Infrared Spectra and Photochemistry of the Primary and Secondary Ozonides of Propene, *trans*-2-Butene, and Methylpropene in Solid Argon

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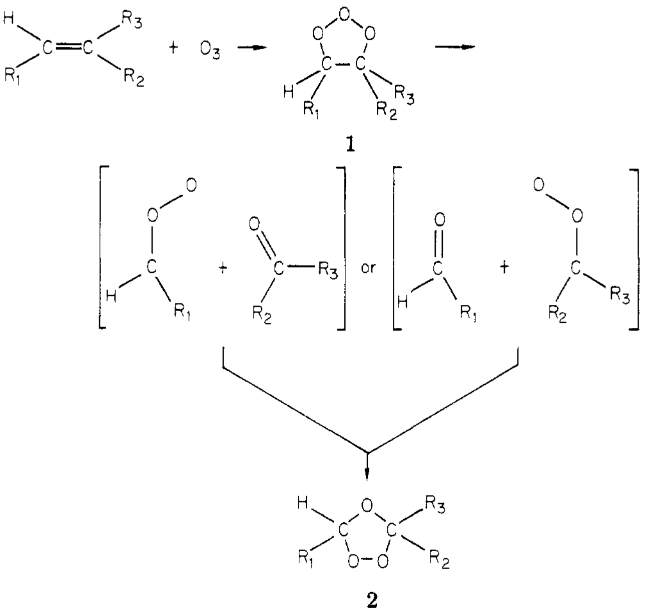
Reactions of propene, *trans*-2-butene, and methylpropene with $^{16}O_3$, $^{16,18}O_3$, and $^{18}O_3$ have been studied in solid xenon at 80–110 K and CF_3Cl solution at 130–150 K. The major reaction product in solution was identified as the secondary ozonide (SOZ) from the matrix infrared spectrum. Reaction products in solid xenon for propene and *trans*-2-butene were SOZ, primary ozonide (POZ), and aldehyde, and for methylpropene the products were POZ, oxide, and acetone. The POZ's were characterized by an intense antisymmetric O–O–O stretching mode at 640–700 cm^{-1}. Photolysis of the propene and 2-butene SOZ's gave formic acetic anhydride, hydroxy ester, and acid–aldehyde dimer decomposition products.

Introduction

A considerable amount of work has involved the reaction between ozone and alkenes which has been thoroughly reviewed by Bailey in a recent monograph.[1] The Criegee reaction mechanism,[2] Scheme I, has been essentially substantiated, and has led to much of the present understanding of the ozonolysis reaction. Recent work in this laboratory has identified the initial ethene–ozone adduct primary ozonide (POZ) as the 1,2,3-trioxolane, **1a**, from infrared spectroscopic studies of six isotopic modifications of this species produced in solid xenon at 80–110 K,[3] whereas only the secondary ozonide **2a** (SOZ) was observed in the volatile product of the reaction of ethene and ozone in CF_3Cl solution near 130–150 K.[4] The present low-temperature reaction techniques require small reagent quantities which allows the use of isotopic precursors; oxygen-18 isotopic substitution enables the C–O and O–O stretching vibrations in both the primary and secondary ozonides to be identified. The reactions of ozone with propene (R), *trans*-2-butene (TB), and 2-methylpropene (MP) have been carried out in solid xenon and Freon solutions in order to obtain matrix infrared spectra of the ozonides of these compounds. The samples were photolyzed as a diagnostic for ozonides and to characterize decomposition mechanisms for ozonides.

Scheme I



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$, $R_2 = R_3 = H$
c, $R_1 = R_2 = CH_3$, $R_3 = H$
d, $R_2 = R_3 = CH_3$, $R_1 = H$

Experimental Section

Two different experimental techniques were used to prepare ozonides. The first employed diffusion and reaction of the reagents in solid xenon warmed to 80–110 K with the closed-cycle cryogenic refrigeration system[5] as described previously,[3] except that higher reagent concentrations were used in the present studies to minimize the xenon film thickness. After deposition of each sample (~1 mmol/h) for 10–14 h on a 50-K window, the infrared spectrum was recorded on a Beckman IR-12, and the window was allowed to warm to 80–110 K over 20–30 min without refrigeration; the window was then recooled to 50 K and another spectrum was recorded. The samples were photolyzed with a water-filtered high-pressure mercury arc in order to characterize the ozonide product bands. In a variation on the above, $Ar/O_3 = 100/1$ and Ar/alkene = 100/1 samples (20 mmol each) were condensed at 16 K over a 15-h period and 0.5 mmol of xenon was added as an overcoat to reduce the argon sample evaporation rate.[6] The samples were held in the 30–40- and 40–50-K ranges for about 1 h until significant reaction occurred as determined from survey scans; the samples were recooled to 16 K and final spectra were recorded.

In the second method, the secondary ozonides of propene, *trans*-2-butene, and 2-methylpropene were prepared in the same manner described previously for the ethene.[4] The alkene and ozone (~0.1 mmol each) were condensed (−196 °C) at the base of a U-tube with excess Freon 13 (chlorotrifluoromethane) as solvent and reaction moderator. The U-tube was slowly warmed by using pentane (−130 °C) and methanol (−98 °C) slush baths. (A "snap" was heard in the U-tube during warming in several synthetic attempts, which indicated that the reaction had gone further than ozonide products.) The reaction mixture was

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[1] Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. I.
[2] Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975,** *14,* 745.
[3] Kohlmiller, C. K.; Andrews, L. *J. Am. Chem. Soc.* **1981,** *103,* 2578.
[4] Hawkins, M.; Kohlmiller, C. K.; Andrews, L. *J. Phys. Chem.* **1982,** *86,* 3154.
[5] Andrews, L. *J. Chem. Phys.* **1968,** *48,* 972, **1971,** *54,* 4935.
[6] Jones, L. H., presented at the International Meeting on Matrix Isolation Spectroscopy, Nottingham, England, 1981.

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TABLE I: New Absorptions (cm^{-1}) Produced on Warming a Xenon Matrix Sample of Propene and Ozone to 80-110 K

$^{16}O_3$	$^{18}O_3$	assignments
505 (506)[a]	499 (499)	SOZ
640 (638)	609	POZ
685		?
718 (718)	699	POZ
828 (834)	812	POX[c]
844 (847)	829 (831)	SOZ
868 (876)	850 (859)	SOZ
955 (967,963)	936 (948,944)	SOZ
974	955	POZ
[1044][b] (1052)	1027 (1032)	SOZ
1116 (1122)	1095 (1098)	SOZ
1138 (1143)	1132 (1138)	SOZ
1347 (1348)	1347	A
1380	1378	POZ
1396 (1397)	1393	SOZ
1722 (1729)	1684	A

[a] Argon matrix values given in parentheses. [b] Obscured by the strong ozone absorption. [c] Propene oxide.

evacuated at −77 °C (dry ice) to remove the Freon 13, excess reactants, and side products. The ethene ozonide cross-ozonolysis product was formed when propene and 2-methylpropene were reacted, but attempts to distill it from the desired secondary ozonides were never completely successful. Attempts to react the olefins and ozone at lower temperatures, and therefore achieve less cross-ozonide products, by using Freon 14 (tetrafluoromethane, CF_4, mp −184 °C; $CClF_3$, mp −150 °C) produced similar yields of products. The ozonide products were evaporated directly from the U-tube into a stream of argon and condensed at 16 K on a CsI optical window. Samples were photolyzed in order to identify photosensitive bands that might be due to the ozonides. In addition, several neat ozonide samples were passed through 30 cm of heated spray-on line and the effluent was condensed with excess argon to study thermal decomposition products.

The propene, *trans*-2-butene, and methylpropene were obtained from Matheson (CP grade). All olefins were condensed at 77 K and outgassed with an oil diffusion pump before use. The ozone was formed from oxygen gas by a static electric discharge (Tesla coil) in a Pyrex tube immersed in liquid nitrogen;[7] liquid O_3 was evacuated with an oil diffusion pump to remove residual O_2 before use. The normal isotopic oxygen gas was obtained from Burdett, U.S.P. grade, and the ^{18}O-enriched oxygen gas (95%) from Yeda (Israel). The xenon (Airco, purified, 99.9%), argon (Burdett, 99.995%), and Freon 13 (DuPont) were used as received.

Results

Infrared spectra of ozonides prepared from three different alkenes in solid xenon and CF_3Cl solutions will be described in turn.

