away from the initial photolytic cage leaving other stable cage partners. Because the photolysis of O_3 below 300 nm can give $O(^{1}D)$, the secondary photolysis of O_{3} in the vicinity of H₂CO, CO, or H₂O may account in part for the observed products such as HCOOH, CO₂, or H₂O₂. However, we do not believe the O_3 photoreactions are of major importance in the present system, since such reactions would result in low CO and H_2O concentrations and high HCOOH and H_2O_2 concentrations, contrary to our observation. Of course, the photolysis in the 290-400-nm range should prevent such secondary photolysis of O_3 . The fact that the observed product distribution from photolysis in the 290-400-nm range⁴⁰ is not significantly different from our present result lends support to the above statement.

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A similar "migration" process may apply to HO_2 . UV photolysis of HO_2 should produce an H atom which can react with another O_2 to regenerate HO_2 or with other photoproducts. The repeated dissociation and recombination of HO_2 in this manner could result in the H atom hopping through the matrix from one O_2 site to another, with no net reduction of HO₂ occurring until the H atom combines with another reactive species.

A product peak appearing at 1762.8 cm⁻¹ is assigned to the carbonyl stretch of formic acid (HCOOH). The yield of HCOOH is quite small and the mechanism of its formation is discussed elsewhere.^{40b} No carbonyl stretch peak corresponding to formyl radical (1863 cm⁻¹, in solid Ar) or hydroxycarbonyl (1833 and 1797 cm⁻¹ in solid CO) has been observed. However, a product peak appearing at 1790.2 cm⁻¹ is identified as formylperoxy radical, HC-(0)00, formed by addition of O_2 to HCO.^{40b} The hydroperoxycarbonyl radical, HOOC(O), which could be formed by addition of HO_2 to CO was not observed.

The absence of CH_3OH in O_2/H_2CO photolysis indicates that O_2 scavenges the radical precursor responsible for CH_3OH formation in the $(H_2CO)_2$ photolysis in solid O_2 , i.e., CH₂OH or HCOH.

The relative absorption strengths of CO_2 and CO may be used to estimate roughly the relative abundance of each of these molecules after photolysis. The gas-phase integrated absorption coefficient for CO is $\sim 2.3 \times 10^2$ cm⁻² atm⁻¹, and that for CO₂ (ν_3) is $\sim 2.0 \times 10^3$ cm⁻² atm⁻¹ at 300 K.⁴⁴ The assumption is made, for these calculations, that the ratio of the gas-phase coefficients (CO_2/CO) , 8.7, does not change significantly in an O₂ matrix at 12 K. Although this assumption may not be valid in some cases, it could give rough estimates of relative product concentrations. When we use this ratio and the measured peak intensities for CO₂ and CO in the matrix, it is estimated that 3 times as much CO_2 as CO is present after 2 h of irradiation.

This relative abundance can in turn give some insight into the reaction sequence in the matrix. The first step should be the formation of HCO and HO_2 , with subsequent reaction of HCO with O_2 to give HO_2 and CO (reaction 7 overall) or HC(0)OO (reaction 8). Next may be the combination of the two HO₂ molecules to give the dimer $(HO_2)_2$ or H_2O_2 (and O_2), followed by photochemical reaction of H_2O_2 with CO to give CO_2 and H_2O (or reaction 5 overall).

⁽⁴⁴⁾ L. A. Pugh and K. N. Rao in "Molecular Spectroscopy: Modern Research", Vol. II, K. N. Rao, Ed., Academic Press, New York, 1976, p 165

^{(45) (}a) D. R. Stull and H. Prophet, Eds., "JANAF Thermochemical Tables", 2nd ed., Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.), No. 37, (1971); (b) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

^{(43) (}a) G. C. Pimentel and A. D. McClellan, "The Hydrogen Bond",
W. H. Freeman, San Francisco, 1960; (b) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand-Reinhold, New York, 1971.

 ⁽⁴⁶⁾ C. J. Howard, J. Am. Chem. Soc., 102, 6937 (1980).
 (47) K. Shibuya, T. Ebata, K. Obi, and I. Tanaka, J. Phys. Chem., 81, 2292 (1977).



Figure 2. Energetics of oxidation processes starting with H₂CO + nO_2 . The standard enthalpies of the reactions at 300 K (ΔH°_{rx}) giving various final products as shown. The numbers in parentheses are estimated values.

