significant role. The parallelism between the H_2-D_2 equilibration activity and reducibility is strong evidence for this scheme. The effect of admixed Pd-carbon also supports the view. H_3PMo and Ag_3PMo have the same polyanion, but H₃PMo is hardly reduced at 150 °C because it does not dissociate H_2 at that temperature. In other words, polyanion can be reduced, if hydrogen atoms are supplied by any means, either by countercations or by mechanically mixed catalysts. The results of the kinetic isotope effect on the reduction rate also suggest the above scheme: the lack of the isotope effect for Ag₃PMo indicates that the former process is sufficiently rapid, but this step is slow for the other molybdophosphates.

Halpern¹¹ reported that some metal cations can activate molecular hydrogen in aqueous solution: molecular hydrogen dissociated by catalysis of some metal cations and resultant H atoms reduce the reducible ionic species such as $Cr_2O_7^{2-}$ or Ce^{4+} . The scheme can be written

$$H_2 + 2Ag^+ \rightarrow 2[AgH]^+$$

 $2[AgH]^+ + [reducible species] \rightarrow$

 $2Ag^{+} + [reduced species]$

 Ag^+ has an isoelectronic structure as Pd^0 , which is one of the strongest H_2 -dissociation catalysts. This is the reason that Ag^+ has activity for H_2 dissociation. Table I lists the active and inactive metal cations reported by Halpern, together with ours. A good parallelism is apparent.

The scheme can only be applied for Ag₃PMo and $Cu_{1.5}PMo$, which have extraordinarily high reducibility. Different mechanisms, in which cations play only secondary roles, must be considered for less reducible catalysts. The compounds whose cation has no activity for H₂ dissociation might be reduced without a direct participation of cations. Akimoto¹² et al. reported that the activities for isobutyric acid oxidation also were affected by countercations, but differences of catalytic activity between the compounds were not so large. they attributed the results to countercation effects on the electronic properties of polyanions.

A brief discussion about the reducibility of polyanion may be appropriate. Polarographic studies¹³ show that Mo-based heteropoly acids have higher oxidation ability than W-based ones. The appearance of the TPR peak at lower temperatures for Mo-based acids is thus acceptable.

One may consider that reduced metal atoms or polyanions, not cations, are actually working as a hydrogen activator. However, when H₂-D₂ mixtures were contacted with reduced H₃PMo at 200 °C, no HD was formed. Therefore, it was concluded that the reduced polyanion does not dissociate molecular hydrogen so well as the oxidized state. The good parallelism between Halpern's work and ours suggests that cations are working as a hydrogen activator.

Matrix Infrared Spectra and Photolysis and Pyrolysis of Isotopic Secondary Ozonides of Ethylene

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The secondary ozonide of ethylene (SOZ) has been prepared in six isotopic modifications by reacting ozone and ethylene in CF₃Cl near -150 °C. The SOZ vibrations are characterized by ¹⁸O, ¹³C, and D isotopic shifts from matrix infrared spectra. Photolysis and pyrolysis of the SOZ is proposed to proceed via excited hydroxymethyl formate (HMF*). Under the conditions of pyrolysis, this activated species decomposes completely to formic acid and formaldehyde, but matrix photolysis of SOZ leads to quenching of HMF* and trapping of the ground-state molecule. An open chain trans and a hydrogen-bonded cis conformer of HMF are observed; photoexcitation decomposes the former to formic anhydride (FAN) and the latter to a specific formaldehyde-formic acid dimer (F/A). The dimer F/A is also observed following pyrolysis of SOZ and codeposition of formic acid and formaldehyde. The origin of CO₂ produced on SOZ pyrolysis and of CO₂, CO, and H₂O produced on SOZ photolysis is discussed. A brief comparison of results from ethylene-ozone gas-phase studies with matrix photolysis of SOZ suggests that ground- or excited-state SOZ may play an important role in the gas-phase ethylene-ozone reaction, even though it is rarely detected.

Introduction

A substantial amount of evidence supports the mechanism proposed by Criegee for the solution-phase reaction of ozone with olefins.¹⁻⁴ The initial five-membered ring, known as the primary ozonide (POZ) or 1,2,3-trioxolane,

1, is highly unstable, and quickly rearranges to the secondary ozonide (SOZ) or 1,2,4-trioxolane, 2. In a recent matrix study,⁵ the POZ was formed in six isotopic modifications by reaction of ethylene and ozone in solid xenon warmed to 80 K. This paper presents the vibrational spectra of six isotopic modifications of the SOZ of ethylene trapped in an argon matrix. In addition, matrix photolysis studies of the SOZ isotopes have given infrared spectro-

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scopic evidence for hydroxymethyl formate, suggested as an SOZ decomposition product in recent gas-phase work.⁶

Infrared spectra of ozonides reported before 1955 are suspect; bands in the carbonyl region have been shown to be due to decomposition products.^{2,7} Criegee et al.⁸ have studied infrared spectra of 18 pure ozonides. Garvin and Schubert⁹ published the first spectra of ozonides prepared by reacting ethylene, propylene, and isobutylene with ozone at -78 °C. Menyailo and Pospelov¹⁰ detected two bands, at 1110 and 1062 cm⁻¹, for ozonides of n-alk-1-enes. Bailey² has reviewed the infrared spectra of ozonides and has reported characteristic bands in the 1115-1015- and 1000-890-cm⁻¹ regions. In the most extensive previous infrared study of secondary ozonides, Kuhne and Gunthard¹¹ examined the spectra of three isotopic modifications of the SOZ of ethylene, $SOZ-d_0$, $SOZ-1,1-d_2$, and $SOZ-d_4$ and made assignments based on empirical considerations and normal coordinate analysis (using C_2 symmetry, as indicated from the microwave spectra¹²). The ozonides were prepared by passing ozone through a solution of ethylene in methyl chloride at -78 °C. Matrix spectra were recorded after the ozonides were purified from the solvent by low-temperature trap-to-trap distillation.

Experimental Section

Apparatus. The 15K cryogenic refrigeration system and vacuum vessel have been previously described.¹³ All spectra were recorded on a Beckman IR-12 spectrophotometer over the range 200-4000 cm⁻¹. Regions of interest were examined with expanded wavenumber scales; reported band measurements are accurate to $\pm 1 \text{ cm}^{-1}$ below 2000 cm^{-1} and $\pm 2 \text{ cm}^{-1}$ above 2000 cm^{-1} . Selected samples were photolyzed with a BH-6 high-pressure mercury-arc lamp (1000 W, General Electric Co. and Illumination Industries, Inc.) for periods ranging from 5 min to 1 h. A 10-cm water filter, used to prevent heating of the matrix during photolysis, provided a 220-1000-nm output. A quartz window, sealed with halocarbon wax, allowed access to the matrix.

Chemicals. Ozone was generated by a static electric discharge (Tesla coil) of oxygen in a Pyrex tube and collected with liquid N₂.¹⁴ The normal isotopic O₂ was obtained from Burdett, U.S.P. grade. Two ¹⁸O-enriched samples, from Yeda R&D Co., Ltd. (Israel), were reported as 50.35% ¹⁸O and 95.57% ¹⁸O. Residual O_2 was removed from the O₃ samples by pumping with an oil diffusion

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pump. The ethylene was obtained from Matheson (CP grade). Isotopic ethylene samples obtained from Merck Sharp and Dohme (Montreal) included C_2D_4 (99% D), CH_2CD_2 (98% D), and ${}^{13}C_2H_4$ (90% ${}^{13}C$). All ethylene samples were condensed at 77 K and pumped with an oil diffusion pump to remove any air impurities. Argon (Burdett, 99.999%) and chlorotrifluoromethane (DuPont, Freon-13) were used as received.