Propene. Ten experiments were performed with 1% propene (R) and 2–4% ozone samples in xenon; the spectra illustrated in Figure 1 represent the most successful of these efforts. Figure 1a shows the spectrum of propene and $^{18}O_3$ reagents (labeled R and O, respectively, in the figure). The sample was first warmed to 90 K and recooled to 50 K; the strongest product band at 609 cm^{-1} was A = 0.27 absorbance units. The sample was cycled to 110 K, and the 609-cm^{-1} band increased slightly (A = 0.32); this spectrum is illustrated in Figure 1b. Note that the R and O bands were replaced by new product absorptions labeled A, PO, S, and P in the figure and collected in Table I. Photolysis for 15 min increased the A bands at 1684, 1425, and 1348 cm^{-1} due to acetaldehyde and decreased the S and PO bands by 40% and the P bands by 70%; new bands appeared at 1186, 1050, and 520 cm^{-1} and a very strong $C^{18}O_2$ band was produced at 648 cm^{-1}. The spectrum from a similar experiment with $^{16}O_3$ is compared in Figure 1c; oxygen isotope shifts ranging from 2 to 38 cm^{-1} were observed for the product bands. Photolysis for 15 min almost destroyed the P bands, reduced the S bands by 60%, left the 827-cm^{-1} PO band unchanged, and produced a strong CO_2 band at 658 cm^{-1}. No evidence was found for **1a** or **2a** in the xenon experiments. Another study with mixed isotopic ozone $^{16,18}O_3$ gave doublets at 1722, 1684 cm^{-1} and 828, 812 cm^{-1}, in agreement with the $^{16}O_3$ and $^{18}O_3$ spectra. The strongest bands at 640 and 609 cm^{-1} in the spectra of the $^{16}O_3$ and $^{18}O_3$ products gave way to a broad doublet with maxima at 634 and 614 cm^{-1} in the $^{16,18}O_3$ experiment; the other product bands were a broad average of the $^{16}O_3$ and $^{18}O_3$ counterparts.

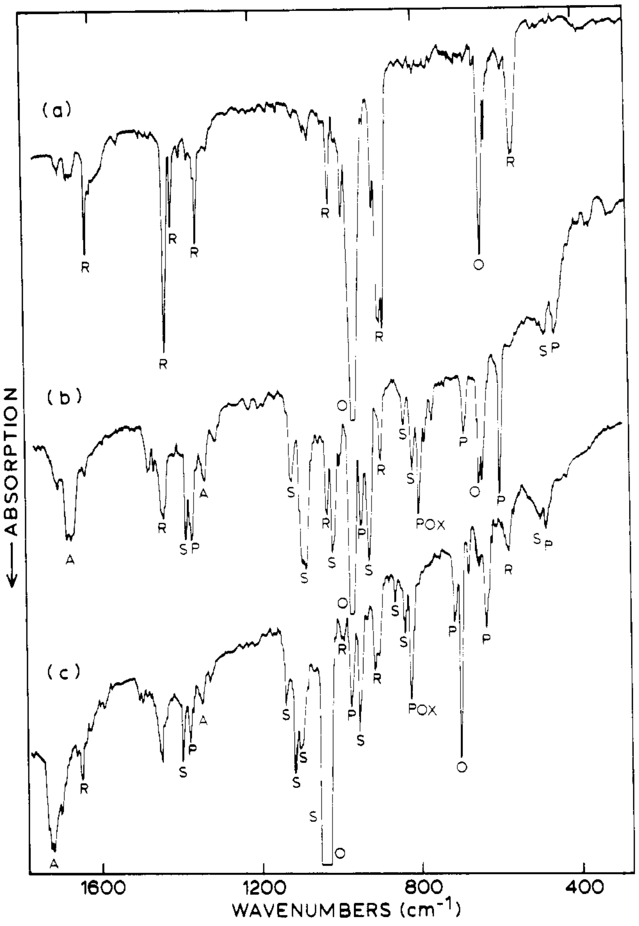

Figure 1. Infrared spectra of propene and ozone and their reaction products in solid xenon at 50 K: (a) 8 mmol of Xe/C_3H_6 = 110/1 sample codeposited at 50 K with 8 mmol of Xe/$^{18}O_3$ = 35/1 sample for 14 h, (b) sample in (a) after temperature cycling to 90 and to 110 K over 20–30-min periods, (c) 10 mmol of Xe/C_3H_6 = 100/1 sample codeposited at 50 K with 3 mmol of Xe/$^{16}O_3$ = 20/1 sample for 12 h then temperature cycled to 90 K. R denotes propene reagent, O denotes ozone.

The ozonolysis of propene in Freon solutions was performed 17 times followed by matrix isolation of the products. Most samples were contaminated by the acetaldehyde (A) decomposition product (labeled A in Figure 2), which gives a characteristic band at 1727 cm^{-1} and sharper bands at 2843, 2737, 1442, 1438, 1350, and 1111 cm^{-1} as measured from argon matrix experiments with CH_3CHO in this laboratory; however, some samples were

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[7] Andrews, L.; Spiker, R. C. *J. Phys. Chem.* **1972**, *76*, 3208.

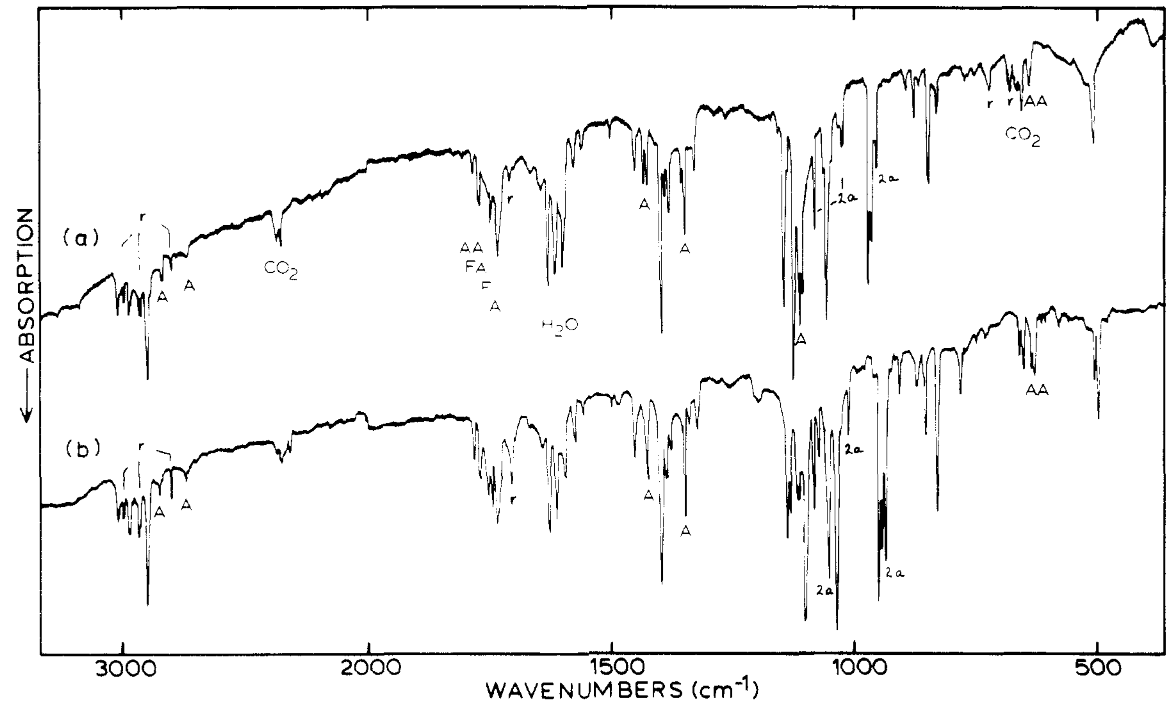

Figure 2. Infrared spectra of the product of the propene-ozone reaction in Freon-13 solution evaporated from U-tube at -77 °C and codeposited with argon at 15 K: (a) $^{16}O_3$, (b) $^{18}O_3$. **2a** denotes ethene-SOZ cross ozonide; r denotes bands that remain on photolysis.

