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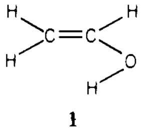
Reactions of Atomic Oxygen with Ethene in Solid Argon. The Infrared Spectrum of Vinyl Alcohol

Michael Hawkins* and Lester Andrews

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901. Received September 22, 1982

Abstract: Matrices formed by the cocondensation of ethene and ozone in argon at 15–20 K were irradiated with the emission from a Hg arc. Primary photoproducts include ethylene oxide, acetaldehyde, and ketene. New absorptions at 413.0, 818.5, 1084.0, 1631.0, 3241.5, and 3625.0 cm^{-1} are assigned, on the basis of ^{18}O, ^{13}C, and deuterium enrichment studies, to fundamental modes of vinyl alcohol, $CH_2{=}CHOH$. The high frequency for the OH torsion (413.0 cm^{-1}) suggests that the C–O bond of vinyl alcohol has some π character while Fermi resonance is observed between the overtone of the out-of-plane CH_2 wag and the C=C stretch. All products are considered to arise from reaction of O atoms with ethene, and there is some evidence for the participation of excited O(^{1}D) atoms. Excited vinyl alcohol or the biradical $\dot{C}H_2CH_2\dot{O}$ are proposed as precursors to ketene.

In previous studies of the reaction between oxygen atoms and solid ethene[1] and ethene in liquid-nitrogen[2] or liquid-argon[3] solutions, acetaldehyde and ethylene oxide were identified as the sole addition products. Both O(^{1}D) and O(^{3}P) atoms undergo addition reactions with ethene,[3,4] and both are observed to abstract hydrogen atoms from alkanes,[5] the higher energy O(^{1}D) species doing so with less discrimination. In addition O(^{1}D) but not O(^{3}P) atoms yield H-atom abstraction products with ethene in liquid argon,[4] and oxygen atom insertion into the C–H bonds of alkanes is characteristic of O(^{1}D) atoms. A third possible "addition" product of the O atom–ethene reaction is vinyl alcohol, $CH_2{=}CHOH$. This molecule has been identified in solution by ^{1}H and ^{13}C NMR[6-8] and ^{1}H and ^{13}C CIDNP enhanced NMR,[9,10] but little is known of its infrared spectrum.[8] The microwave spectrum of the gaseous species[11] provides experimental evidence for a preferred planar syn structure, **1**, in agreement with ab initio molecular orbital calculations.[12,13] Although both theoretical[14] and experimental[15] results show vinyl alcohol to be less thermodynamically stable than acetaldehyde, the barrier to isomerization via intramolecular rearrangement is predicted to be high (85 kcal/mol),[14] and its half-life in a Pyrex container at room temperature has been measured as 30 min.[11] Thus, once formed, vinyl alcohol should be stable in a matrix environment.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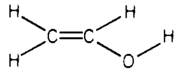
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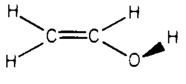
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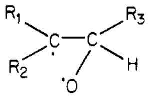
There remains considerable disagreement concerning the mechanistic details of the addition of O(^{3}P) atoms to ethene and alkenes in general.[16] Cvetanovic favors the intermediacy of a triplet biradical **4** while Klein and Scheer propose that a H-bonded complex **5** controls the stereochemistry and rearrangement processes of the addition reaction. Unfortunately there has been no direct observation of the biradical **4** in these systems, and both mechanisms are successful in explaining many of the details of product distribution and stereochemical behavior.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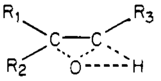
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Here follows a study of the ethene–oxygen atom reaction in solid argon at 15 K that traps sufficient vinyl alcohol for observation of its infrared spectrum.

Experimental Section

Apparatus. The cryogenic refrigeration system and vacuum vessel have been described elsewhere.[17] All spectra were recorded on a Beckman IR-12 spectrophotometer over the range 200–4000 cm^{-1}. Regions of interest were examined by using expanded wavenumber scales, allowing measurement of band positions to an accuracy of ±1 cm^{-1}. The

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[5] See, for example: Yamazaki, H.; Cvetanovic, R. J. *J. Chem. Phys.* **1964**, *41*, 3703 and Jewell, S. P.; Holbrook, K. A.; Oldershaw, G. A. *Int. J. Chem. Kinet.* **1981**, *13*, 69, for details of O(^{1}D) and O(^{3}P) + C_3H_8, respectively.

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[17] Andrews, L. *J. Chem. Phys.* **1968**, *48*, 972; **1971**, *54*, 4935.

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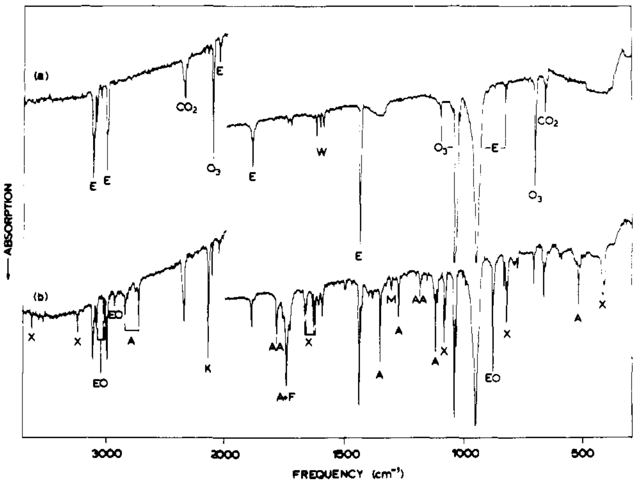