Procedure. About 5 mmol of the ethylene was condensed at the base of a "U-tube" (0.25-in. stainless steel) by allowing liquid N_2 to just cover the bottom of the tube. The N₂ level was raised about 2 cm, and about 25 mmol (or more) of chlorotrifluoromethane was condensed in the tube. The N_2 level was raised another 2 cm, and about 5 mmol of ozone was condensed in the tube. This "sandwich" technique was necessary to ensure the roomtemperature ozone could not be in contact with the ethylene. The dewar containing the N_2 was then quickly replaced with a dewar containing a n-pentane slush (-130 $^{\circ}$ C), or (better) *n*-pentane was added to the N₂-containing dewar. After the N_2 liquid evaporated, the *n*-pentane slowly melted. The reaction temperature was probably controlled by the melting of the Freon-13 (approximate mp -150 °C). The solvent, excess reagents, and volatile products were removed by pumping at -98 °C (methanol slush). The ozonide was deposited onto the CsI window as the methanol slush slowly warmed to -78 °C (dry ice) along with excess argon (argon/ozonide $\approx 200/1$ estimated) from a second spray on line ($\sim 2 \text{ mmol/h}$). The temperature of the U-tube was kept at -78 °C for 5 h or until all the ozonide was evaporated as determined from infrared spectra. In the pyrolysis experiments, 10-20% of the ozonide was allowed to evaporate onto the window, as described above, for quality control. The remainder was transferred under vacuum and evaporated from a cold finger through 120 cm of stainless-steel tubing with the last 30 cm heated, and the effluent was codeposited on the cold CsI window with argon.

Results

Infrared spectra and photochemistry of matrix-isolated isotopic secondary ozonides will be presented and compared to the spectra of SOZ pyrolysis products trapped in solid argon.

SOZ Infrared Spectra. The infrared spectrum of the secondary ozonide produced by the liquid-phase reaction of ethylene and ozone is shown in Figure 1. The top trace, Figure 1a, shows the spectrum of codeposited ethylene and ozone samples (Ar/R = 200/1); no reaction products were observed. Diffusion studies were attempted by warming the window but the argon evaporated before any product formation (successful results were obtained with xenon instead of argon, as described in an earlier paper⁵). Similar matrix samples were photolyzed producing ethylene oxide (878 and 1274 cm⁻¹) and acetaldehdye (518, 1120, 1353, and 1745 cm⁻¹). Figure 1b shows the spectrum of the ethylene secondary ozonide produced by the liquid-phase ozonolysis of ethylene in Freon 13. No primary ozonide or reaction intermediates were observed. Formaldehyde, labeled F at 2864, 2797, 1743, 1499, 1246, and 1167 cm⁻¹, was usually observed as a decomposition product; the SOZ band positions, in excellent agreement with Kuhne and Gunthard,¹¹ are listed in Table I.

The infrared spectra obtained with the use of isotopic oxygen are contrasted in Figure 2. Comparison of the ¹⁶O and ¹⁸O spectra in parts a and c of Figure 2 reveals obvious ¹⁸O counterparts for the ¹⁶O product bands as listed in Table I. The mixed ^{16,18}O SOZ, shown in Figure 2b, produced a doublet for the 952-cm⁻¹ band, a doublet of triplets

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Figure 1. Infrared spectra of ozone and ethylene mixtures in solid argon at 15 K: (a) $Ar/C_2H_4 = 200/1$ and $Ar/O_3 = 200/1$ samples codeposited from separate manifolds; (b) ethylene secondary ozonide evaporated into condensing argon stream, F denotes formaldehyde absorptions from SOZ decomposition during deposition; (c) sample from (b) after 75 min of full high-pressure mercury arc photolysis; (d) ethylene secondary ozonide evaporated through a 120-cm tube at 24 °C for 8 h and with last 30 cm heated to 140 °C for 4 h. A denotes formic acid absorptions.



Figure 2. Expanded scale spectra contrasting oxygen isotopic secondary ozonides of ethylene in solid argon at 15 K: (a) SOZ prepared from ${}^{16}O_3$; (b) SOZ synthesized with ${}^{16,18}O_3$ (50 % ${}^{18}O$); (c) SOZ formed from ${}^{18}O_3$ (95 % ${}^{18}O$).



Figure 3. Expanded scale spectra contrasting carbon isotopic secondary ozonides of ethylene in solid argon at 15 K: (a) SOZ prepared from natural isotopes; (b) SOZ prepared from ¹³C₂H₄ (90 % ¹³C).



Figure 4. Expanded scale spectra contrasting hydrogen and deuterium isotopic secondary ozonides of ethylene in solid argon: (a) SOZ prepared from C_2H_4 ; (b) SOZ made with CH_2CD_2 ; (c) SOZ synthesized from C_2D_4 . F denotes formaldehyde absorptions.

for the 1078-cm⁻¹ band, and triplets for the 808- and 1029-cm⁻¹ bands. The 927-cm⁻¹ band also appears to be a triplet, although it is partially obscured by the strong 940-cm⁻¹ band. The weaker 698- and 736-cm⁻¹ bands both appear to be sextets.

Infrared spectra for the ¹³C SOZ and the ¹²C SOZ are compared in Figure 3. The ¹³C counterparts are readily apparent and are listed in Table I. The strong ¹³C SOZ bands at 934, 1009, and 1059 cm⁻¹ show satellite bands at 944, 1019, and 1071 cm⁻¹, respectively, due to the mixed ^{12,13}C ethylene, in the intensity ratio (81/18) expected for the vibration of two equivalent carbon atoms.

The spectra obtained for the SOZ- d_0 , $-1,1-d_2$, and $-d_4$ are compared in Figure 4. Slight decomposition of the SOZ- d_2 sample gave sharp weak bands at 1743 and 1698 cm⁻¹ for CH₂O and CD₂O, respectively. As expected, the bands in

the 2000-3000-cm⁻¹ region show large shifts, although no straightforward mapping of the bands is apparent. The SOZ band positions agree with the measurements of Kuhne and Gunthard; however, only small amounts of cross ozonides SOZ- d_0 and $-d_4$ were formed in the present synthesis of SOZ- $1,1-d_2$, in marked contrast to the earlier synthesis.¹¹

SOZ Photolysis and Pyrolysis. Mercury arc photolysis of several SOZ isotopes produced a large number of product bands which are listed in Table II. In an attempt to distinguish between sets of bands, the duration of photolysis and irradiating wavelength were varied. Pyrex-filtered radiation (290–1000 nm) had no effect on the sample but the full arc (220–1000 nm) gave product bands within 5 min; these continued to increase in intensity at similar rates during further irradiation for 70 min. Ra-



Figure 5. Expanded scale isotopic spectra of secondary ozonkle photolysis products in the 1820–1660- and 1190–970-cm⁻¹ regions: (a) ${}^{16}O_3$, 40-min Hg arc irradiation; (b) ${}^{16,18}O_3$ (50% ${}^{18}O)$, 5-min Hg arc irradiation (1190–970 cm⁻¹) or 30-min (1820–1660 cm⁻¹); (c) ${}^{18}O_3$ (95% ${}^{18}O)$, 20-min Hg arc irradiation; (d) ${}^{13}C_2$ SOZ, 15-min Hg arc irradiation (1820–1660 cm⁻¹) or 75-min (1190–970 cm⁻¹). HMF, FAN, and F/A denote hydroxymethyl formate, formic anhydride, and formic acid–formaldehyde dimer, respectively.

diation transmitted through a saturated $NiSO_4/CoSO_4$ solution (235-335 nm) effected a similar distribution of product bands with the same relative intensities.

Pyrolysis of SOZ at 140 °C followed by trapping the products in solid argon gave samples with complementary spectra which aid in sorting the product bands in Table II. Both monomeric formic acid and formaldehyde were major products of the pyrolysis of SOZ. Consequently, formic acid and formaldehyde were each condensed with argon in separate experiments in order to identify absorptions arising from these species. In addition, two experiments were performed in which a mixture of formic acid and argon and formaldehyde were codeposited from two separate lines.

The photolysis of SOZ creates several new species. In addition to CO_2 , CO, and H_2O , bands appear in four regions of the spectrum considered characteristic of -O-H

(3150–3500 cm⁻¹), >C=O (1700–1820 cm⁻¹), and >C-O-(950–1250 cm⁻¹) stretching vibrations and skeletal deformations involving carbon and oxygen atoms (300–550 cm⁻¹). A close inspection of the spectra illustrated in parts c and d of Figure 1 reveals new product absorptions in three categories: (i) those appearing only on photolysis of SOZ ($h\nu$), (ii) those appearing in both photolysis and pyrolysis experiments ($h\nu/\Delta$), and (iii) those produced only by pyrolysis of SOZ (Δ).