TABLE II: Photosensitive Absorption Bands (cm^{-1}) for SOZ's of Propene, 2-Butene, and Methylpropene

propene		2-butene		methylpropene	
$^{16}O_3$	$^{18}O_3$	$^{16}O_3$	$^{18}O_3$	$^{16}O_3$	$^{18}O_3$
506	499	479	473	421	415
829	784	698		514	504
847	831	847	816	630	618
876	859	861	842	719	692
963	944			798	763
967	948	895	879	835	792
1052	1035	1075	1070	851	828
1122	1098	1117	1103	950	938
1142	1137	1146	1135	985	973
1328	1323	1341	1341	1069	1044
1378	1377	1368	1367	1160	1155
1396	1395	1392	1391	1230	1227
1450	1448	1448	1448	1252	1252
2896	2896	2915	2914	1375	1374
2970	2970	2926	2925	1383	1384
		2950	2949	1460	1460
				2724	2722
				2896	2895

TABLE III: New Absorptions (cm^{-1}) Produced by Photolysis of Propene SOZ in Solid Argon

$^{16}O_3$	$^{18}O_3$	identification
523	507	D
538		D
934	907	HE
945	923	HE
998	976	FAN
1019	1006	HE
1048	1021	HE
1060	1047	HE
1079	1067	HE
1091		FAN
1173 (Δ)[a]	1142	D
1185 (Δ)	1155	D
1188	1172	*trans*-HEF
1200	1193	*cis*-HEF
1245 (Δ)	1234	D
1252	1247	*cis*-HMA
1281	1273	HE
1305	1305	CH_4
1375		FAAN
1500		D
1727	1696	D
1744	1712	*cis*-HEF
1761	1723	*cis*-HMA (<30% FAN)
1784 sh	1747 sh	*trans*-HEF
1786	1749	FAAN
1803	1763	FAAN
1812 w	1771 w	FAN
2142	2090	CO
2158 (Δ)	2107	(CO)D
2344	2308	CO_2
3189 (Δ)	3180	D
3474	3465	*cis*-HEF

[a] Δ denotes bands produced by SOZ thermal decomposition.

completely free of decomposition products. Weak bands were also observed at 1780, 1769, and 1743 cm^{-1} for acetic acid[8] (AA), formic acid[4] (FA), formaldehyde[4] (F) decomposition products; clearly the acetaldehyde-formic acid decomposition products are favored over formaldehyde-acetic acid. Figure 2, a and b, contrasts samples prepared from $^{16}O_3$ and $^{18}O_3$, respectively. The samples were photolyzed for 10 and 60 min to identify photosensitive species, and spectra were recorded after each photolysis. The bands labeled S in Figure 2 and listed in Table II decreased together on photolysis and they are attributed to the same species; oxygen isotopic shifts were found for a number of the new product absorptions. The bands labeled **2a** in the figure are due to the **2a** cross-ozonide produced by reaction of CH_2O from the first intermediate and CH_2OO from the second intermediate in Scheme I. Experiments with $^{16,18}O_3$ gave multiplets for the strongest bands at 1122, 1052, and 967 cm^{-1}, but the resolution was not sufficient to specify the number of components; the strongest band exhibited its strongest components at 1116 and 1103 cm^{-1}, intermediate between the 1122- and 1099-cm^{-1} peaks for the $^{16}O_3$ and $^{18}O_3$ species.

Strong, new photolysis product absorptions were observed in the spectra; the regions 930–1320 and 1690–1860

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[8] Berney, C. V.; Reddington, R. L.; Lin, K. C. *J. Chem. Phys.* **1970**, *53*, 1713.

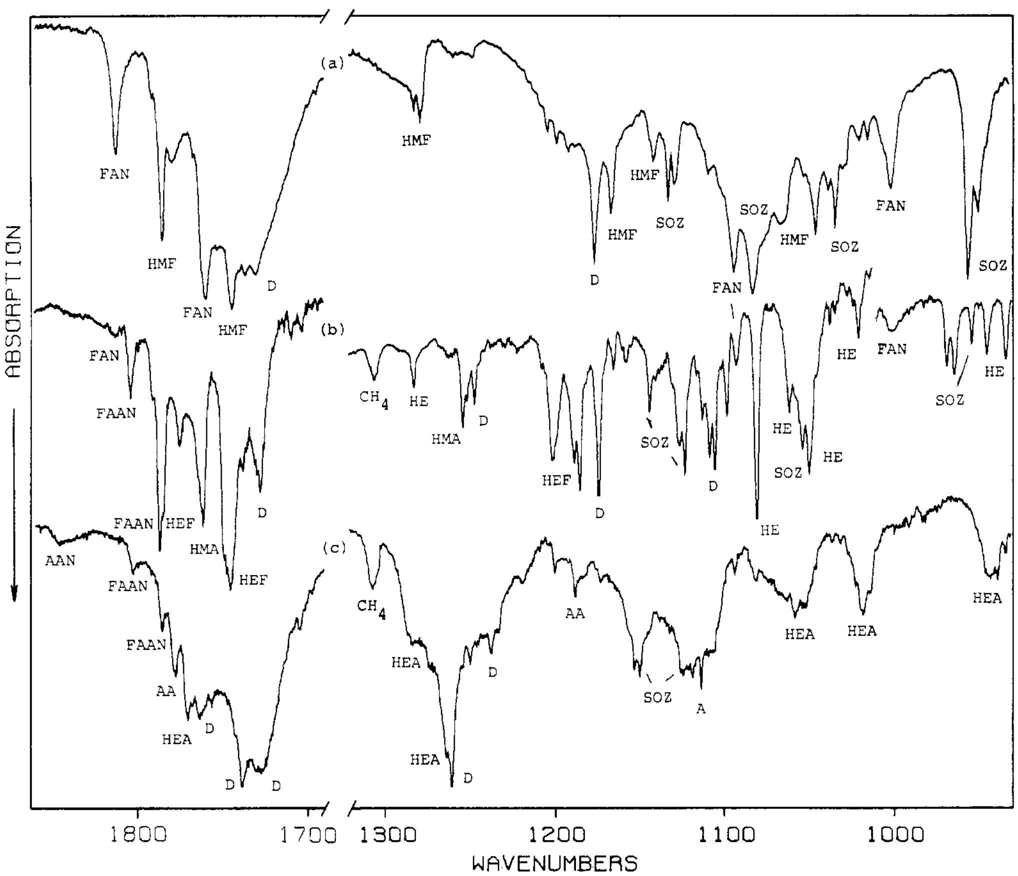

Figure 3. Infrared spectra of the matrix photolysis products of SOZ samples in 930–1320- and 1690–1860-cm^{-1} spectral regions: (a) ethene-SOZ, (b) propene-SOZ, (c) 2-butene-SOZ.

cm^{-1} shown in Figure 3b are of particular interest here. The photolysis product bands are given in Table III for $^{16}O_3$ and $^{18}O_3$ experiments. Thermal decomposition of the SOZ passing through a 180 °C spray-on line gave substantially increased yields of the acid and aldehyde decomposition product absorptions. Some of the photolysis product bands were also produced on thermal decomposition, which are denoted Δ in Table III.

Propene and ozone samples (1% in argon) were condensed at 20 K, and 0.5 mmol of xenon was added as an overcoat. The sample was warmed to 35 K, and new medium-intensity bands appeared at 1741, 1723, 1411, 952.0, and 831.5 cm^{-1} (A = 0.10) and very weak bands were detected at 1118, 718 and 638 cm^{-1} (A = 0.005). The sample was warmed to 50 ± 2 K, and the latter bands increased substantially: 1118 cm^{-1} (A = 0.07), 718 cm^{-1} (A = 0.03), 638 cm^{-1} (A = 0.04), and a new 1140-cm^{-1} band (A = 0.04) was observed. The matrix was lost before other regions could be scanned.

trans-2-Butene. Four experiments were done with 1% *trans*-2-butene (TB) and 2–5% ozone in xenon with warming cycles to 80–90 K. The product bands listed in Table IV were observed during sample condensation at 50 K, and they increased substantially on warming the solid xenon to allow reagent diffusion and reaction. Product absorptions from a comparable experiment with $^{18}O_3$ given in the table show isotopic shifts for most of the new bands.

The ozonolysis of TB in Freon solutions was done 15 times followed by evaporation of the product from the U-tube at −25 to −30 °C. Spectra are shown in Figure 4 for the cleanest $^{16}O_3$ and $^{18}O_3$ experiments; an experiment with $^{16,18}O_3$ gave broad product bands covering the $^{16}O_3$ and $^{18}O_3$ product position. The samples were photolyzed by a high-pressure mercury arc for 10- and 70-min periods to identify and group photosensitive bands which are listed in Table II. The absorptions labeled r in Figure 4 remained on photolysis, which clearly separates them from the photosensitive bands in Table II. Strong new photolysis product absorptions in 930–1320- and 1690–1860-cm^{-1} regions are illustrated in Figure 3 for the $^{16}O_3$ experiment; all photolysis product bands are listed in Table V for both oxygen isotopic species. Thermal decomposition of neat SOZ samples flowing through a spray-on line heated to 180 °C for 16 h gave substantial acetic acid and acetaldehyde decomposition products and the absorptions noted Δ in Table V.