Figure 1. The infrared spectrum of an argon matrix containing ethene ($Ar/C_2H_4 = 400$) and ozone ($Ar/O_3 = 200$) recorded after (a) deposition at 17 K and (b) a total of 95 mins full Hg arc irradiation: A = acetaldehyde, AA = acetic acid, E = ethene; EO = ethylene oxide, F = formaldehyde, K = ketene, M = methane, W = water, and X = vinyl alcohol.

temperature of the CsI cold window in the range 15–25 K was determined by a H_2 vapor pressure gauge attached to the second stage of the refrigerator cold tip and was varied by adjusting the voltage applied to three heater buttons (Minco Products, Inc., Minneapolis, MN) mounted on the copper window support. Samples were photolyzed for periods up to 680 min by using the 220–1000-nm output of a BH-6 high-pressure mercury-arc lamp (1000 W, Illumination Industries Inc.). A 10-cm water filter reduced the amount of infrared radiation incident upon the matrix during photolysis while replacement with aqueous $NiSO_4$, $CoSO_4$, or $NiSO_4/CoSO_4$ solutions afforded selective transmission of near-UV light ($\lambda < 340$ nm).

Chemicals. Ozone was generated by a static electric discharge (Tesla coil) of oxygen in a Pyrex tube and condensed with liquid N_2. Residual O_2 was removed by pumping at 77 K with an oil diffusion pump. Normal isotopic O_2 was obtained from Burdett, U.S.P. grade. Two samples enriched in ^{18}O to 50.35% and 95.57%, respectively, were supplied by Yeda R & D Co., Ltd. (Israel). Ethene supplied by Matheson (C.P. Grade) and the isotopically enriched ethenes C_2D_4 (99% D), CH_2CD_2 (98% D_2), and $^{13}C_2H_4$ (90% ^{13}C) obtained from Merck Sharp & Dohme (Montreal) were degassed by freeze-thawing and pumping at 77 K.

Procedure. Ozone and ethylene were diluted with argon and codeposited through two separate spray-on lines. The matrix ratios for each reagent mixture were varied between 100:1 and 300:1 and both gases deposited at an average rate of 1.5 mmol/h for 16 h. Matrices deposited at 20 K exhibited better infrared and ultraviolet transmission properties than did those deposited at 15 K, the higher temperature apparently not impairing the degree of isolation of either precursor or product.

Results

$C_2H_4 + O_3$. Samples of ethene ($Ar/C_2H_4 = 200$) and ozone ($Ar/O_3 = 100$) were codeposited at 17 K for 15 h. The infrared spectrum recorded immediately after deposition is shown in Figure 1a. In addition to the precursors ethene (E) and O_3, small quantities of matrix-isolated water and carbon dioxide were detected, as evidenced by bands at 1592, 1610, and 1624.5 cm^{-1} and 663.0 and 2346.0 cm^{-1}, respectively. Irradiation of the matrix for a total of 95 min with the full output of the Hg arc (220–1000 nm) destroyed more than 70% of the O_3 as determined from the change in intensity of the $\nu_2(O_3)$ absorption at 704 cm^{-1} (Figure 1b). The photolysis of O_3 was accompanied by the appearance of a large number of bands throughout the entire spectral range of 300–3700 cm^{-1}. The positions of these absorptions are listed in Table I together with their intensities.

The product band labeled K at 2150.0 cm^{-1} in Figure 1b is near an intense doublet (2149.0 and 2143.5 cm^{-1}) characteristic of irradiated samples of acetylene codeposited with ozone.[18] In subsequent experiments, deposition of ethylene oxide (EO) or acetaldehyde (A) in argon revealed that many of the new features in Figure 1b could be attributed to these two molecules. Furthermore 60-min irradiation of a matrix formed by codeposition of ozone and acetaldehyde in argon ($Ar/O_3 = 200$, $Ar/CH_3CHO = 635$) with the full output of the Hg arc gave rise to new product bands. Acetaldehyde absorptions decreased, and new bands appeared at 1180.5, 1183.0, 1306.5, 1381.5, 1386.0, 1781.5, 1784.0, and ca. 3564 cm^{-1} close to those observed after photolysis of C_2H_4/O_3 samples at 1183.5, 1305.5, 1381.0, 1386.5, 1782.5, 1786.5, and 3567.0 cm^{-1} (Table I) and marked AA and M in Figure 1b.

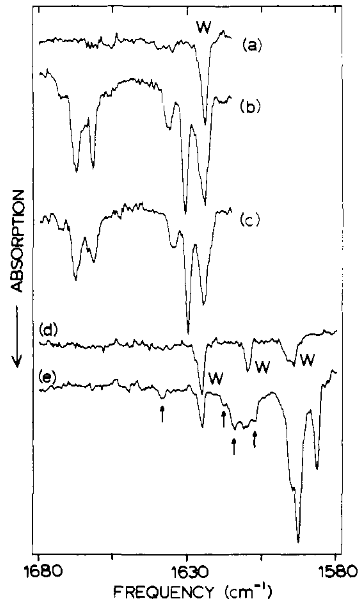

Figure 2. The effect of full Hg arc irradiation on the infrared spectrum of an argon matrix containing ethene and ozone between 1580 and 1680 cm^{-1}: (a) before and (b) after 95-min irradiation of an $Ar/C_2H_4 = 400$, $Ar/O_3 = 200$ sample; (c) $Ar/C_2H_4 = 500$, $Ar/^{18}O_3$ (96% ^{18}O) = 300, $h\nu$, 60 min; (d) before and (e) after 190-min irradiation of an $Ar/^{13}C_2H_4$ (90% ^{13}C) = 400, $Ar/O_3 = 200$ sample (W = water; arrows denote weak absorptions due to vinyl-$^{13}C_1$ alcohol).