Bands Unique to SOZ Photolysis. The absorptions summarized in Table II and denoted $h\nu$ are produced only on photolysis of SOZ. A sharp band at 3471 cm⁻¹ shows a -8 cm⁻¹ shift on ¹⁸O-isotopic substitution and two bands at 3474 and 2681 cm⁻¹ are observed after photolysis of SOZ-1,1-d₂. The region 1700–1820 cm⁻¹ contains four intense and relatively sharp bands (Figure 5a). Two of these, at 1761.5 and 1812.0 cm⁻¹, are due to formic anhy-

TABLE I: Absorptions (cm⁻¹) for Isotopic Secondary Ozonides of Ethylene and Ozone in Solid Argon at 15 K

C ₂ H ₄ ¹⁶ O ₃	C ₂ H ₄ ^{16,18} O ₃	$C_{2}H_{4}^{18}O_{3}$	${}^{13}C_{2}H_{4}O_{3}$	CH ₂ CD ₂ O ₃	$C_2D_4O_3$
698	698, 693, 684, 679, 673, 668	668	693	683	672
736	736, 729, 722, 717, 711, 703	703	732	721	706
808	807, 787, 765	764	805	783	758
927	(927), 915, 907	906	912	847	830
952	952, 940	938	934	919, 910	848
1029	1029, 1021, 1013	1013	1008	986, 965	904, 911
1078	1078, 1076, 1071, 1058, 1055, 1052	1052	1058	1067	929
1129	1128, 1125	1124	1119	1143, 1132, 1103	972, 981
1196		1189			1020
1201		1197		1201	1057
1346	1346, 1341	1340	1343		1134, 1142
1387	1389	1388	1378	1309	1159
2716	2717, 2712	2710	2706	2080, 2111, 2134	2091, 2117, 2131
2895	2896	2895	2889	2189, 2210	2181, 2204
2967	2961	2967	2957	2240, 2250	2249, 2257
2973			2966	2898	
2989	2990	2990	2981	2968, 2990	

dride (FAN),¹⁵ a conclusion supported by shifts in frequency of 38.5 and 41.0 cm⁻¹, respectively, on ¹⁸O-isotopic substitution. On photolysis of mixed ^{16,18}O SOZ the band at 1812.0 cm⁻¹ gives way to two poorly resolved triplets (Figure 5b); two components of the first are observed at 1772.0 and ca. 1778 cm⁻¹ and the second exhibits bands at 1802.5, 1807.0, and 1812.0 cm⁻¹. The other two bands (HMF), observed at 1745.5 and 1786.0 cm⁻¹, both show ¹⁸O-and ¹³C-isotopic shifts (Figure 5b–d, Table II) characteristic of the C=O stretching vibration in organic carbonyl compounds. These absorptions maintain a similar relative intensity in all isotopic modifications of the molecule. The ¹³C counterparts of the absorption at 1786.0 cm⁻¹ (Table II) exhibit three bands at 1773.0, 1759.0, and 1745.0 cm⁻¹.

In the region 950-1250 cm^{-1} (Figure 5a), two bands (FAN) at 997 and 1091 cm⁻¹ are again due to formic anhydride. Of the other features, the strongest and most consistent absorptions are observed at 1035.0, 1042.5, 1068.0, 1139.0, and 1163.5 cm⁻¹ and are denoted HMF. Shifts of -38.0 and -37.5 cm⁻¹ on ¹⁸O substitution exhibited by the bands at 1035.0 and 1042.5 cm⁻¹, respectively, are greater than expected (ca. 25 cm⁻¹) for a C-O fundamental vibration, while the 1042.5-cm⁻¹ absorption has a ¹³C shift which is much smaller than expected. Both ¹⁸O- and ¹³Cisotopic shifts for each of the other three bands are close (within 7 cm⁻¹) to the diatomic values. Photolysis of SOZ-1,1- d_2 produces bands which may be assigned to formic- d_1 anhydride;¹⁵ a strong absorption at 1090.0 cm⁻¹ and weaker ones at 1027.5/1031.5, 978.5/974.5, and 953.0 cm⁻¹ agree well with previous measurements. Bands at 1101 and 1052 cm⁻¹ produced by photolysis of SOZ- d_4 are similarly assigned. Photolysis of SOZ-1,1- d_2 leads to four other absorptions at 1209.5, 1158.0, 1058.5, and 1020.0 cm⁻¹ while a single band at 1210.0 cm⁻¹ is observed after SOZ- d_4 photolysis.

In the low-frequency region $(300-550 \text{ cm}^{-1})$ of the spectrum two bands show consistent relative intensities. That at *ca*. 325 cm⁻¹ exhibits a shift of -5 cm^{-1} in experiments with ¹⁸O₃ SOZ and ¹³C₂ SOZ while a band at 536.0 cm⁻¹ shows a large (ca. 18 cm⁻¹) ¹⁸O-isotopic shift and a small (ca. 2 cm⁻¹) ¹³C-isotopic shift.

Several other absorptions are unique to the infrared spectrum of photolyzed SOZ. Bands at 704.0, 864.0, 879.0, 1277.5, and 3091 cm⁻¹ exhibit isotopic shifts as listed in Table II. The band at 879.0 cm⁻¹ is due to ethylene oxide. The absorption at 1277.5 cm⁻¹ invariably lies on the low-frequency flank of a much broader feature extending for

some 30 cm⁻¹. Although ethylene oxide exhibits a band at 1274.5 cm⁻¹ its intensity relative to the 879.0-cm⁻¹ absorption renders it unlikely that the band at 1277.5 cm⁻¹ is attributable to ethylene oxide.

Bands Associated with Photolytic and Thermal Decomposition of SOZ. Absorptions denoted $h\nu/\Delta$ in Table II were observed after UV irradiation and thermal decomposition of SOZ. Two observations are particularly noteworthy: (i) there are no bands coincident in the two sets of experimets in the low-frequency region between 300 and 550 cm⁻¹ and (ii) there are no coincidences of intense sharp bands between 1700 and 1820 cm⁻¹, but a broad intense absorption in the region $1700-1745 \text{ cm}^{-1}$ is often a common feature. The most intense band in this category, denoted F/A in Figure 5, is observed at 1173.5 cm^{-1} after photolysis and 1174.5 cm⁻¹ after pyrolysis of SOZ. Its ¹⁸O-isotopic shift of 32.0 cm⁻¹ is too large for a pure –C–O– stretching vibration, while its ¹³C shift of 14.0 cm⁻¹ is too small. Pyrolysis and photolysis of SOZ- $1,1-d_2$ lead to bands at 1175.5 and 1174.5 cm^{-1} , respectively; the mixed ^{16,18}O SOZ yields a quartet of absorptions at 1174.5, 1171.0, 1146.5, and 1143.0 cm⁻¹ on pyrolysis and a similar set shifted by 1.0-1.5 cm⁻¹ to lower frequency on photolysis. An intense absorption was observed at 1174.5 cm⁻¹ after codeposition of formic acid and formaldehyde with argon.

A broad intense band (fwhm = 11 cm⁻¹) at 3188 cm⁻¹ is shifted to 3174.5 cm⁻¹ on photolysis of ¹⁸O₃ SOZ. The mixed ^{16,18}O SOZ yields a very broad, unresolved band centered at 3181 cm⁻¹ while no ¹³C shift can be detected. Pyrolysis gives rise to a band of similar half-width but at the slightly higher frequency of 3193.5 cm⁻¹ and a broad feature at 3194 cm⁻¹ is present in infrared spectra of formic acid-formaldehyde mixtures.

In both photolysis and pyrolysis experiments, four other absorptions appear at 859.5, 1495.5/1500.5, 2834.5, and 2939 cm⁻¹. The doublet at 1495.5/1500.5 cm⁻¹ is characteristic of photolysis experiments; an intense 1499-cm⁻¹ CH₂O band was dominant in pyrolysis experiments. However, while pyrolysis of SOZ leads to bands at 2798 and 2864 cm⁻¹ also characteristic of monomeric formaldehyde, these features are absent from photolysis experiments. Furthermore codeposition of formic acid and formaldehyde generates each of the above four bands present after photolysis and pyrolysis of SOZ.