TABLE IV: Product Absorptions (cm^{-1}) That Increased on Temperature Cycling Xenon Samples Containing *trans*-2-Butene and Ozone from 50 to 80–90 K

$^{16}O_3$			$^{18}O_3$,	
cm^{-1}	A_{50}	$A_{50-90-50}$	cm^{-1}	identification
470	0.04	0.12	455	POZ
478	0.02	0.06	470	(479, Ar) SOZ
521	0.20	0.60	513	(522, Ar) ?
693	0.23	0.67	658	POZ
799	0.03	0.10	790	?
809	0.03	0.10	790	(812, Ar) BOX[a]
849	0.03	0.10	816	?
887	0.05	0.18	870	(889, Ar) BOX[a]
894	0.04	0.12	876 sh	(895, Ar) SOZ
902	0.16	0.40	883	POZ
919	0.03	0.08	902	(922, Ar) ?
996	0.09	0.20	$^{18}O_3$	POZ
1114	0.26	0.8	1099	(1117, Ar) SOZ
1142	0.13	0.4	1130	(1146, Ar) SOZ
1348	0.07	0.2	1348	(1349, Ar) A
1384	0.06	0.2	1384	POZ
1392	0.09	0.3	1391	(1392, Ar) SOZ
1722	0.2	0.4	1684	(1728, Ar) A

[a] Butene oxide.

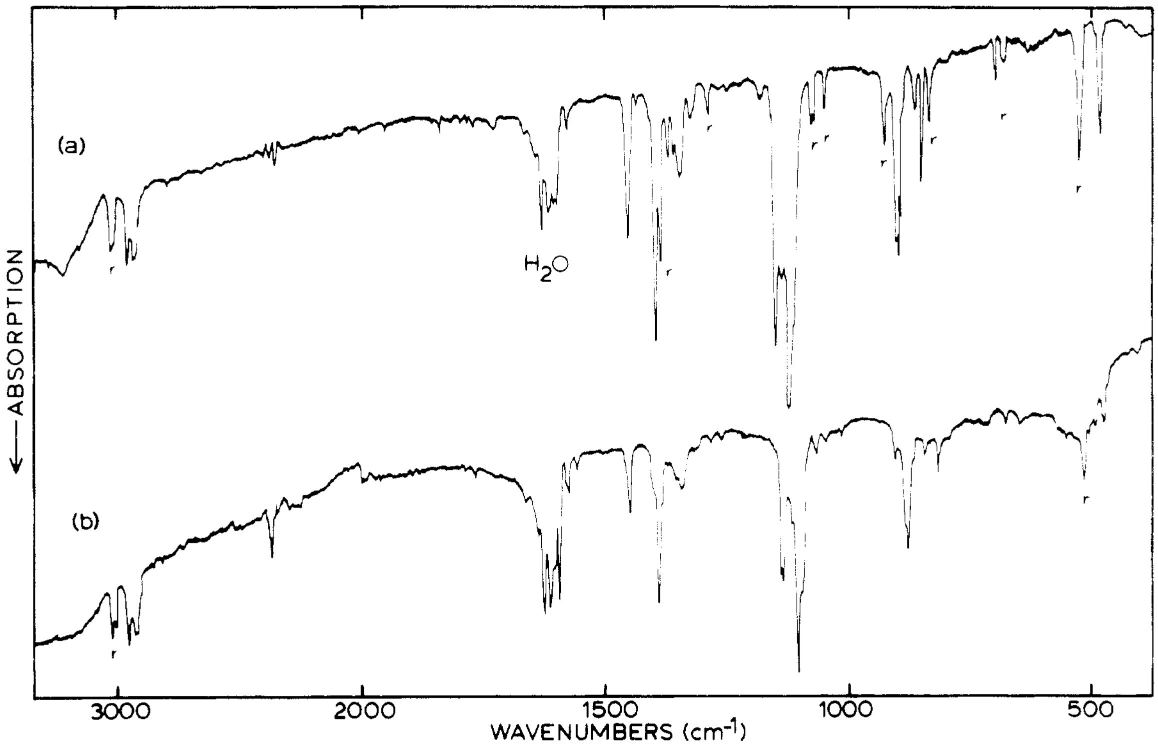

Figure 4. Infrared spectra of the reaction product of *trans*-2-butene and ozone in Freon-13 solution evaporated from U-tube at −25 °C and codeposited with argon at 15 K: (a) $^{16}O_3$, (b) $^{18}O_3$. r denotes bands that remain on photolysis.

TABLE V: New Absorptions (cm^{-1}) Produced by Photolysis of 2-Butene SOZ in Solid Argon

$^{16}O_3$	$^{18}O_3$	identification
940	910	*cis*-HEA
1016	1007	*cis*-HEA
1055	1050	*cis*-HEA
1112		A
1185	1164	AA
1258 (Δ)	1241	D
1261	1254	*cis*-HEA
1282	1276	*cis*-HEA
1305	1305	CH_4
1348	1348	A
1375	1373	FAAN
1431	1430	A
1728 (Δ)	1695	D
1738 (Δ)	1702	D
1764 (Δ)	1726 sh	D
1772	1728	*cis*-HEA
1780		AA
1786	1749	FAAN
1803	1763	FAAN
1846	1811	AAN
2142	2090	CO
2344	2308	CO_2

[a] Δ denotes bands produced by SOZ thermal decomposition.

Samples of TB and O_3 (1% in argon) were codeposited at 16 K, and the spectrum revealed very strong reagent bands and weak new bands at 1115 (A = 0.02) and 812 cm^{-1} (A = 0.01). The sample was warmed to 25 K and 0.5 mmol of xenon was condensed onto the sample; the 1115- (to A = 0.06) and 812-cm^{-1} (to A = 0.02) bands increased, new bands were detected at 893 (A = 0.03) and 1144 cm^{-1} (A = 0.01), and a scan out to 2000 cm^{-1} revealed a 1729-cm^{-1} (A = 0.13) carbonyl band. Warming the sample to 35 K and recording spectra over a 30-min period revealed marked growth in the 1144- (A = 0.08), 1115- (A = 0.23), 812- (A = 0.05), and 1728-cm^{-1} (A = 0.22) bands and the appearance of new absorptions at 889 (A = 0.06), 694 (A = 0.12), 904 (A = 0.05), and 998 cm^{-1} (A = 0.04). The sample was warmed to 43 K for 15 min; the spectrum showed substantial reduction in reagent absorptions, reduction at 1728 cm^{-1} (to A = 0.12), a threefold growth of 694-, 904-, and 998-cm^{-1} bands, a twofold growth of the 888- and 812-cm^{-1} bands, and a 30% increase in the 1115- and 1144-cm^{-1} bands, the latter of which are within 2 cm^{-1} of absorptions due to the evaporated ozonolysis product. New bands were also observed at 518 (A = 0.13), 480 (A = 0.05), and 471 cm^{-1} (A = 0.09) similar to the xenon experiments.

Methylpropene. Three experiments were done with methylpropene (MP) and ozone in xenon. Weak product bands were observed at 1779, 1740, 1718, and 795 cm^{-1} after sample deposition at 50 K; these bands increased substantially upon cycling the sample to 80 K and strong *new* bands were produced at 1372, 1229, 1160, 989, 953, and 674 cm^{-1} ($A \approx 0.2$) and a medium-intensity band was produced at 847 cm^{-1}.