UV irradiation of matrices containing ozone and either ethylene oxide or acetaldehyde gave rise to no bands which could be compared to those labeled X in Figure 1b which are unique to irradiated C_2H_4/O_3 samples (Table I). In all experiments these features grew concurrently and with constant relative intensities.

The absorptions at 3625.0 and 3241.5 cm^{-1} were accompanied by three bands at 1667.5, 1662.0, and 1631.0 cm^{-1} (Figure 1b). The spectra of parts a and b in Figure 2 together show in more detail that the water band at 1624.5 cm^{-1}, present before photolysis, also increased on irradiation. In addition this sample gave rise to a complex set of bands between 790 and 840 cm^{-1}. Before photolysis two absorptions were observed at 831.5 and 825.0 cm^{-1} (E, Figure 3a). After photolysis (Figure 3b) five new bands appeared at 814.0, 817.0, 818.5, 821.5, and 823.5 cm^{-1}, two of which coincide with bands exhibited by a sample of ethylene oxide in argon at 817.0 and 822.0 cm^{-1} (EO, Figure 3c). In two separate experiments the infrared spectrum of a matrix containing ethene and ozone in the region 800–1400 cm^{-1} was recorded before and after 5-min irradiation with the 220–340-nm Hg arc emission transmitted by a saturated $NiSO_4/CoSO_4$ solution filter. In both cases bands denoted X at 814.0, 818.5, 823.5, 1079.0, and 1084.0 cm^{-1} exhibited a much greater intensity relative to the acetaldehyde and ethylene oxide bands at 1121.0 and 879.0 cm^{-1}, respectively, than is depicted in Figure 1b. Subsequent photolysis with radiation transmitted by a saturated solution of $CoSO_4$ resulted in a growth of all bands, the absorptions at 1121.0 and 879.0 cm^{-1} now increasing at a much greater rate than before. Finally after a total of 135 min of both filtered and unfiltered photolysis and the O_3 content all but exhausted one sample was irradiated for 680 min with the full Hg arc. While absorptions associated with acetaldehyde and ethylene oxide remained unchanged, those at 814.0, 818.5, 823.5, 1079.0, and 1084.0 cm^{-1} and a triplet also denoted

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(18) Hawkins, M.; Kohlmiller, C. K.; Andrews, L., unpublished results.

Table I. Absorptions (cm^{-1}) Appearing on Photolysis of Argon Matrices Containing Ethene and Ozone

12-16	12-18^{a}	13-16^{b}	d_4^{c}	d_4,^{18}O	intensity^{d}	identificatn
407.0	406.0	407.5	307.0	307.0	0.10	X
413.0	411.5	413.0	310.0	312.5	0.14	X
417.0	416.0	417.5	314.0		0.11	X
			436.0	436.0		K
519.0	508.5	511.0	444.0	436.0	0.15	A
587.5	588.5				W	K
596.0	593.5				W	K
663.0	653.0	644.5	663.0			CO_2
774.5	772.0	770.0			W	A
814.0	814.0	805.5			0.09	X
817.0	804.0	795.0	807.0	793.0		EO
818.5	818.5	810.0	651.0^{o}	651.0^{o}	0.22	X
821.5	808.5	799.5	810.5	797.0	0.09	EO
823.5	823.5	814.5			W	X^{s}
875.5	850.0					EO
879.0	854.5	864.5^{i}	755.0	745.5	0.45	EO
881.5	855.5	866.5	757.0	747.0		EO
1079.0^{f}	1067.0	1070.5	922.5	904.0	0.16	X
1084.0	1071.0	1075.5	925.5	908.0	0.25	X
1112.0	1111.0	1089.0	939.5	938.0	0.09	A
1121.0	1120.0	1097.5^{j}	943.5	941.0	0.29	A
1124.5	1123.5				0.08	A
1126.5		1116.5	966.5	949.3		EO
			898.5	980.5		EO
1154.5	1146^{g}	1149.5	903		W	EO
1183.5	1170.5	1170.0			0.05	AA
			1298.5	1287.5		AA
			1306.5	1295.0		AA
1274.0	1267.5	1245.5^{k}	1015.0		0.14	EO
1305.5	1305.5	1298.0	995.3		W	M
	1321.5	1317.0				
1350.0	1350.0	1339.5			0.13	A
1353.5	1353.5	1343.0^{l}			0.30	A
1381.0	1378.0	1368.0			W	AA, K
1386.5	1382.0				W	AA
1399.5	1400.5	1399.0	1025.5	1024.5	W	A
1430	1428.0	1426.5	1155.0	1149.0	0.08	A
1435	1433.0	*m*	1160.0	1154.5	0.17	A
1470	1470	1467.0			W	EO
			1313.0	1306.0		EO
1499	1488.5	1499.0			W	F
1624.5	1624.0	1586.0	1583.5	1580.5	0.13	H_2O, X^{p}
1631.0	1629.5	1592.0^{q}	1589.5	1585.5	0.14	X
1636.5	1635.5				W	X^{s}
1662.0	1661.5				0.10	X
1667.5	1667.5				0.10	X
			1691.5	1677.5		A
			1700.0	1688.5		A
1731.0	1703.0	1692.0	1726.0	1695.5	0.15	A
1745.0	1714.5	1705.0	1735.5	1704.5	0.48	A, F
	1724.0	1718.0				
1782.5	1750.5		1768.0	1735.5	0.13	AA
		1741.0 (br)				AA
1786.5	1754.0		1770.0	1738.0	0.15	AA
2150.0^{h}	2123.0	2086.5	*r*	*r*	0.40	K
2346.0	2310.0	2280.0	2346.0	2310.0		CO_2
2730.5	2723.5	2724.5	2061.5	2057.0	0.16	A
2821.5	2820.0	2815.0			W	A
2841.5	2835.0	2833.5			0.09	A
2923.5	2922.5	2917.0			W	EO
2931.5	2930.0	2921.0			0.05	EO
2968.5	2967.0				W	EO
3011.0	3010.0	3001.0	2181.5	2179.5	0.10	EO
3020.5	3019.0	3012.0^{n}	2213.0	2210.5	0.07	EO
3078.0	3077.0	3067.0	2326.0		0.07	EO
3241.5	3240.5	3229.0	2411.0	ca. 2412	0.11	X
3528.5	3518.5	3530.5	2649.0	2632.0	W	
3567.0	3560.0	3566.5	2632.0	2615.0	W	AA
3625.0	3615.5	3624.5	2677.0	2661.5	0.08	X