Bands Unique to the Pyrolysis of SOZ. Spectra of products of the thermal decomposition of SOZ are dominated by absorptions associated with monomeric formic acid $(A)^{16}$ and formaldehyde $(F)^{17}$ (Figure 1d). Comparison

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TABLE II: New Absorptions (cm⁻¹) Produced by Photolysis of Ethylene SOZ

12-16 ^a	absorbance ^b	12-18 ^c	13-16 ^d	character ^e	assignment ^f
~ 325	~0.10	~ 320	320.0	hν	HMF
~ 370	~ 0.05	~369	~370	hν	
471.0	0.07	~471	470.0	hν	
497.0	w		494.0	hv	
536.0	0 10	~518	534.0	hu	HMF
541.0	web	010	001.0	hu	FAN
666 5	~0.11	656 5		h_{ν}/Λ	CO
675 5	~ 0.11	000.0		h_{ν}/Δ	E_{1A}
670.0	~ 0.14			$h\nu/\Delta$, COD	
679.0	~0.10		704.0	$h\nu/\Delta$, COD	F/A
704.0	0.12	~ 102	704.0	$h\nu$	
859.5	0.25	800.0	607.0	$n\nu/\Delta$, COD	F/A D(A
864.0	0.25	860.0	862.0	nv	F/A
879.0	0.10	868.0		hν	CH ₂ OCH ₂
883.0	w, sh			$h\nu/\Delta$	
997.0	0.25	976.5	978.5	hν	FAN
1012.0	0.07	985.5	995.0	$h\nu$	
1015.5	0.07			$h\nu$	
1024.5	0.11 sh			$h\nu$	
1025.0	0.09 sh			$h\nu$	
1035.0	0.11 sh	997.0		$h\nu$	HMF
1042.5	0.42	1005.0	1031.0	$h\nu$	HMF
1068.0	0.18 br, sh	1040.5	1048.0	hν	HMF
1091.0	0.53	1060.5		h u	FAN
1126.5	0.20	1093.0		$h\nu/\Delta$	
1139.0	0.15	1117.0	1116.0	$h\nu$	trans-HMF
1163.5	0.30	1141^{g}	1142.5	$h\nu$	cis-HMF
1173.5	0.66	1141.0	1159.5	$h\nu/\Delta$, COD	\mathbf{F}/\mathbf{A}
1275.5	sh			$h\nu$	CH,OCH,
1277.5	~0.16	1271.0	1274.5	hν	HMF
1281.0	sh			hv	
~1288	br	~1279	~1289	hv	HMF
1340.0	w			hy	
1421 5	w	1417 0		hv	
1495 5	0.20	1484.5	1494 5	h_{ν}/Λ COD	F/A
1500.5	0.16	1489.0	1500.0	h_{ν}/Δ COD	F/A
1731 5	br sh	1607 5	1000.0	h_{μ}/Λ COD ^m	F/A
1737 5	br sh	1708 5		$h_{\nu}/\Delta, COD^{m}$	F/A
1745 5	~0.02	1710.0^{h}	1717 0	h_{ν}	
1740.0	~0.95	1792.0	1792.0	<i>hv</i>	E A NI
1701.0	by sh	1725.0	1723.0	<i>hv</i>	PAN
1786.0	0.40	1740 01	1715 OK	h	turne UNE
1/80.0	0.49	1749.0°	1740.0	nv h	LFURS-FIMF
1812.0	0.21	1771.0	~1776	nv	FAN
2139	0.05	2089	2093	nv	00
2143	0.05			hν	
2158	0.05	2107	2110	nv	(CO) (M)
2344	~ 0.22	2308	2278	$h\nu/\Delta$	CO_2
2364			A.D.C.A.	$h\nu$	$(CO_2)(M)$
2834 (5)	0.12	2833	2829	$h\nu/\Delta$, COD	F/A
2939	0.10	2932	2929	$h\nu/\Delta$, COD	\mathbf{F}/\mathbf{A}
3091	0.10	3054	3042	$h\nu$	
3188	0.29	3174	~3193	$h\nu/\Delta$, COD	F/A
3471	0.10	3463		hv	cis-HMF
3710	~0.09			$h\nu, \Delta$	$({\rm H}_{2}{\rm O})$ (M)
3757	~0.09			$h\nu$, Δ	H,Ò
					-

^a Absorptions in normal isotopic experiments. ^b Band absorbance after 38-min full Hg arc photolysis. w < 0.05, br = broad, sh = shoulder. ^c Absorptions produced by photolysis of ${}^{18}O_3$ SOZ. ^d Absorptions produced by photolysis of ${}^{13}C_2$ SOZ. ^e $h\nu$, appears on photolysis only; $h\nu/\Delta$, appears on both photolysis and pyrolysis; COD, present after codeposition of formic acid and formaldehyde with argon. ^f Product assignments: FAN = (CHO)₂O, HMF = hydroxymethyl formate, *cis*-HMF = H-bonded HMF, *trans*-HMF = open chain HMF, F/A = formic acid-formaldehyde dimer. ^g Obscured by the intense formic acid-formaldehyde absorption at 1141.0 cm⁻¹. ^h In mixed ^{16,18}O experiments, a 1743- and 1715-cm⁻¹ doublet was observed for this species. ⁱ In mixed ^{16,18}O experiments, broad 1760- and 1724-cm⁻¹ bands were observed. ^j In mixed ^{16,18}O experiments, a 1785-cm⁻¹ band and 1750-cm⁻¹ shoulder were observed. ^k Tentative assignment of bands at 1745.0, 1759.0, 1773.0, and 1786.0 cm⁻¹ to four isotopomers of *trans*-HMF. 90% ¹⁵C enrichment should yield a 81:9:9:1 quartet (Figure 5d), respectively. ^l In mixed ^{16,18}O experiments a triplet at 1802.5, 1807.0, and 1812.0 cm⁻¹ and two components of a second triplet at 1772.0 and ca. 1778 cm⁻¹ are observed. ^m Observed at 1729.0 and 1738.0 cm⁻¹ in pyrolysis and codeposition experiments.

of Figure 6b with Figure 6c illustrates the fact that, in pyrolysis experiments, absorptions in the region 1700-1820 cm⁻¹ may be entirely attributed to the presence of formic acid and formaldehyde. Bands at 1768.0 (A, monomeric formic acid), 1747.5, and 1723.0 cm⁻¹ appear in the spectra

(17) Khoshkhoo, H.; Nixon, E. R. Spectrochim. Acta, Part A 1973, 29, 603.

of formic acid isolated in argon; that at 1743.0 cm⁻¹ (F) is due to monomeric formaldehyde while those at 1739.0 and 1729.0 cm⁻¹ labeled F/A are characteristic of samples containing both formic acid and formaldehyde. Experiments in which formic acid was isolated in argon matrices invariably yielded a greater number of absorptions than normally associated with the monomer. Those which are also observed in SOZ pyrolysis (but not photolysis) ex-

 TABLE III:
 Observed and Calculated Isotopic Shifts

 (cm⁻¹) for Major SOZ Absorptions Obtained with the
 Diatomic Oscillator Approximation

12- 16	13-	-16	18- 18	12-	-18	
obsd	calcd	obsd	calcd	calcd	obsd	assignment
698	682	694	658	681	668	ring bending
736	720	733	694	718	703	ring bending
808	790	805	762	789	764	O-O stretch
927	906	912	874	905	906	C-O _p sym
952	931	934	897	929	938	C-Oe sym
1029	1006	1008	970	1004	1013	C-Op anti
1078	1054	1058	1016	1052	1052	C-O _e anti
1129	1104	1119	1064	1102	1125	CH ₂ deformation
1346	1316	1343	1269	1314	1340	CH, bending
1387	1356	1378	1308	1354	1387	CH_2 bending

periments are listed in Table V, together with a summary of absorptions due to formaldehyde. The band at 1115.0 cm⁻¹ was often the most intense band in the spectrum of both formic acid and SOZ pyrolysis experiments. Carbon dioxide is a product of the pyrolysis of SOZ but carbon monoxide is not observed.

Discussion

Vibrational fundamentals of the SOZ of ethylene will be characterized by the isotopic data, the SOZ matrix photolysis products will be identified, and possible mechanisms for their formation will be considered.