The radical combination reaction of HO_2 with HCO could give HC(O)OOH. Some of these steps may require a second UV photon. The products CO_2 and H_2O should be very stable under the experimental conditions. Therefore the amount of CO_2 and H_2O continues to increase, while the other, less stable, photoproducts maintain a steady-state concentration.

Energetics. While there is much to be done to elucidate the detailed kinetics and mechanisms of the oxidation processes, the energetics of various oxidation reactions can be examined. The standard enthalpies of the reactions of $H_2CO + nO_2$ at 300 K to give various oxidation products are shown in Figure 2. The values of ΔH°_{rx} for ideal gases at 300 K are used for convenience, since the corresponding ΔH°_{rx} values at 12 K would not be much different for the purpose of discussion here. The values of $\Delta H_{\rm f}^{\circ}_{300\rm K}$ were obtained from standard references.⁴⁸ The recent value of $\Delta H_{\rm f}^{\,\circ} = 2.5$ kcal/mol for HO₂⁴⁶ was used in estimating the value of $\Delta H_{\rm f}^{\circ} = -5.0$ kcal/mol for the hydrogen-bonded dimer (HO₂)₂.^{40b} The $\Delta H_{\rm f}^{\circ}$ values of performic acid and formylperoxy radical were estimated from the group additivity rule to be -72.4 and -32.4 kcal/mol, respectively.46b It was assumed that each O-H···O hydrogen bond is worth approximately -5 kcal/mol in performic acid and $(HO_2)_2$.

The conversion of HCO to $H(C=0)O_2$ is 42 kcal/mol exothermic. The conversion of HCO to $HO_2 + CO$ is 34 kcal/mol exothermic, and its activation energy is nearly zero (-0.3 kcal/mol).^{12,47,48} This might explain the absence of HCO in the O_2 matrix. It is interesting to note that the reaction of $H_2CO + 2O_2$ to give $2HO_2 + CO$ is only ~ 4 kcal/mol endothermic compared to the thermoneutral process leading to $H_2 + CO + 2O_2$. This means that HO_2 and $(HO_2)_2$ can act as relatively stable intermediates with high energy contents. In other words, HO_2 and $(HO_2)_2$ are effective in energy storage, and their further conversion to other lower-lying oxidation products shown in Figure 2 is interrupted in solid O_2 at low temperature. The chain initiation and propagation processes normally present in low-temperature combustion reaction in the gas phase are greatly suppressed by the rapid vibrational relaxation of excited species resulting from photochemically initiated oxidation processes. Therefore, solid O2 provides an environment in which a variety of reactive intermediates containing excess oxygen atoms (polyoxides) are stabilized. As Ar dilutes O_2 in mixed matrices, this stabilizing effect is significantly reduced, and it favors the formation of more stable products such as H_2O_2 , H_2O , and CO_2 .

In summary, it can be stated that in the O_2/H_2CO photolysis more than half of the photooxidation products are CO_2 and H_2O , the result of complete oxidation. The more abundant minor products are CO, H₂O₂, HO₂, and $(HO_2)_2$, due to incomplete oxidation. O_3 , HCOOH, HC-(O)OOH, and HC(O)OO radical (1790-cm⁻¹ absorption)^{40b} are less abundant minor products. The absence of HCO radical is probably due to an efficient reaction of HCO with O_2 . In the Ar/ O_2/H_2CO photolysis, HO₂ and other radical products are less abundant, indicating shorter lifetimes of the "transient" species. This may be due to a greater mobility of H atoms in Ar matrix than in O_2 matrix. The O_2/H_2CO matrix corresponds to a "lean-fuel" mixture. Secondary photolysis may play a nonnegligible role in the final product distribution in the present study, and monochromatic and time-dependent photolysis will be desirable in future studies. A more complete mechanistic rationale for oxidation processes must await further investigation, which is underway. However, it is amply demonstrated here that the use of matrix FT IR spectroscopy in the study of photooxidation of simple molecules such as H₂CO can provide new experimental information on reactive intermediates important in oxidation processes as well as on molecular complexes formed in photolytic systems.

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⁽⁴⁸⁾ B. Veyret and R. Lesclaux, J. Phys. Chem., 85, 1918 (1981).