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[a] Ozone synthesized from 95.6% ^{18}O-enriched O_2. [b] 90% ^{13}C-enriched ethene containing 81% $^{13}C_2H_4$ and 18% $^{13}C_1$-C_2H_4. [c] 99% D-enriched ethene. [d] The intensities of bands due to X are taken from expanded scale spectra of the normal isotopic species. Others are taken from the survey spectrum of Figure 1b and are generally lower than expanded-scale values by $\leqslant$10% between 300 and 2000 cm^{-1} and $\leqslant$25% between 2500 and 4000 cm^{-1}. Intensities less than 0.05 are labeled W. br = broad. [e] Labels identify the following molecules: A = acetaldehyde, AA = acetic acid, EO = ethylene oxide, F = formaldehyde, K = ketene, M = methane, and X = vinyl alcohol. [f] A weak third band at 1075.0 cm^{-1} is also observed in C_2H_4/$^{16}O_3$ experiments. See also footnote s. [g] Average of a doublet at 1143.0 and 1149.0 cm^{-1}. [h] After photolysis of C_2H_4/$^{16,18}O_3$ (50% ^{18}O). [i] A third band at 871.5 cm^{-1} is due to ethylene-$^{13}C_1$ oxide. [j] Two bands at 1107.5 and 1111.5 cm^{-1} are due to acetaldehyde-$^{13}C_1$. [k] A second band at 1260.5 cm^{-1} is due to ethylene-$^{13}C_1$ oxide. [l] A second doublet at 1354.0 and 1351.0 cm^{-1} is due to acetaldehyde-$^{13}C_1$. [m] Obscured by ethene-$^{13}C_2$. [n] A second band of equal intensity is observed at 3006.5 cm^{-1}. [o] The more intense component of a doublet with a shoulder observed at 653.5 (^{16}O) or 653.0 (^{18}O) cm^{-1}. [p] Only absorptions at 1624.5 and 1624.0 cm^{-1} contain a contribution from H_2O. [q] Four weaker bands at 1606.5, 1613.0, 1617.0, and 1639.0 cm^{-1} are also observed, attributed to $^{13}C_1$-X. [r] Three doublets of absorptions observed for CD_2CO at 2112.5, 2119.0, 2151.5, 2156.0, 2261.0, and 2266.0 cm^{-1} with corresponding bands for $CD_2C^{18}O$ at 2090.0, 2094.0, 2128.1, 2259.0, and 2262.0 cm^{-1}. [s] Tentatively assigned to a third matrix site of X.

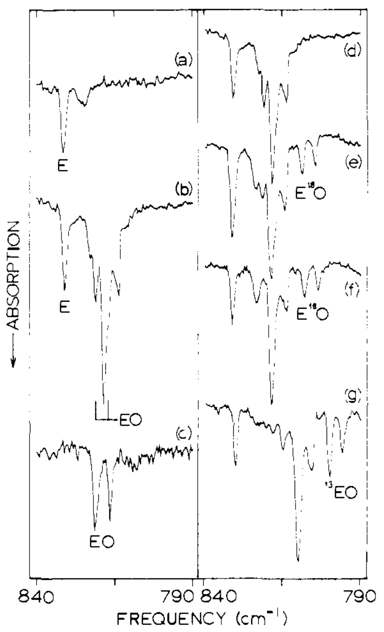

Figure 3. The infrared spectrum of the region 790–840 cm^{-1} after full Hg arc irradiation of an argon matrix containing ethene and ozone: (a) before and (b) after 95-min irradiation of an Ar/C_2H_4 = 400, Ar/O_3 = 200 sample; (d) Ar/C_2H_4 = 400, Ar/O_3 = 200, *hν*, 95 min; (e) Ar/C_2H_4 = 500, Ar/$^{16,18}O_3$ (50% ^{18}O) = 340, *hν*, 60 min; (f) Ar/C_2H_4 = 500, Ar/$^{18}O_3$ (96% ^{18}O) = 300, *hν*, 60 min; (g) Ar/$^{13}C_2H_4$ (90% ^{13}C) = 400, Ar/O_3 = 200, *hν*, 190 min. Spectrum c is that of an ethylene oxide/O_3 sample before irradiation (E = ethene, EO = ethylene oxide).