Secondary Ozonide. Vibrational fundamentals were observed for six isotopic SOZ molecules. Table III lists the observed band shifts, and the calculated shifts, assuming isolated simple bond stretching modes. The spectrum of the mixed ^{16,18}O SOZ shows a clear symmetric triplet (1:2:1) for the 808-cm⁻¹ band, indicating that two equivalent oxygen atoms participate in the mode. The large ¹⁸O shift is almost that predicted for an isolated O–O stretch (see Table III), and the ¹³C shift is very small. Therefore this band is assigned to the O–O stretching mode. Other molecules with similar modes are listed in Table IV.

The bands at 927 and 1029 cm⁻¹ show approximately the correct shifts in the ¹⁸O and ¹³C experiments to be isolated C–O stretching modes. In the mixed ^{16,18}O experiments, these bands show a triplet structure (assuming part of the 927-cm⁻¹ band is obscured), indicating the participation of two equivalent oxygen atoms. The 927- and 1029-cm⁻¹ bands are therefore assigned to the carbon–peroxide oxygen, C–O_p, stretching modes. The more intense, higher-energy band is usually the antisymmetric motion, and the assignments of similar molecules agree with these assumptions.

The strongest ethylene secondary ozonide bands, at 952 and 1078 cm⁻¹, also show isotopic shifts corresponding to C–O stretching modes. In the mixed 16,18 O experiment, the



Figure 6. Expanded scale spectra of SOZ photolysis, SOZ pyrolysis, and formic acid-formaldehyde codeposition products in the region 1820-1700 cm⁻¹: (a) 40-min Hg arc irradiation; (b) pyrolysis at 77 °C; (c) codeposition of formic acid and formaldehyde. HMF, FAN, F/A, F, and A denote hydroxymethyl formate, formic anhydride, formic acid-formaldehyde dimer, formaldehyde, and monomeric formic acid, respectively.

952-cm⁻¹ band is split into a doublet (the lower frequency absorptions are due to site effects), and the 1078-cm⁻¹ band

TABLE IV: Molecules Containing O-O, C-Op, and C-Oe Linkages and the Assigned Stretching Modes (cm⁻¹)

mode			CH3- OOCH3	CF ₃ - OOCF ₃			CH3OCH3
O-O stretch	808	647 anti, 846 sym	779	890	780		
C-O _p sym	927	927	914	975	925		
C-O _p anti	1029	983	1032	1065	1110, 1150		
C-Oe sym	952				, -	912	929
C-O, anti	1079					1076	1116
ref	this work	5	а	b	с	d	e

^a Bell, M. E. B.; Laane, J. Spectrochim. Acta, Part A 1972, 28, 2239. ^b Durig, J. R.; Wertz, D. W. J. Mol. Spectrosc., 1968, 25, 467. ^c Salomon, M. F.; Salomon, R. G. J. Am. Chem. Soc. 1979, 101, 4290 (our assignments). ^d Eyster, J. M.; Prohofsky, E. W. Spectrochim. Acta, Part A, 1974, 30, 2041. ^e Hamada, K.; Morishita, H. Z. Phys. Chem., 1975, 97, 295.

is split into a doublet of triplets. Since the major splitting of both is a doublet, one oxygen atom dominates this mode, and these bands are assigned to the carbon-ether oxygen, $C-O_e$, stretching modes. The further splitting of the 1078-cm⁻¹ band shows the minor effect of the peroxide oxygen atoms in this vibration. The higher energy more intense band is therefore the antisymmetric motion, which is expected to be affected by the remainder of the ring more than the symmetric mode.

The two lowest energy bands, 698 and 736 cm^{-1} , can be mapped throughout the isotopic changes; these bands exhibit large ¹⁸O, small ¹³C, and small D shifts. These absorptions are probably due to ring bending predominantly involving the oxygen atoms.

The bands at 1346 and 1387 cm⁻¹ are in the region of CH_2 bending motions, and the isotopic data—very large shifts (>200 cm⁻¹) in the d_4 experiment, and very small shifts (<10 cm⁻¹) in the ¹⁸O and ¹³C experiments—support these assignments. The three bands at 1129, 1196, and 1201 cm⁻¹ also exhibit deuterium shifts much larger than $^{18}\mathrm{O}$ or $^{13}\mathrm{C}$ shifts and are therefore assigned as CH_2 deformations.

Kuhne and Gunthard¹¹ have presented a detailed analysis of the CH₂ stretching modes, including the Fermi resonance interactions, based on spectra of the SOZ- d_0 , $-1,1-d_2$, and $-d_4$ molecules and therefore band assignments in the 3000-cm⁻¹ region will not be repeated here; the 6-10-cm⁻¹ ¹³C shifts and the absence of ¹⁸O shifts on the 2974, 2968, and 2894-cm⁻¹ bands confirm their earlier assignment as C-H stretching modes.

It is interesting to note that the present reaction of CH₂CD₂ and ozone at -150 to -130 °C in CF₃Cl solution gave practically no cross ozonides whereas the conventional reaction in methyl chloride at -78 °C allowed substantial formation of h_4 and d_4 ozonides.¹¹ Cross ozonides were not produced in the reaction of CH_2CD_2 with O_3 in solid xenon at 80-100 K.⁵ A concerted, intramolecular rearrangement of POZ to SOZ may be favored at these lower temperatures. It is of course possible that the colder solvent cage prevents diffusion of the CH₂O and CH₂OO products of the initial ozonolysis reaction and allows the original precursor integrity to be maintained in the final SOZ product.

Identification of Matrix Photolysis Products. There is a general concensus that the pyrolysis or photolysis of secondary ozonides involves the possible intermediacy of a 1,5 diradical, 3.¹⁸⁻²⁰ The distribution of products de-



pends upon the relative rates of several different modes of rearrangement and/or decomposition of this species. In cases where R_1 and $\dot{R}_3 = H$, intramolecular H-atom abstraction yields an unstable hydroxyalkyl ester;¹⁸ simultaneous scission of R_2 and R_4 generates the unstable formic anhydride molecule and products characteristic of alkyl radical abstraction and addition reactions.^{18,19} Some fully substituted ozonides have been observed to undergo a Baeyer-Villiger or Wieland type rearrangement resulting



in the generation of an ester and a ketone.^{19,20} Scheme I illustrates the species expected (5-7) if the SOZ diradical 4 were to undergo each of the reactions described above. Thus hydroxymethyl formate (HMF), 5, formic anhydride (FAN), 6, and formic acid and formaldehyde (from 5 or 7) are anticipated products.

Photolysis of SOZ generates FAN and carbon monoxide. Formic anhydride is known to decompose into formic acid and carbon monoxide at room temperature.¹⁵ Bands at 1786.0 and 1745.5 cm⁻¹ also appear while free formic acid and formaldehyde are not observed. No FAN or carbon monoxide are detected on pyrolysis of SOZ and the additional bands at 1786.0 and 1745.5 cm^{-1} do not appear. Absorptions characteristic of monomeric formic acid and formaldehyde are intense, however. We conclude that pyrolysis of SOZ generates an undetectable amount of FAN, even as an intermediate.

It is reasonable to assume that an SOZ molecule isolated in a matrix cage is unlikely to give rise to a photoproduct of molecular formula greater than that of SOZ itself, i.e., $C_2H_4O_3$. Reference to literature spectra establishes that the bands at 1786.0 and 1745.5 cm^{-1} and other new absorptions are not due to acetic acid, hydroxyacetic acid (CH₂OH·CO₂H), glycolaldehyde (CH₂OH·CHO), glyoxal (CHO·CHO), or glyoxylic acid (CHO·CO₂H). The carbonyl bands may, however, be associated with (i) the same molecular species or (ii) different molecular species, including conformers. Restrictions imposed by the molecular formula and relative intensity measurements for several isomers (parts a, c, and d of Figure 5) render it improbable that the absorptions are either associated with a dicarbonyl species or comprise a Fermi doublet. Two different species are therefore favored and the observation of four bands between 1745.0 and 1786.0 cm⁻¹ on photolysis of ¹³C₂ SOZ (Figure 5d) suggests that one of them contains two inequivalent carbon atoms; a ¹³C enrichment of 90% is expected to reveal a quartet of absorptions in the ratio 81:9:9:1.