Methylpropene was reacted with ozone in Freon solutions and the products were evaporated from the U-tube at −77 to −10 °C and codeposited with argon in 14 separate experiments. Several ozonide samples were evaporated into the matrix in three fractions according to volatility; it was found that the **2a** cross-ozonide was the major product in the light fraction but was substantially reduced in the heavier product fraction. Figure 5 illustrates the spectra of the heavier product fraction from (a) $^{16}O_3$ and (b) $^{18}O_3$ reactions. Sample decomposition was evidenced by acetic acid (AA) at 1779 cm^{-1}, formic acid (FA) at 1766 cm^{-1}, formaldehyde (F) at 1743 cm^{-1}, and acetone (K) at 1724 cm^{-1} in the spectrum from the $^{16}O_3$ reaction; the acetone and formic acid decomposition products clearly dominate. The samples were photolyzed to identify photosensitive absorptions which are listed in Table II; the weaker bands labeled r in the figure remained on photolysis. The acetone, CO, and CO_2 bands in the figure increased markedly on photolysis; new photolysis products included strong bands at 1803, 1786, and 1098 cm^{-1} and

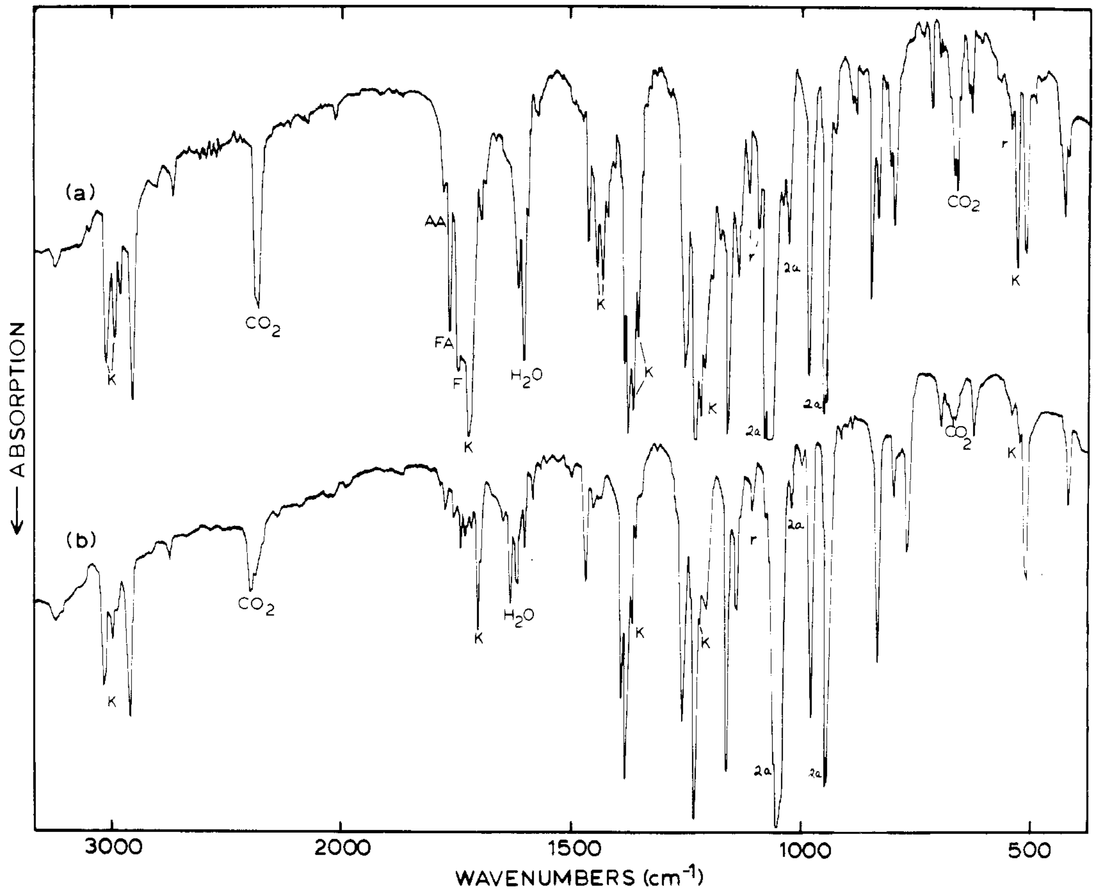

Figure 5. Infrared spectra of the reaction product of methylpropene in Freon-13 solution evaporated from U-tube at −77 to −10 °C and codeposited with argon at 15 K: (a) $^{16}O_3$, (b) $^{18}O_3$. r denotes bands that remain on photolysis. **2a** denotes cross ozonide.

medium-intensity bands at 1499, 1305, and 608 cm^{-1} in the $^{16}O_3$ experiments and 1765, 1749, 1491, 1305, 1091, and 599 cm^{-1} in the $^{18}O_3$ sample. Thermal decomposition of the heavy fraction in the spray-on line at 190 °C gave a substantial yield of the AA, FA, F, and K decomposition products and new bands at 1761, 1735 (strong, broad), 1245, and 1049 cm^{-1}.

A reaction was done with MP, and $^{16,18}O_3$, and the lighter product fraction again contained major **2a** products; in the heavier fraction, the strongest product bands were observed at 1252, 1228, and 1158 cm^{-1}, a partially resolved doublet of triplets at 1069, *1067*, 1065, 1050, *1046*, and 1044 cm^{-1} (most intense components italicized), a partially resolved multiplet at 985, *983*, *976*, and 973 cm^{-1}, and a partially resolved multiplet at 950, 947, *944*, *941*, and 938 cm^{-1}.

Discussion

The ozonides prepared by two different techniques for each alkene will be identified, POZ and SOZ species will be compared for different alkenes, and the photolysis products and mechanism will be discussed.

Propene. Identification of the ozone–propene reaction products in solid xenon depends on photolysis behavior to group the bands and on the spectrum of propene SOZ, which has been studied in the gas phase. There is general agreement that propene SOZ exhibits strong absorptions at 1400, 1120, 1050, 970, and 840 cm^{-1} in the gas phase.[9-11] The argon matrix spectra in Figure 2 exhibit sharp bands near the gas-phase values, which supports the identification of propene SOZ. The observation of substantial oxygen-18 shifts and a partially resolved multiplet consistent with a doublet of triplets for the strongest 1122-cm^{-1} band support the observation of propene SOZ. The bands given in the first two columns of Table II photolyzed together and they are assigned to the SOZ of propene, **2b**. Vibrational assignments, which follow from the characteristic oxygen-16–18 shifts and comparison to ethene SOZ assignments,[4] will be discussed in a later section.

The xenon matrix experiment has an excellent possibility of stabilizing the POZ **1b** as well as further reaction products.[3] The 1722-cm^{-1} band, which shifted to 1684 cm^{-1} with oxygen-18, is in sufficient agreement with the spectrum of acetaldehyde in solid argon to indicate this assignment. The 828-cm^{-1} band, which shifted to 812 cm^{-1} with oxygen-18 and exhibited a doublet at 828 and 812 cm^{-1} characteristic of a single oxygen vibration in the mixed isotopic experiment, is assigned to propene oxide based on observation of this compound at 837 cm^{-1} in the gas phase[12] and 834 cm^{-1} in solid argon.[13] The growth of propene oxide upon diffusion and reaction of ozone and propene in solid xenon suggests that the POZ may decompose by eliminating O_2 to form the oxide in addition to the Scheme I rearrangement giving the SOZ. Nine of the bands in Table I are due to the SOZ based on comparison with the argon matrix observations. The 685-cm^{-1} band is uncharacteristically sharp, and without an oxygen-18 counterpart, it cannot be assigned here.

The remaining five bands at 1380, 974, 718, 640, and 488 cm^{-1} are assigned to the POZ species **1b**. The strongest band at 640 cm^{-1} in solid xenon exhibits a 31-cm^{-1} oxy-

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gen-18 shift to 609 cm^{-1}, which indicates an almost pure O–O vibration; this band is assigned to the antisymmetric O–O–O stretching mode in **1b**. The broad doublet with maxima at 634 and 614 cm^{-1} in the mixed isotopic experiment is probably an unresolved doublet of triplets characteristic of a three oxygen species with two equivalent oxygen atoms. The analogous absorption of species **1a** at 647 cm^{-1} shifted to 615 cm^{-1} with oxygen-18 and exhibited a partially resolved doublet of triplets at 647, 641, 636, 630, 623, and 616 cm^{-1} in the mixed isotopic experiments.[3] The strong 974-cm^{-1} band shifted to 955 cm^{-1} with oxygen-18, which identifies a C–O stretching mode analogous to the 983- and 927-cm^{-1} bands of species **1a**. The 718- and 488-cm^{-1} bands showed appropriate oxygen-18 shifts for C–O–O and O–O–O bending modes, and they are near similar 727- and 409-cm^{-1} bands for species **1a**. The 1380-cm^{-1} band exhibited a small oxygen-18 shift and it is near strong $-CH_3$ deformation vibrations in the SOZ species, which suggests this assignment.