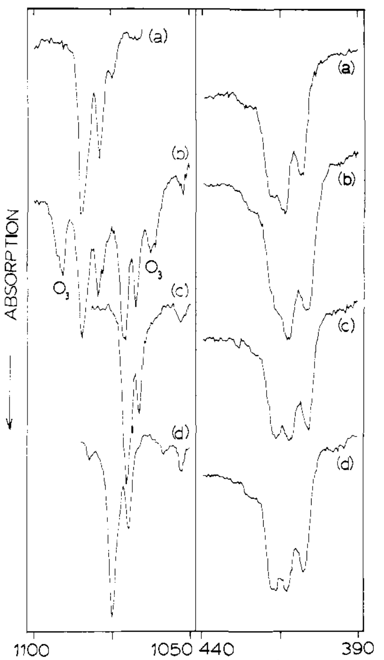

Figure 4. The infrared spectra in the 390–440-cm^{-1} and 1050–1100-cm^{-1} regions after full Hg arc irradiation of an argon matrix containing ethene and ozone: (a) Ar/C_2H_4 = 400, Ar/O_3 = 200, *hν*, 95 min; (b) Ar/C_2H_4 = 500, Ar/$^{16,18}O_3$ (50% ^{18}O) = 340, *hν*, 60 min; (c) Ar/C_2H_4 = 400, Ar/$^{18}O_3$ = 200, *hν*, 60 min, (d) Ar/$^{13}C_2H_4$ (90% ^{13}C) = 400, Ar/O_3 = 200, *hν*, 190 min (O_3 = ozone).

X (Figure 1b) at 407.0, 413.0, and 417.0 cm^{-1} decreased in intensity by ca. 15%.

^{18}O- and ^{13}C-Enriched Reagents. Photolysis of argon matrices containing C_2H_4 + $^{18}O_3$ (95.57% ^{18}O), C_2H_4 + $^{16,18}O_3$ (50.35% ^{18}O), or $^{13}C_2H_4$ + O_3 (90% ^{13}C) resulted in the appearance of bands due to isotopically enriched acetaldehyde and ethylene oxide, which are listed in Table I. Absorptions complementary to those labeled X, AA, M, and K in Figure 1b were also observed. Of the bands denoted X, those at 1079.0 1084.0, and 3625.0 cm^{-1} show 12.0-, 13.0-, and 9.5-cm^{-1} shifts respectively with $^{18}O_3$. With scrambled $^{16,18}O_3$ the 1079.0- and 1084.0-cm^{-1} bands gave way to a doublet of doublets with corresponding components of equal intensity and at the same frequencies as in the pure $^{16}O_3$ and $^{18}O_3$ samples (Figure 4a–c). Both bands at 1079.0 and 1084.0 cm^{-1} also exhibited a ^{13}C shift of 8.5 cm^{-1} with $^{13}C_2H_4$ (Figure 4d) while that at 3625.0 cm^{-1} showed none, over and above the limits of experimental error.

Several of the related bands X exhibited very small ^{18}O shifts. Thus the absorptions at 407.0, 413.0, and 417.0 cm^{-1} were located at 406.0, 411.5, and 416.0 cm^{-1} on photolysis of C_2H_4/$^{18}O_3$ samples and in matrices containing scrambled $^{16,18}O_3$ the fwhm of the triplet increased from 14.0 to 16.0 cm^{-1} (Figure 4a–c). The positions of these bands were unchanged when $^{13}C_2H_4$ was employed (Figure 4d). Similarly a shift of 1.5 cm^{-1} was observed for the band at 1631.0 cm^{-1} on ^{18}O substitution while the water absorption at 1624.0 cm^{-1} again increased in intensity on UV irradiation (Figure 2c). The ^{13}C counterpart of the 1631.0-cm^{-1} absorption was observed at 1592.0 cm^{-1} (Figure 2d,e), a feature which was more intense than the 1631.0-cm^{-1} band and which exhibited a weaker shoulder at 1586.0 cm^{-1}. The bands at 1667.5 and 1662.0 cm^{-1}, which showed no ^{18}O shift, had now disappeared (Figure 2b,e), and weak absorptions at 1606.5, 1614.5, 1617.0, and 1639.0 cm^{-1} were observed. Finally, the absorption at 3241.5 cm^{-1} in the natural isotope experiments exhibited a 1.0-cm^{-1} ^{18}O and 12.5-cm^{-1} ^{13}C shift while there was no detectable frequency shift for the bands at 814.0, 818.5, and 823.5 cm^{-1} on ^{18}O enrichment and shifts of 8.5, 8.5, and 9.0 cm^{-1}, respectively, on ^{13}C enrichment.

The band at 2150.0 cm^{-1} and labeled K in Figure 1b was observed to be shifted to 2123.0 cm^{-1} on ^{18}O enrichment, and ^{13}C enrichment resulted in a decrease of 63.5 cm^{-1} to 2086.5 cm^{-1}. Ultraviolet irradiation of a sample of acetylene and scrambled $^{16,18}O_3$ (50% ^{18}O) gave rise to a doublet of absorptions at 2150.0 and 2123.0 cm^{-1} with shoulders at 2142.5 and 2115.5 cm^{-1}, respectively.[18] The small ^{18}O shift confirms that the bands K are due to ketene and not to perturbed carbon monoxide.