Hydroxymethyl formate, 5, should exhibit absorptions in its infrared spectrum characteristic of -O-H, >C==O, and C-O stretching vibrations and of O=C-O- and -C-O-C- deformations. Eleven bands unique to photolysis experiments are so assigned (Table II). Two conformers of the HMF molecule are implicated, 9 and 10. Hydrogen bonding to a carbonyl group lowers the C=O vibrational frequency.²¹ The band at 1745.5 cm⁻¹ is assigned, there-

⁽¹⁸⁾ Story, P. R.; Morrison, W. H., III; Hall, T. K.; Farine, J.-C.; Bishop, C. E. Tetrahedron Lett. 1968, 52, 3291. Story, P. R.; Hall, R. K.;
 Morrison, W. H., III.; Farine, J.-C. Ibid. 1968, 52, 5397.
 (19) Stery, P. R.; Morrison, W. H.; Butler, J. M. J. Am. Chem. Soc.

^{1969, 91, 2398.}

⁽²⁰⁾ Ullman, E. F.; Henderson, W. A. J. Am. Chem. Soc. 1967, 89, 4390.



fore, to cis-HMF, 9, and that at 1786.0 cm⁻¹ to trans-HMF, 10. The assignment is supported by the ¹³C data which implies a species with two inequivalent carbon atoms. Furthermore, the ratios $\nu(^{12}C=O)/\nu(^{13}C=O)$ and $\nu(C=^{16}O)/\nu(C=^{16}O)$ are smaller for the 1745.5-cm⁻¹ absorption, as expected for a H-bonded system. H bonding to an ester has also been observed to increase the vibrational frequency of the acyl-oxygen bond, 11, by 17-25 cm⁻¹.²¹ The



corresponding vibrations in HMF are located at 1163.5 and 1139.0 $\rm cm^{-1}$ for 9 and 10, respectively, their relative intensities paralleling those of the two carbonyl bands (Table II). The two remaining C-O stretching modes are not expected to be influenced by H bonding to such a great extent as the acyl-oxygen vibration. An absorption at 1068.0 cm⁻¹ is assigned to a mode involving C-OH stretching motion; the corresponding band in gaseous methanol shows only a small shift of -3 cm⁻¹ on condensation to the liquid phase. A second, more intense absorption at 1042.5 cm⁻¹ is assigned to a complex stretching mode of vibration involving the O-C-O-C skeleton, on account of its large ¹⁸O shift and small (but significant) ¹³C shift. The four absorptions at 1209.5, 1158.0, 1058.5, and 1020.0 cm⁻¹ characteristic of SOZ-1,1- d_2 photolysis are tentatively assigned as counterparts to the 1163.5; 1139.0; 1068.0; and 1042.5-cm⁻¹ bands of HMF. Since C-D deformations may also occur in this region, specific correlations cannot be made between the two isotopic experiments particularly without knowledge of band positions from ${}^{18}O_3$ SOZ- d_4 photolysis. It seems likely that the 1209.5-cm⁻¹ band (1210.0 cm⁻¹ from SOZ- d_4 photolysis) is a counterpart of either the 1163.5- (cis-HMF) or 1139.0cm⁻¹ (trans-HMF) band and thus one or possibly both of the latter exhibit a positive deuterium shift. A similar effect is observed in the infrared spectra of deuterated formic acid.¹⁶ The remaining assignments to HMF are unambiguous. The band at 3471 cm^{-1} is some 150 cm^{-1} lower than expected for a primary alcohol but in the correct region for an intramolecularly H-bonded alcohol.²² It is thus assigned to cis-HMF, 9, while the corresponding absorption for trans-HMF, 10, is probably weaker and is not observed. Absorptions at 536.0 and 325 cm⁻¹ are assigned to O=C-O- and -C-O-C- deformations, respectively, on the basis of isotopic shift and the position of similar modes in FAN (541.0 cm⁻¹) and methyl formate (325 cm⁻¹).²³ Finally two bands located at 1277.5 and 1288 cm⁻¹ are assigned to in-plane deformations of the C-O-H group of HMF. That at 1277.5 cm⁻¹ is sharp and characteristic of a free OH group. That at 1288 cm⁻¹ is broad and its slightly increased frequency indicative of a H-

Scheme II



bonded species.²¹ The intensity of this absorption relative to those of *cis*-HMF, however, is not always consistent and may contain components originating in both inter- and intramolecular H bonding of the hydroxyl group of HMF.

Formation of HMF. A 120° rotation of a -CH₂O group in 4 around its bond to the ether-oxygen atom provides a simple pathway to hydroxymethyl formate via intramolecular H-atom abstraction (Scheme II). Hull and co-workers have demonstrated that the activation energy for thermal decomposition of ozonides with α -H atoms is lower than that expected for decomposition via a diradical 4.²⁴ They proposed that simultaneous fission of the O-Obond and H-atom transfer lead to a stabilized transition state, 12, a process having an activation energy of 27.5 kcal/mol in the case of SOZ. This transition state is a ready precursor for HMF in the H-bonded form, 9. Values for the bond energies in methanol, the O-O bond enthalpy in MeO-OMe, and the C=O bond enthalpy in formaldehyde allow an estimate of at least -38 kcal/mol to be made for ΔH of $2 \rightarrow 9$, Scheme II. When added to an activation energy of 27.5 kcal/mol, this enthalpy change requires that the HMF product is formed in a vibrationally excited state, 65.5 kcal/mol above the ground state. Under the conditions of pyrolysis of SOZ it is probable that "hot" HMF decomposes to formic acid and formaldehyde. Although the extent of HMF excitation is greater than the estimated activation energy of 22 kcal/mol for decomposition to FAN,⁶ the absence of detectable amounts of FAN or CO in pyrolysis experiments implies that the former pathway for HMF decomposition is faster. When generated in a matrix by photolysis of SOZ, however, rapid vibrational relaxation of the "hot" HMF can occur, thus stabilizing and trapping the molecule in either the cis or trans form.

Su and co-workers proposed HMF as a possible intermediate in the gas-phase reaction between ethylene and ozone,⁶ based on absorptions at 900-1200 and 1700-1800 cm⁻¹ in a residual FT-IR spectrum. Using a similar technique of spectral subtraction, Niki and co-workers²⁵ also correlated transitory infrared bands in the gas-phase ethylene-ozone reaction with HMF and made a tentative assignment of absorptions at 1760 and 3583 cm⁻¹ to trans-HMF and at 1737 and 3405 cm⁻¹ to cis-HMF (Table V). While bands at 1047 and 1167 cm^{-1} and, to a lesser extent, those at 1737 and 1760 cm⁻¹ agree tolerably well with bands assigned in this work to cis- and trans-HMF. those at 1116 and 2943 cm⁻¹ are not associated with this species. Together with the other bands, for which we observe no counterparts, these absorptions imply the presence of at least three species in the residual gas-phase spectrum of Niki et al. Substantially better agreement is found, however, with the position of a number of absorptions reported by Kuhne et al. from a study of the same reaction using a linear reactor²⁶ (Table V); their bands at 1163, 1747, and 1786 cm^{-1} fall within 1.5 cm^{-1} of those assigned to HMF in Table II. These authors, however,

⁽²¹⁾ Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, 1960.

⁽²²⁾ Tichy, M. Adv. Org. Chem. 1965, 5, 115.

⁽²³⁾ Marmar, E. B.; Pouchan, C.; Dargelos, A.; Chaillet, M. J. Mol. Struct. 1979, 57, 189.

⁽²⁴⁾ Hull, L. A.; Hisatsune, I. C.; Heicklen, J. J. Phys. Chem. 1972, 76, 2659.

⁽²⁵⁾ Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. J. Phys. Chem. 1981, 85, 1024.

⁽²⁶⁾ Kuhne, H.; Vaccani, S.; Bauder, A.; Gunthard, Hs. H. Chem. Phys. 1978, 28, 11.