The argon matrix reaction of propene and ozone provides an interesting counterpoint to the xenon matrix study. The propene oxide was formed at lower temperature (35 K) and in greater yield (831-cm^{-1} band) than the SOZ and POZ as identified by 1140- and 1118-cm^{-1} (within 4 cm^{-1} of the absorptions due to evaporated material) and 718- and 638-cm^{-1} bands, respectively. A temperature of about 50 K was required for significant yields of the SOZ and POZ to be formed in solid argon.

The three strongest bands at 974, 718, and 640 cm^{-1} in solid xenon assigned here to the POZ species **1b** are in agreement with major bands at 971, 715, and 635 cm^{-1} in the solid film studies of Hull et al.[14] These earlier workers were unfortunately unable to identify major bands in their film spectrum due to the SOZ and propene oxide, which is required before assignments to the POZ can be made.

2-Butene. The secondary ozonides of 2-butene have the O–O half-chair conformation with two different trans arrangements (biequatorial and biaxial methyl group orientations) and two different cis arrangements (axial–equatorial and equatorial–axial methyl groups).[15] These conformational differences will, however, make very little difference in the infrared spectrum. The gas-phase spectrum[10] exhibits strong bands at 2905, 1385, and 1115 cm^{-1} and medium bands at 1445, 1345, and 890 cm^{-1}, which are near major bands in the matrix spectrum (Figure 3) prepared from *trans*-2-butene and that reported by the Swiss group[16] for the SOZ prepared from *cis*-2-butene. As far as can be determined from the literature spectrum, the matrix spectra of the SOZ prepared from the 2-butene isomers are identical. The absorptions assigned to 2-butene SOZ in Table II decreased substantially on mercury arc photolysis as expected for an ozonide species; the absorptions denoted r remained on photolysis, including bands at 3015, 832, and 522 cm^{-1} common to the present and the Swiss matrix spectra, which suggests that these bands are due to a different species. In particular, the 522-cm^{-1} band in all of the present argon and xenon matrix studies, the solid film experiments,[14] and the Swiss sample[16] was relatively more intense in samples containing more CO_2, which suggests a higher oxidation product than the ozonide. Finally, the oxygen isotopic shifts for the bands in Table II are appropriate for vibrations of an SOZ species.

Most of the absorptions produced upon diffusion and reaction of *trans*-2-butene and ozone in solid xenon are due to the SOZ species **2c**. The bands at 1722 and 1348 cm^{-1} arise from acetaldehyde, and the 919- and 521-cm^{-1} bands cannot be identified from the present data. The 808-cm^{-1} band is assigned to *trans*-2-butene oxide based on its observation at 812 cm^{-1} in the argon diffusion experiments and at 815 cm^{-1} in photolysis studies[13] and in a prepared sample.[16] The strongest four remaining xenon matrix bands at 996, 902, 693, and 470 cm^{-1} are appropriate for assignment to the POZ species **1c**. The 996- and 902-cm^{-1} bands are near 983- 927-cm^{-1} bands assigned to C–O stretching modes in the POZ species **1a**. The $^{18}O_3$ counterparts of the 996-cm^{-1} band was lost under $^{18}O_3$ itself, but the 902-cm^{-1} band shifted to 883 cm^{-1}, which is appropriate for a C–O stretching mode. The strongest 693-cm^{-1} product band was not completely resolved from $^{16}O_3$ at 702 cm^{-1}, and likewise the 658-cm^{-1} counterpart was not completely resolved from $^{18}O_3$ at 663 cm^{-1}; the large oxygen-18 shift (35 cm^{-1}) is appropriate for an almost pure O–O vibration (39 cm^{-1} for ν_2 of O_3 in these experiments), and the 693-cm^{-1} band is assigned to the antisymmetric O–O–O stretching vibration in **1c**. The weaker, lower frequency band at 470 cm^{-1} shows an appropriate oxygen-18 shift for a predominantly O–O–O bending mode.

The argon matrix reaction of ozone and *trans*-2-butene complements the xenon reactions and demonstrates that three different species were produced, the SOZ, POZ, and oxide. The 998-, 904-, 694-, and 471-cm^{-1} bands in solid argon are assigned to the POZ and are in excellent agreement with similar bands at 996, 902, 693, and 470 cm^{-1} in solid xenon and with sharp bands at 995, 900, 690, and 465 cm^{-1} in the earlier solid film studies. The solid film experiments with *cis*-2-butene and ozone also contain SOZ absorptions, which are common to the *trans*-2-butene studies, and sharp bands at 970, 890, 710, and 440 cm^{-1} which are near but distinctly different from the *trans*-POZ film bands. The O–O half-chair conformation[15] of the SOZ is such that cis and trans orientations of two methyl groups make no observable differences in the matrix infrared spectra of the two isomers; however, the O-envelope conformation[17] of the POZ clearly shows a spectroscopic difference for the cis and trans orientations of two methyl groups in the 2-butene POZ's, which provides experimental evidence to support the O-envelope POZ conformation proposed by recent ab initio MO calculations on the 2-butene POZ isomers.[17]

Methylpropene. The ozonolysis of methylpropene is seldom studied because reaction of the dioxymethylene intermediate CH_2OO with ketones is less favorable than with aldehydes;[1] however, Criegee et al.[18] circumvented this problem by performing ozonolysis of $(CH_3)_2C{=}C(CH_3)_2$ in CH_3Cl at −80 °C, which, with formaldehyde added, gave the methylpropene SOZ **2d**. A gas-phase spectrum of **2d** containing strong bands at 1370, 1220, and 1060 cm^{-1} and medium-intensity bands at 1160, 990, 950, 850, 830, and 790 cm^{-1} has been reported by Garvin and Schubert[9] using direct ozonolysis of methylpropene in isobutane at −78 °C. After bands due to the major decomposition product acetone (K) and cross-ozonide (**2a**) are identified, the new photosensitive absorptions in Figure 5 and the indicated columns in Table II due to the Freon solution ozonolysis product, which agree well with the gas-phase spectrum, are assigned to the SOZ **2d**. The oxygen-18 isotopic shifts are supportive of the assignment. The present observations of substantial ethene SOZ and acetone products of the MP

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ozonolysis reaction is consistent with the low reactivity of CH_2OO with acetone and the instability of $(CH_3)_2COO$ although some of the latter intermediate does react with formaldehyde to give the **2d** product observed here, based upon the Criegee observation described above.

The strongest band in the spectrum of **2d** at 1069 cm^{-1} exhibits a doublet of triplets in $^{16,18}O_3$ samples similar to the strong 1078-cm^{-1} band[4] for **2a**, which identifies the SOZ species; this band is likewise assigned to the antisymmetric $C-O_e$ stretching mode. The multiplets observed for the 985- and 950-cm^{-1} bands are also consistent with the SOZ stoichiometry. These latter bands, and the 851-cm^{-1} band, are assigned to C–O stretching modes, based on their oxygen-18 shifts. The 835-cm^{-1} band, which exhibited a large oxygen-18 shift to 792 cm^{-1}, is assigned to the O–O stretching mode. The 1230-cm^{-1} band, which exhibited a 3-cm^{-1} oxygen-18 shift, is unique to the SOZ species **2d**; this band is near the antisymmetric C–C stretching mode[19] of acetone in solid argon at 1217 cm^{-1}, which supports this assignment.

The reaction of ozone and methylpropene in solid xenon is particularly interesting owing to the absence of the strongest band assigned to the SOZ (1069 cm^{-1} in argon) and the observation of seven new product bands at 1372, 1229, 1160, 989, 953, 847, and 674 cm^{-1}, the first six of which are near SOZ bands (1375, 1230, 1160, 985, 950, and 851 cm^{-1} in argon). Note that the 989- and 953-cm^{-1} xenon bands are higher than the 985- and 950-cm^{-1} argon bands, which is indicative of different species, since xenon bands usually fall 6–9 cm^{-1} *below* argon matrix counterparts for the same species (see **2a** in ref 4). The above seven bands are assigned to the POZ species **1d**, which is expected to be the first step in the low-temperature reaction. This assignment leads to the conclusion that the SOZ species **2d** *is not* formed from **1d** at 80 K in solid xenon, a conclusion consistent with reduced reactivity of acetone and dimethyldioxymethylene.