C_2H_4 + O_3: d_2, d_4, and ^{18}O Isotopomers. Ultraviolet irradiation of deuterium enriched samples (C_2D_4 = 99% D or CH_2CD_2 = 98% CD_2) of ethene and ozone gave rise to deuterated acetaldehyde,[19] ethylene oxide,[20] and ketene.[21] The acetaldehyde-d_0 absorption at 519.0 cm^{-1} (A, Figure 1b) gave way to a band at 444.0 cm^{-1} appropriate to acetaldehyde-d_4. Irradiation of a CH_2CD_2/O_3 sample for 185 min however gave rise to two absorptions at 457.5 and 496.0 cm^{-1}, their intensities being in the ratio 2.6:1. The intensities of these bands did not decrease after further irradiation for 585 min. In the same experiment absorptions characteristic of *gem*-ethylene-d_2 oxide but not of *cis*- or *trans*-ethylene-d_2 oxide were observed.[20b]

All bands denoted X in Figure 1b suffered large shifts in frequency on deuterium enrichment. Irradiation of C_2D_4/O_3 samples gave rise to absorptions at 651.0, 922.5, 925.5, 2411.0, and 2677.0 cm^{-1}; these bear a frequency ratio with the corresponding bands of the protonated samples of 1.26 (818.5 cm^{-1}), 1.17 (1079.0 cm^{-1}), 1.17 (1084.0 cm^{-1}), 1.34 (3241.5 cm^{-1}), and 1.35 (3625.0 cm^{-1}), respectively. While the bands at 651.0 and 2411.0 cm^{-1} show no shift in position on photolysis of C_2D_4/$^{18}O_3$ samples, those at 922.5, 925.5, and 2677.0 cm^{-1} exhibit ^{18}O shifts of 18.5, 17.5, and 15.5 cm^{-1}, respectively (Table I). Furthermore, samples of CH_2CD_2/O_3 gave rise to bands at 971.0 and 978.5 cm^{-1} that decreased in intensity by ca. 26% on prolonged full arc photolysis.

The triplet of absorptions at 407.0, 413.0, and 417.0 cm^{-1} observed after photolysis of C_2H_4/O_3 samples gave way to a similar triplet located at 307.0, 310.0, and 314.0 cm^{-1} in experiments using

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[20] (a) Lord, R. C.; Nolin, B. *J. Chem. Phys.* **1956**, *24*, 656. (b) Cant. N. W.; Armstead, W. J. *Spectrochim. Acta, Part A* **1979**, *31A*, 839. (c) Nakanaga, T. *J. Chem. Phys.* **1980**, *73*, 5451.

[21] Moore, W. B.; Pimentel, G. C. *J. Chem. Phys.* **1963**, *38*, 2816.

Table II. The Observed Vibrational Frequencies (cm^{-1}) and Assignments for Vinyl Alcohol Isolated in Argon Matrices at 15-20 K

frequency							
d_0	^{18}O	$^{13}C_1$	$^{13}C_2$	d_2	d_4	$d_4,^{18}O$	assignt
407.0	406.0		407.5	392.5, 318.0	307.0	307.0	
413.0	411.5		413.0	398.0, 322.0	310.0	312.5	τ(OH)
417.0	416.0		417.5	400.5, 326.5	314.0		
814.0	814.0		805.5				
818.5	818.5		810.0		651.0	651.0	$\gamma(CH_2)$
823.5	823.5		814.5				
1079.0	1067.0		1070.5	972.0	922.5	904.0	ν(CO), δ(COH)
1084.0	1071.0	1083.0	1075.5	978.5	925.5	908.0	
1624.5	1624.0	1614.5	1586.0		1583.5	1580.5	ν(CC)
1631.0	1629.5	1617.0, 1606.5	1592.0	1630.0, 1611.0	1589.5	1585.5	
1662.0	1661.5	1639.0		1657.5			$2\gamma(CH_2)$
1667.5	1667.5						
3241.5	3240.5		3229.0		2411.0	2412	$\nu_a(CH_2)$
3625.0	3615.5		3624.5		2677.0	2661.5	ν(OH)

C_2D_4 (Figure 5a,c). Little or no ^{18}O shift was observed for this band, as was the case for samples containing C_2H_4 and $^{16}O_3$ or $^{18}O_3$ (Figure 4a,c; Table I). Figure 5b shows that doublet of triplets is observed between 300 and 425 cm^{-1} after irradiation of a sample containing CH_2CD_2 and ozone. The components of these features occur at 318.0, 322.0, 326.5, 392.5, 398.0, and 400.5 cm^{-1} and are thus not coincident with the bands in parts a and c of Figure 5, appropriate to the fully protonated and fully deuterated samples, respectively. Finally the region 1570–1680 cm^{-1} of the infrared spectrum of irradiated samples is shown in Figure 5a–d. The bands at 1667.5 and 1662.0 cm^{-1} observed for C_2H_4/O_3 samples are not present in spectra b–d of Figure 5. Furthermore the intense absorption at 1631.0 cm^{-1} has given way to an intense doublet at 1583.5 and 1589.5 cm^{-1} (Figure 5c) and a third, much weaker absorption at 1603.0 cm^{-1}. A sample of $C_2D_4/^{18}O_3$ affords a doublet of absorptions at 1580.5 and 1585.5 cm^{-1} (Figure 5d) while two bands at 1652.5 and 1646.0 cm^{-1} are also observed in these experiments.