TABLE V:	Comparison of B	Bands (in cm ⁻¹)	Observed in the l	Infrared Spectrum	of the Gas-Phase H	thylene-Ozone Reaction	n
(ref 25 and 2	26) and This Worl	k					

			this wor	k
ref 25	ref 26	freq		character ^a and assignment
	504, 644, 668, 689		NO	
	653, 680	653.6, 656.3 675.5, 679.0		$\stackrel{\Delta}{h u/\Delta}$, COD; F/A
823, 922		,	NO	
1047, 1116	1126, 1163, 1173	1042.5, 1163.5		$h\nu$; HMF
1167		1126		Δ , COD; A $h\nu/\Delta$
1350	$1244,^c \ 1305,^d \ 1348$	1173	NO	$h\nu/\Delta$, COD; F/A
1737, 1760	1729, 1730, 1737, 1747, 1756, 1760, 1786	1731.5, 1737.5 1745.5		$h\nu/\Delta$, COD; F/A $h\nu$; cis-HMF
		1761.0		$h\nu$; FAN
2943		1786.0 2939		$h\nu$; trans-HMF $h\nu/\Delta$, COD; F/A
3405	3599, 3604		NO	
3583			\mathbf{A}^{b}	

^a $h\nu$, SOZ photolysis; Δ , SOZ pyrolysis; COD, codeposition of formic acid and formaldehyde in argon; NO, not observed; A, deposition of formic acid in argon. ^b See Table VI. ^c Possibly formaldehyde. ^d Possibly methane.

ventured no suggestion as to their identification.

Formation of Formic Anhydride. The proposition by Su et al.⁶ that HMF may be a precursor to FAN is of particular interest in this study. Although absent in pyrolysis experiments, FAN is a major product of photolysis of SOZ. Since photons of wavelength 300 nm are equivalent to an energy of 95.3 kcal/mol, irradiation of SOZ at wavelengths shorter than 300 nm will generate "hot" HMF excited to a greater extent than during pyrolysis. Thus in this case also, decomposition to FAN is possible. If the mechanism of decomposition of HMF is common to the two sets of experiments, however, we would expect evidence of FAN in the pyrolysis of SOZ. There are two possible explanations for such a discrepancy. First, in a matrix, excited HMF may decompose to formic acid and formaldehyde or relax to its ground state faster than it decomposes to FAN. Generation of FAN then occurs via irradiation of HMF, possibly to eliminate H. from the hydroxyl group. Secondly the matrix may favor decomposition of the excited HMF via the transition state leading to FAN. Su et al. suggested that HMF decomposes to FAN via a four-center transition state 13. While it is



possible that the matrix stabilizes 13 and hence lowers the activation energy for this mode of decomposition, this transition state is also highly ordered. Thus the preexponential factor in the rate constant is small. The trans configuration of HMF, 10, however, as trapped in the matrix, may be quite close to the configuration of the transition state 13. The preexponential factor is increased and the rate of decomposition to FAN enhanced. Unfortunately the present findings do not allow distinction between these possibilities. However, the H atoms in FAN generated on photolysis of SOZ are bonded to the same carbon atoms as in SOZ; this is demonstrated by the fact that SOZ- d_2 yields a mixture of FAN- d_1 A and $-d_1$ E¹⁵ and no absorptions due to FAN- d_0 or d_2 .

The possibility that FAN is generated by a β -scission

mechanism involving the diradical 4 (Scheme I) cannot be discredited. However, the suitability of the intermediate 12 as the transition state leading to HMF formation from SOZ and the failure of Hull et al. to trap diradical intermediates in the gas-phase pyrolysis of ozonides favors a mechanism for the photolysis and pyrolysis of SOZ which does not involve the diradical 4.

Formic Acid-Formaldehyde Dimer, F/A. Formic acid and formaldehyde produced on decomposition of photoexcited HMF in a matrix are expected to be trapped in close proximity. When formed in the gas phase during pyrolysis of SOZ, formic acid and formaldehyde separate resulting in the matrix trapping of monomers of the two species. A few formic acid-formaldehyde pairs may be isolated, however, either through residual association in the gas phase or association caused by surface diffusion in the condensing matrix. If the latter effect is dominant then codeposition of formic acid and formaldehyde is expected to yield products similar to those observed in pyrolysis of SOZ.

Several bands were observed in photolysis, pyrolysis, and codeposition experiments (Table II). These are assigned to the formic acid-formaldehyde dimer, F/A, 14. In



photolysis and pyrolysis of SOZ, excited *cis*-HMF is an attractive precursor to the dimer 14. Concerted H-atom transfer and cleavage of the alkyl ester C–O bond may involve a transition state 15 similar in structure to HMF itself. Bands at 675.5, 679.0, 859.5, 1173.5, 1731.5, 1737.5, 2939, and 3188 cm⁻¹ assigned to 14 should be compared with those observed for formic acid dissolved in CCl₄ solutions containing dioxane- d_8 at -20 °C.²⁷ Assignments made to a formic acid–dioxane adduct were 672, 865, 1166, 1730, 2915, and 3050 cm⁻¹ and were the strongest observed product absorptions. Those at 1166, 1730, and 3050 cm⁻¹ were assigned to the C–O, C=O, and O–H stretching vibrations of complexed formic acid. In the present experiments the band at 1173.5 cm⁻¹ exhibits ¹⁸O and ¹³C shifts characteristic of an C–O stretching mode. More

⁽²⁷⁾ Wolff, H.; Muller, H.; Wolff, E. J. Chem. Phys. 1976, 64, 2192.

significantly, however, photolysis or pyrolysis of the mixed ^{16,18}O SOZ results in a quartet of bands at 1174.5, 1171.0, 1146.5, and 1143.0 cm⁻¹ with separations of 3.5, 24.5, and 3.5 cm^{-1} . The infrared spectrum of mixed ^{16,18}O HCO₂H near 1105 cm⁻¹ also exhibits a quartet of bands separated by 4.1, 24.9, and 3.7 $\text{cm}^{-1.16}$ The appearance of a band between 1165 and 1180 cm⁻¹ in complexes of formic acid and in deuterated formic acid results from reduced interaction between the C-O stretching and C-O-H deformation vibrations. While this is achieved in deuteration by increasing the actual atomic mass of the hydrogen atom, H bonding in formic acid complexes serves to increase the effective mass of the hydroxy H atom. Thus the frequency of the band at 1173.5 cm⁻¹ further supports the assignment to a H-bonded formic acid complex, F/A. Furthermore the intensity and broadness of the band at 3188 cm^{-1} , which exhibits isotopic shifts characteristic of an O-H stretching vibration, implicates a H-bonded species. The low-frequency favors assignment to a carboxylic hydroxyl group rather than to an alcohol.

The absence of an absorption in photolysis experiments at 1743.0 cm⁻¹ characteristic of monomeric formaldehyde implies that any formaldehyde generated is complexed, probably via the carbonyl group. A dimer F/A in which the acidic H atom of formic acid is H bonded to the O atom of formaldehyde would be expected to show little perturbation of the acid carbonyl vibration and no perturbation of vibrations associated with the CH₂ group of formaldehyde. On photolysis of SOZ the absence of any absorption within 30 cm⁻¹ of the formic acid band at 1768.0 cm⁻¹ and of bands characteristic of monomeric formaldehyde at 1169.0, 1246.5, 2797, and 2864 cm⁻¹ (Table VI) imply that either formaldehyde is not formed or it too is H bonded via the methylene group. Two observations suggest the generation of perturbed formaldehyde on photolysis of SOZ. First a strong doublet at 1495.5 and 1500.5 cm^{-1} is close to the 1499.0-cm^{-1} fundamental of monomeric formaldehyde. A small perturbation would be expected for this mode, the symmetric in-plane CH₂ deformation, for formaldehyde in the complex 14. Secondly, two bands at 1729.0 and 1738.0 cm⁻¹ (Table VI), observed during codeposition and pyrolysis experiments, lie close to broader bands at 1731.5 and 1737.5 cm⁻¹ characteristic of SOZ photolysis. Deposition of formaldehyde alone yields a weak band at 1738.5 cm⁻¹ assigned to dimer¹⁷ while an absorption at 1732.0 cm⁻¹ in the spectrum of formic acid in argon grows in intensity on annealing the matrix. The bands at 1729.0 and 1738.0 cm⁻¹ in codeposition experiments are much more intense than the formaldehyde dimer and formic acid aggregate bands. Thus the presence of one molecule enhances the intensity of bands characteristic of aggregated species of the other. It is thus tempting to assign the absorptions at 1729.0 and 1738.0 cm^{-1} to the carbonyl vibrations of 14. Comparison of Figure 6b and Figure 6c, however, reveals that these bands show different relative intensities in codeposition and pyrolysis experiments, although consistent relative intensities in a series of pyrolysis experiments. Suffice it to say, however, that the presence of two bands between 1728.0 and 1739.0 cm⁻¹ in codeposition, pyrolysis, and photolysis experiments strongly suggests the presence of a specific formic acid-formaldehyde dimer. In the absence of more definitive information, these bands are assigned to 14 as are those at 1731.5 and 1737.5 cm⁻¹ in photolysis experiments.