Observations from the earlier solid film studies[14] support the above interpretation. After thermal cycling (88–143–88 K) a sample consisting of a film of ozone condensed on top of a film of methylpropene, sharp, strong new bands were produced at 1226, 1155, 980, 950, 790, and 670 cm^{-1} and slightly broader and weaker bands were observed at 1060, 940, and 845 cm^{-1}. A further thermal cycle (88–173–88 K) destroyed the 950- and 670-cm^{-1} bands, replaced the 1226-, 1155-, 980-, and 795-cm^{-1} bands with strong broader bands at slightly lower frequency, markedly increased bands at 1060, 940, and 840 cm^{-1}, and produced new weaker bands at 715 and 500 cm^{-1}.[14] The latter bands, which increased at the expense of the former sharp bands, are in near agreement with argon matrix absorptions of the SOZ species **2d**, and their formation on warming to 173 K supports this assignment. Apparently, a temperature in the 150–170-K range is required for the formation of the SOZ **2d**. The former sharp bands are due to the POZ species **1d**, as originally proposed by Hull et al.[14] The bands at 1372, 1229, 1160, 989, 953, 847, 795, and 674 cm^{-1} produced in solid xenon on warming (50–80–50 K) without the strongest SOZ band are in excellent agreement with the solid film bands at 1226, 1155, 980, 950, 840, 790, and 670 cm^{-1} produced on first warming (88–143–88 K), which reinforces both identifications of the POZ **1d**.

Absorptions at 1779, 1740, and 1718 cm^{-1} in solid xenon which increased on warming are due to acetic acid, formic acid, and acetone, respectively, with the latter most dominant. These expected decomposition products of the POZ verify that the CH_2OO and $(CH_3)_2CO$ intermediates were formed on warming (50–80–50 K), but without reaction to give the SOZ, the CH_2OO intermediate rearranged to HCOOH. The observation of acetic acid indicates rearrangement requiring substantial activation energy, which is available from the exothermicity of the initial reaction (about 50 kcal/mol).[20] The 795-cm^{-1} band that increased on warming in the xenon experiments and the 790-cm^{-1} band produced in the first warming and decreased in the second warming in film experiments are assigned to methylpropene oxide, based on agreement with the strong 796-cm^{-1} gas-phase absorption.[21]

TABLE VI: Comparison of Strong Infrared Absorptions (cm^{-1}) for Primary Ozonides of Several Alkenes

E[a]	R[b]	TB[b]	MP[b]	TME[c]	DIPE[d]	assignments
409	488	470				O-O-O bend
647	640	693	675	721	693	antisym O-O-O str
727	718					ring skeletal bend
846						sym O-O-O str
927	*e*	902	953	852	925	C-O str
983	974	996	989	953	954	C-O str
1214						CH_2 def
			1160	1148		CH_3 bend
			1229	1197		antisym $C-CH_3$ str
	1380	1384	1372	1370		$-CH_3$ sym def

[a] POZ in solid xenon at 50 K, ref 3. [b] POZ in solid xenon, this work. [c] Tetramethylethylene POZ in solid film at 88 K, ref 14. [d] *trans*-diisopropylethylene POZ in liquid CS_2 at 168 K, ref 22. [e] Probably obscured by propene.

Comparison of Primary and Secondary Ozonide Spectra. Table VI compares the strong infrared absorptions for the POZ's of four simple alkenes in solid xenon with the POZ of tetramethylethylene (TME) in a solid reagent film[14] and the POZ of *trans*-diisopropylethylene (DIPE) in CS_2 at 168 K.[22] Since TME does not give an SOZ,[1] the sharp absorptions produced on warming the film are in all likelihood due to the POZ as originally assigned. Further warming in the CS_2 solution spectrum of DIPE ozonolysis products decreased the bands assigned to the POZ and increased SOZ bands. The POZ spectra contain a strong characteristic band in the 640–720-cm^{-1} region, which exhibits a large oxygen-18 shift (in the xenon matrix studies) appropriate for the antisymmetric O–O–O stretching mode. Clearly the SOZ does not have such an absorption. The C–O stretching modes for POZ's fall in the 850–1000-cm^{-1} region, which overlaps the 850–1120-cm^{-1} range of C–O stretching modes for SOZ species. Other modes involving the methyl groups are, of course, common to both ozonides.

A number of theoretical calculations have been done to determine the POZ structure. Semiempirical methods are rather inconclusive with regard to POZ conformation; however, ab initio MO calculations with large augmented basis sets clearly predict a symmetrical O-envelope conformation for the POZ.[17] Interaction between the antisymmetric O–O–O stretching mode and C–O stretching modes should be less in the O-envelope conformation than in other puckered ring structures or a C–C half-chair conformation with the C–C center of mass in the O–O–O plane. Accordingly, the observation of an almost pure antisymmetric O–O–O stretching mode (based on oxy-

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TABLE VII: Comparison of Strong Infrared Bands (cm^{-1}) for Secondary Ozonides of Simple Alkenes

E	P	TB	MP	$^{16}O-^{18}O$[a]	assignments
	506	479	514	-, 7, 6, 10	O-C-CH_3 bending
698		698	630	30, -, -, 12	ring bending
736			719	18, -, -, 27	ring bending
808	829	847	835	44, 45, 31, 42	O-O stretch
927	847	861	851	21, 16, 19, 23	sym C-O_p stretch[b]
952	967	895	950	14, 19, 16, 12	sym C-O_e stretch[b]
1029	1052		985	16, 17, -, 12	anti C-O_p stretch
1078	1122	1117	1069	26, 24, 14, 25	anti C-O_e stretch
1129	1142	1146	1160	4, 5, 11, 5	CH_2 def, C-O stretch
1346	1328	1341		6, 5, 0, -	CH_2 bending, C-O stretch
1387	1378	1368	1383	0, 1, 1, 1	CH_2 bending
	1396	1392	1375	-, 1, 1, 0	sym -CH_3 deformation
	1450	1448	1460	-, 2, 0, 0	anti -CH_3 deformation
2895	2896	2915	2896	1, 0, 1, 1	anti C-H_2 stretch

[a] Isotopic shifts, $\nu O^{16}-\nu O^{18}$, given for each SOZ, respectively. [b] O_p refers to the peroxide oxygens and O_e refers to the ether oxygen in the SOZ molecule.

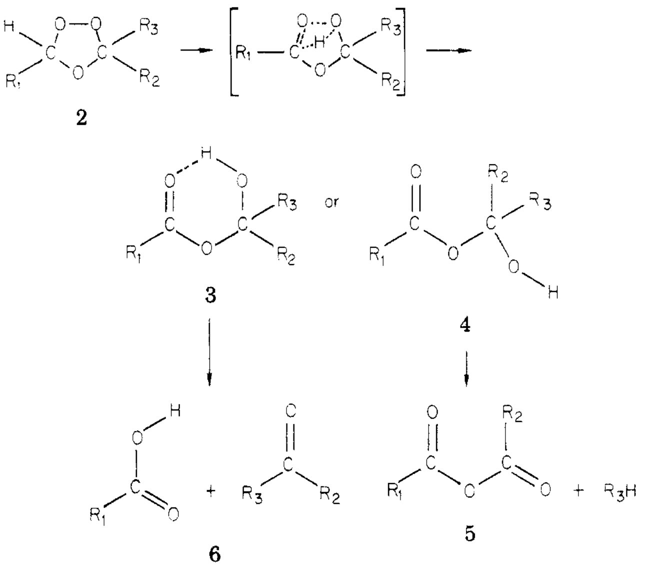
gen-18 displacement) for the POZ provides some experimental evidence for the O-envelope conformation.

The SOZ absorptions considered here and their oxygen-16–18 shifts are compared in Table VII with recent ethene SOZ observations from this laboratory.[4] Characterization of modes for the latter species was based on six isotopic molecules, which provides a model for modes of the present SOZ's where only oxygen isotopic shifts are available. Table VII shows a striking similarity in the spectra of the ethene and propene SOZ's, the major difference coming in modes involving the $-CH_3$ group and a minor difference in slightly increased ring bond stretching modes for the methyl-substituted compound. The mixing of ring bond stretching modes changes in the TB compound as demonstrated by different oxygen-16–18 shifts in the 847-, 1117-, and 1146-cm^{-1} bands as compared to the modes given for the other SOZ's. The ring bond stretching modes of the MP species are similr to the E compound in position and isotopic shift; the ring bending modes are, however, affected substantially by the dimethyl substituents as expected.