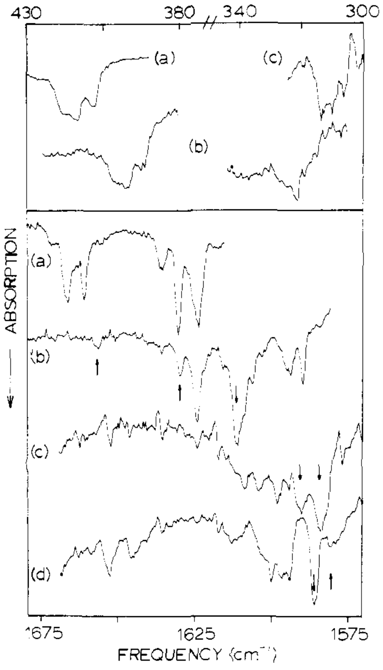

Figure 5. The infrared spectra in the 300–430-cm^{-1} and 1570–1680-cm^{-1} regions after full Hg arc irradiation of an argon matrix containing ethene and ozone: (a) $Ar/C_2H_4 = 400$, $Ar/O_3 = 200$, *hν*, 95 min; (b) $Ar/CH_2CD_2 = 400$, $Ar/O_3 = 200$, *hν*, 185 min; (c) $Ar/C_2D_4 = 380$, $Ar/O_3 = 210$, *hν*, 60 min; (d) $Ar/C_2D_4 = 375$, $Ar/^{18}O_3 = 215$, *hν*, 60 min. In the lower traces b–d, arrows denote vinyl alcohol absorptions for clarity.

Discussion

Discussion of the results will be in two parts. First the several photoproducts characteristic of C_2H_4/O_3 samples will be identified. Attention will then be paid to the mechanism of the reaction between O atoms and ethene in an argon matrix with reference to the nature of the products and thermodynamic restrictions.

Identification of the Photoproducts. By reference to their known infrared matrix spectra, acetaldehyde, ethylene oxide, and ketene have been identified as primary products of the O + C_2H_4 matrix reaction. Absorptions labeled AA and M in Figure 1b that were found to be present after photolysis of O_3 in C_2H_4/O_3 or CH_3CHO/O_3 samples may be similarly identified as acetic acid[22] and methane, respectively. The appearance of both species in irradiated CH_3CHO/O_3 samples argues strongly that both result from secondary reaction between photoproduced acetaldehyde and atomic oxygen in C_2H_4/O_3 samples.

The identification of the species responsible for the bands denoted X is not as straightforward, however. The magnitude of the ^{18}O and ^{13}C isotopic shifts exhibited by the intense doublet of absorptions at 1084.0 and 1079.0 cm^{-1} suggests, together with the absolute frequencies, the presence of a C–O bond in species X. Furthermore this vibration involves a single oxygen atom as evidenced by the appearance of a doublet of doublets in the scrambled $^{16,18}O_3$ experiments. The lack of a more complex isotopic pattern on 50% ^{18}O enrichment for any of the product bands suggests that the molecule X contains only a single oxygen atom. The absorption at 3625 cm^{-1} is characteristic of the –OH group, a conclusion supported by the 9.5-cm^{-1} ^{18}O and 0.5-cm^{-1} ^{13}C isotopic shift exhibited by this band. Bands at 818.5 and 3241.5 cm^{-1} show 8.5- and 12.5-cm^{-1} ^{13}C shifts, respectively, in addition to large deuterium shifts and are therefore assigned to C–H deformation and stretching modes, respectively. The first is too low in frequency and the second too high for these to be attributed to methyl, CH_3, vibrations. That they should be assigned to motions of a $=CH_2$ group gains support from the presence of the absorption at 1631.0 cm^{-1} that lies in the correct region of the spectrum to be a $>C=C<$ stretching vibration. Furthermore the large ^{13}C and deuterium shifts and very small (1.5 cm^{-1}) ^{18}O shift for the latter band support this assignment. The complex pattern of bands between 1570 and 1670 cm^{-1} appearing after irradiation of samples containing $^{13}C_2H_4$ (90% ^{13}C) and CH_2CD_2 give further credance to this assignment, as discussed in the following section. The identification of vibrational bands in the infrared spectrum of X characteristic of $>C=C<$, $=CH_2$, –OH, and –CO– stretching modes and a $=CH_2$ deformation together with the stoichiometry of the reaction between an O atom and the ethene molecule argues strongly that species X is vinyl alcohol, $CH_2=CHOH$. This conclusion is in general agreement with previous observations[8] of the spectrum of vinyl alcohol in $CFCl_3$ solution or in the condensed phase at 77 K. Bands at 815, 3240, and 3620 cm^{-1} were assigned, among others, to the enol while a band at 1710 cm^{-1} is better reassigned to the carbonyl group of acetaldehyde shifted from the matrix frequency of 1731.0/1745.0 cm^{-1} by H-bonded interactions.

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(22) Berney, C. V.; Redington, R. L.; Lin, K. C. *J. Chem. Phys.* **1970**, *53*, 1713.

Table III. Characteristic Observed Vibrational Frequencies (cm^{-1}) for Selected Vinyl Ethers CH_2=CHOR[a].