Finally bands at 1499.0, 1743.0, and 2797 cm⁻¹ are the strongest which are characteristic of monomeric formaldehyde.¹⁷ Photolysis and pyrolysis of SOZ and codeposition experiments all yield a band at 2834 cm⁻¹ (Table

TABLE VI: Absorptions (cm^{-1}) Characteristic of Formic Acid (A) and Formaldehyde (F) Observed in Pyrolysis and Codeposition Experiments

А	F	$A + F^b$
630.0 M ^a	1169.0	712.5
636.5 M	1246.5	1189.5
1104.5 M	1499.0	1217.0
1115.0	1743.0	1729.0^{c}
1228.0 M	2719	
1374.5 M	2797	
1723.0	2810 (5)	
1747.5	2864 `´	
1765.5 M	~2996	
1768.0 M		
1808.0		
2953		
3539		
3551 M		
3573		

^a M indicates monomer band. ^b Bands not observed after SOZ photolysis. ^c Compare with a band at 1731.5 cm⁻¹ on SOZ photolysis, Table II.

II), and it is assigned to a CH stretching mode of perturbed formaldehyde in F/A, 14. Thus there is good evidence that codeposition of formic acid and formaldehyde and photolysis or pyrolysis of SOZ lead to the formation of a discrete-dimer F/A, 14. While codepositon and pyrolysis experiments yield large amounts of monomeric formic acid and formaldehyde in addition, decomposition of photoexcited SOZ in a matrix cage leads to exclusive formation of F/A, 14.

Formation of CO_2 , CO, and H_2O . In pyrolysis experiments there is no evidence for the generation of FAN and CO. This implies that FAN is not a source of formic acid in SOZ pyrolysis and decomposition of HMF via 15 may account for all formic acid observed in these experiments. Su et al. determined that a greater amount of excited formic acid decomposes to give CO than CO₂.⁶ According to these measurements, if the CO₂ observed on pyrolysis of SOZ came from hot formic acid, some CO should be detected. The absence of a detectable amount of CO under these conditions implies that the source of formic acid and hence its degree of excitation may influence the manner of its decomposition. Thus it remains the most likely source of CO_2 in SOZ pyrolysis experiments. Certainly FAN is not observed to yield CO_2 on decomposition either thermally or photolytically.¹⁸

Photolysis of SOZ, however, generates both CO₂ and CO (Figure 1c) but the identity of the precursor is uncertain. The CO bands at 2139 and 2143 cm⁻¹ are assigned to monomeric CO or dimer species, (CO)(X), in which X may be CO, CO₂, or $H_2O^{.28}$ A third band at 2158 cm⁻¹ is invariably observed after SOZ photolysis and can be assigned to a species (CO)(M), in which M is an unknown molecule, on account of its ¹³C- and ¹⁸O-isotopic shifts (Table II). In two photolysis experiments the CO_2 band at 2344 cm⁻¹ was accompanied by a second band at 2364 cm^{-1} which is assigned to a species (CO₂)(M). It is reasonable to suppose that decomposition of hot HMF formed during photolysis of SOZ would lead to activated formic acid as in SOZ pyrolysis. However, this process should also generate monomeric formaldehyde and none is observed. Similarly, photolysis or decomposition of hot FAN to CO should yield monomeric formic acid. Thus production of CO and CO_2 in this way implicates separate isolation of formic acid and formaldehyde. Bands associated with these species, however, are perturbed and assigned to the

⁽²⁸⁾ Dubost, H. Chem. Phys. 1976, 12, 139.

dimer 14. We conclude therefore that (i) CO and CO_2 are produced from FAN and HMF, respectively, and trapped as $CO-HCO_2H$ and CO_2-H_2CO or, alternatively, (ii) the precursor decomposes to both CO and CO_2 . The first alternative requires that the vibrations of HCO₂H and H₂CO are considerably perturbed from those of the monomers. In addition, the bands due to CO and CO_2 would be expected to show a perturbation and, while the bands at 2158 and 2364 cm⁻¹ satisfy this condition, those at 2140, 2143, and 2344 cm⁻¹ do not. A rationale for the second and more attractive alternative is to assume that either SOZ itself or ground-state HMF can absorb a photon and decompose via a pathway separate from those discussed previously. Formic anhydride might also be included as a possible precursor for photolytic decomposition to CO₂ and CO although with less conviction based on the observations of Story and co-workers.¹⁸

Finally, a growth in intensity of absorptions due to H_2O between 1590 and 1625 cm^{-1} and at 3710 and 3757 cm^{-1} is observed. Water or molecular hydrogen are expected to be complementary products to CO and CO₂ on decomposition of SOZ, HMF, or FAN.

Conclusions

The reaction of ethylene with ozone in CF₃Cl solution at -150 to -130 °C yields SOZ such that CH_2CD_2 gives practically no h_4 and d_4 ozonides. Oxygen-18 and carbon-13 isotopic substitution complement the deuterium studies of Kuhne et al. and allow a more definite assignment of vibrations involving these atoms.

The matrix photolysis and gas-phase pyrolysis of SOZ lead to the isolation of different products. In both cases, however, decomposition of the SOZ is proposed to proceed via intramolecular H-atom transfer to yield a vibrationally excited hydroxymethyl formate (HMF) molecule. Under the conditions of pyrolysis this activated species decomposes completely, and formic acid and formaldehyde are the major products trapped in the matrix. Carbon dioxide is also detected, probably a product of the decomposition of "hot" formic acid. There is no evidence for the intermediacy of formic anhydride in SOZ pyrolysis, despite its recent identification among products of the gas-phase ethylene-ozone reaction.

In situ photolysis of SOZ encourages rapid vibrational relaxation of "hot" HMF and the molecule is trapped in either the cis or trans conformation. Evidence is presented for the photodecomposition of hydrogen-bonded cis-HMF to a specific formic acid-formaldehyde dimer. The same species is also observed in codeposition of formic acid and formaldehyde and in SOZ pyrolysis experiments. Formic anhydride, probably formed by H_2 elimination from vibrationally excited trans-HMF, constitutes the second major photolysis product. The presence of CO_2 , CO, and H₂O without detection of monomeric formic acid or formaldehyde implies another mode of decomposition for SOZ, HMF, or FAN in which the former small molecules are the sole products.

A brief comparison with results from ethylene-ozone gas-phase studies reveals that some unassigned bands agree closely with several of those identified in this work as due to HMF and the formic acid-formaldehyde dimer. Thus the two sets of experiments are complementary and the present results suggest that ground- or excited-state SOZ may play an important role in the gas-phase ethyleneozone reaction even though it is rarely detected.

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Electrochemical Properties of Small Clusters of Metal Atoms and Their Role in Surface Enhanced Raman Scattering

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Starting with equations for the shift of the reversible redox potential of small metal particles with size, the electrochemical properties of these particles are discussed. Approximate equations are given for the relationship between the particle size and the surface charge, the potential of zero charge, the surface potential, work function and quantities related to this function. The influence of these properties on redox reactions, electrosorption, and chemisorption are discussed. The results are used to explain experimental observation in connection with the surface enhanced Raman effect.

Introduction

It is well known that small particles have properties quite different from the properties of the bulk materials.¹ Recently, it was found by Henglein² that small metal particles possess unusual catalytic properties in radiolysis and this was explained qualitatively by a shift in the redox potential. In a series of papers, Henglein et al.³ investigated the catalyzed reduction of several organic molecules, the catalysts being metal clusters of silver, gold, and copper. Another series of experiments, demonstrating the

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