A final comment on alkene reactivity is in order. The present argon matrix reaction experiments clearly showed that *trans*-2-butene is substantially more reactive with ozone than propene. Previous ozone–ethene studies[3] found that a higher 70–80 K was needed for reaction. This increase in alkene reactivity with methyl substitution parallels gas-phase reaction rate constants.[23]

Secondary Ozonide Photolysis. Decomposition of SOZ's is generally thought to proceed by cleavage of the weakest ring bond, the O–O linkage. However, kinetic studies[24] of thermal decomposition of simple SOZ's and matrix photolysis[4] products of ethene SOZ provide evidence for a concerted intramolecular H-atom transfer reaction to give both cyclic (**3**) and open (**4**) structural isomers of hydroxymethylformate (HMF), which can decompose to anhydrides (**5**) or the usual aldehyde and acid products (**6**) as depicted in Scheme II. The latter products can be trapped in the matrix cage to give a unique cyclic dimer in the case of photolysis, or they can be isolated as monomers in the case of SOZ thermal decomposition before entrapment by the matrix. The matrix photolysis of **2b**, **2c**, and **2d** SOZ's gives products that are consistent with the mechanism outlined in Scheme II, as will be described next.

Scheme II



The appropriate acid and aldehyde (or ketone) decomposition products **6** were observed for each SOZ studied here. In the case of **2b**, **3** with R_2 or R_3 = CH_3 is twice as probable as R_1 = CH_3, and the decomposition products **6** FA and A are favored over F and AA, as observed in the spectrum. Butene SOZ (**2c**) produces only A and AA, and **2d** gives primarily K and FA, as found in these experiments. Of more significance, the major anhydride product of **2b** photolysis, formic acetic anhydride (FAAN), was identified[16] by strong absorptions at 1803, 1786, and 1375 cm^{-1}; a smaller yield of formic anhydride (FAN) was identified[25] by absorptions at 1812, 1761, 1091, and 998 cm^{-1} along with methane at 1305 cm^{-1}. Although it might appear that **3** and **4** can form more readily when R_1 = H and R_2 or R_3 = CH_3, the major photolysis product (FAAN) can be formed with CH_3 in any substitutent position, but the minor FAN product requires R_2 or R_3 = CH_3. the major anhydride product of **2c** photolysis is FAAN (along with the additional CH_4 product), and acetic anhydride (AAN), identified by the weaker 1846-cm^{-1} band,[16] is a minor product. This shows that CH_4 elimination is favored from **4c** (R_1 = R_2 or R_3 = CH_3), whereas H_2 elimination was favored from **4b** (R_1, R_2, or R_3 = CH_3). The only anhydride photolysis product in **2d** (R_2 = R_3 = CH_3) experiments was FAAN, and the CH_4 product was also observed. The anhydride products **5** are believed to arise from rearrangement of **4** through a four-center transition state[4,26] depicted below for the **4c** decomposition. It is expected that CH_4 elimination from **4′** would be favored over H_2 elimination owing to the weaker C–C bond compared to the C–H bond. It is surprising, therefore, that FAAN is the major photolysis product of **4b**, which requires H_2 elimination. Although CH_4 elimination from **4b** (R_2 or R_3 = CH_3) should be favored over H_2 elimination, only H_2 elimination is possible from **4b** (R_1 = CH_3). In

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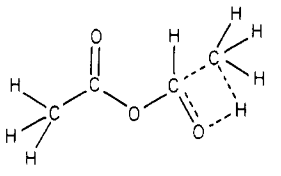

4′

addition to the statistical factor, steric effects may govern the formation of the transition state 4′ proposed for anhydride formation. In this regard, it is perhaps noteworthy that the anhydride yield decreased markedly in matrix photolysis of the series **2a** > **2b** > **2c**.

The definitive observation of FAAN and CH_4 as major photolysis products of the SOZ's studied here, along with smaller yields of FAN and AAN in propene and 2-butene experiments, respectively, strongly implicates the hydroxy esters **3** and **4** as intermediate steps in the photochemical reaction sequence (Scheme II). Other photolysis product absorptions observed in **2b** and **2c** experiments are consistent with **3** and **4** and will be discussed below. It is likely that the hydroxy ester intermediates in **2d** photolysis are not trapped in the matrix but decompose directly to the observed **5** and **6** products; no evidence for **3** and **4** was found in **2d** photolysis experiments. Thermal decomposition of **2d** gave the **6** products (primarily formic acid and acetone) and their dimers, and absorptions at 1761, 1245, and 1049 cm^{-1}, which are appropriate for methyl acetate.[27] This simple ester is probably formed by rearrangement of the less stable $(CH_3)_2COO$ intermediate, which suggests that an additional direct mode of **2d** decomposition to CH_2O and the $(CH_3)_2COO$ biradical contributes to the overall reaction.

The **2b** photodecomposition is complicated due to asymmetry in the propene reagent and the two distinctly different positions for a methyl substituent in **3** and **4**. Substitution at R_2 or R_3 to give a β-hydroxyethyl formate (HEF) is not expected to significantly change the strong carbonyl and acyl C–O vibrations from HMF values.[4] Strong bands in the carbonyl region at 1785 and 1744 cm^{-1} are appropriate for the trans and cis isomers **4** and **3**, respectively, as are new bands at 1188 and 1200 cm^{-1} in the acyl C–O region. New bands in the 1000–1100-cm^{-1} region are reasonable for the other C–O vibrations in **3** and **4**, but since they cannot be identified with a specific one of the possible hydroxy esters (HE), the general HE identification will be used in Table II. New absorptions at 945 and 934 cm^{-1}, appropritate for methyl group rocking modes, and 1281 cm^{-1}, possibly a C–O–H bending mode, are probably due to HE. The 3474-cm^{-1} band and its 3465-cm^{-1} oxygen-18 counterpart are appropriate for a hydrogen-bonded O–H vibration in **3**; similar bands were observed at 3471 and 3463 cm^{-1} for *cis*-HMF.[4] Substitution at R_1 to give hydroxymethyl acetates (HMA) isomers **3** and **4** is expected to blue shift both carbonyl and acyl C–O vibrations, based upon comparisons between methyl formate and acetate,[26] and formic[4] and acetic[8] acids. Accordingly, the 1761- and 1252-cm^{-1} bands are assigned to *cis*-HMA (**3**), but no counterparts were observed for the *trans*-HMA species (**4**). It is conceivable that **4b** is not trapped in the matrix owing to rapid reaction to give FAAN and H_2. Finally, the generally broader bands denoted D in Table III and the isolated FA, AA, A, and F decomposition products **6** were also observed in SOZ thermal decomposition experiments, which supports the identification of D as acid–aldehyde hydrogen-bonded dimers trapped in the same matrix cage.

Photolysis of **2c** can give only one isomer of **3** and **4** owing to methyl substitution at each carbon. The major product bands at 1772 and 1261 cm^{-1} follow the pattern established above and are assigned to *c*is-hydroxyethyl acetate (HEA); again no evidence was found for the trans isomer, suggesting its direct decomposition to anhydride and methane products **5**. The remaining photolysis product bands at 3395, 1055, 1016, and 940 cm^{-1} are probably due to HEA as well. Broad bands at 1764 and 1728 cm^{-1}, observed with thermal decomposition, are probably due to carbonyl vibrations in AA and A in a hydrogen-bonded dimer.

The effect of methyl substitution in the SOZ photolysis products can be summarized by reviewing the spectra in Figure 3. Major photolysis products of the propene and 2-butene SOZ's include FAAN and CH_4, which were not produced from the ethene SOZ. In addition, the acyl C–O vibrations are shifted to the 1250-cm^{-1} region in acetate and methyl rocking modes appear in the 900-cm^{-1} region, which are unique to the propene and 2-butene SOZ photolysis products.

Conclusions

The ozonolysis of propene, *trans*-2-butene, and methylpropene has been studied with $^{16}O_3$, $^{16,18}O_3$, and $^{18}O_3$ in two reaction media, solid xenon at 80–110 K and CF_3Cl solution at 130–150 K. The major solution reaction product was identified from matrix infrared spectra as the SOZ based on isotopic data and gas-phase spectra. Major reaction products for propene and *trans*-2-butene in solid xenon were SOZ, POZ, oxide, and aldehyde species; however, methylpropene gave POZ, oxide, and acetone products. The POZ's are characterized by an intense antisymmetric O–O–O stretching mode in the 640–700-cm^{-1} region, which exhibits a large oxygen isotopic shift. Photolysis of propene and 2-butene SOZ's gave formic acetic anhydride as a major product and additional absorptions consistent with hydroxy ester products. These observations support earlier evidence for an intramolecular H-atom transfer mechanism for SOZ decomposition.

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