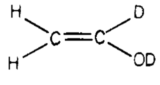
R	freq and assignmt				
	2γ(CH_2)	C=C	C–O	γ(CH)	γ(CH_2)
H	1665[c]	1628[c]	1084		818
CH_3	1665	1620	1223	965	817
C_2H_5	*b*	1610	1205	967	810
n-C_3H_7	*b*	1615	1203	968	811
i-C_3H_{17}	*b*	1614	1203	969	812
C_4H_9	*b*	1613	1200	962	810
C_8H_7	*b*	1610	1205	963	810
$C_6H_5CH_2$	*b*	1611	1200	960	820
C_6H_5	1635	1653	1235	965	806
CH_2=CHSEt	~1720	1585	719	960	860

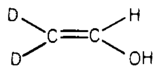
[a] Taken from ref 24. This work R = H. [b] These molecules exhibit a second band at higher frequency than the C=C stretch and of similar but slightly lower intensity. [c] Average frequency for observed doublet.

Vibrational Assignment in Vinyl Alcohol. The observed vibrational frequencies and assignments are given for seven isotopomers of vinyl alcohol in Table II. Assignment of the –OH stretching mode is self-evident while that of the antisymmetric CH_2 stretching mode at 3241.5 cm^{-1} is a little more tentative. This frequency is higher than the corresponding mode of vinyl halides, CH_2=CHX (X = F, Cl, or Br), at 3112–3140 cm^{-1},[23] vinyl ethers, CH_2=CHOR (R = Me, Et, *n*-Pr, or *n*-Bu), at 3100-3125 cm^{-1},[24] or ketene, CH_2=C=O, at 3155 cm^{-1}.[21] The ^{13}C and ^{18}O shifts exhibited by the band, however, deem it unlikely that it is a combination or overtone band and the ratio $\nu(CH)/\nu(CD)$ of 1.34 is appropriate for the antisymmetric C–H stretch of a =CH_2 group.

The frequencies of several absorptions characteristic of vinyl ethers as determined by Mikawa[24] are listed in Table III, together with those observed for vinyl alcohol in this work. Thus assignment of the intense absorption at 818.5 cm^{-1} to the out-of-plane CH_2 wag in vinyl alcohol is supported by the observation of a similar band for each vinyl ether. The bands assigned at ca. 1205 cm^{-1} to the C–O stretch in vinyl ethers represent what is better described as an antisymmetric C–O–C stretching vibration. In vinyl alcohol the presence of a hydrogen atom rather than a larger hydrocarbon group reduces this vibration to a C–O stretch, which is found at a lower frequency of 1084.0 cm^{-1}. Both the ^{18}O and ^{13}C shift exhibited by this band are substantially less than those expected for a pure C–O stretch, implying mixing of the normal vibrations. The in-plane COH and CH′ deformations probably contribute to this vibrational mode for two reasons: (i) both deformations are expected to occur at 1250–1400 cm^{-1} and are therefore sufficiently similar in frequency to the C–O stretch and (ii) the three normal vibrations involve four atoms in close proximity. Interaction with hydrogen deformation vibrations is reflected in the large shift exhibited by the 1084.0-cm^{-1} band in d_2 (978.5 cm^{-1}) and d_4 (925.5 cm^{-1}) vinyl alcohol. Deuteration is expected to alter the extent and character of any vibrational mixing. Thus the band at 925.5 cm^{-1} in CD_2=CDOD shifts to 908.0 cm^{-1} in CD_2=$CD^{18}OD$, a shift fewer than 5 cm^{-1} less than that expected for a pure C–O stretch. Evidently, this vibrational mode contains much more C–O stretching character than does that at 1084.0 cm^{-1} in CH_2=CHOH.

Mixing of the vibrational modes between 900 and 1400 cm^{-1} in vinyl alcohol and in CH_2=CHOH in particular is not confined to normal vibrations involving the α-carbon atom however. Use of ethene-d_2 should give two isotopomers **6** and **7**. The absorption


6


7

observed at 978.5 cm^{-1} is assigned to **6** while the corresponding band for **7** is expected to appear at ca. 1030 cm^{-1} and is probably obscured by the intense ozone band at 1040 cm^{-1}. The shift of 53 cm^{-1} on deuteration of **6** to vinyl-d_4 alcohol is much greater than that predicted by treating the vinyl and hydroxyl groups as point masses. This suggests that deformations of the =CH_2 group participate in these vibrational modes.

Table IV. Observed Vibrational Frequencies (cm^{-1}) for the OH Torsion of Selected Carboxylic Acids and Alcohols

	OH		OD		τ(OH)/τ(OD)[a]
MeOH[b]	d_0 271.5	d_3 259.0	d_1 215.7[c]	d_4 198.0[c]	1.37
EtOH[d]	d_0 211		d_1 175.5		
CH_2=CHOH	d_0 413.0	d_2 398.0	d_2 322.0	d_4 310.0	1.33
HCO_2H[e]	d_0 637.6	d_1 628.3	d_1 506.3	d_2 490.4	1.30
CH_3CO_2H[f]	d_0 535	d_3 479	d_1 422	d_4 409	1.31

[a] Calculated from d_0 and perdeutero isotopomers. [b] Reference 25. [c] Calculated value. [d] Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc.* 1970, *66*, 1932. [e] Redington, R. L. *J. Mol. Spectrosc.* 1977, *65*, 171. [f] Reference 22.

More information about the bonding in vinyl alcohol is afforded by the broad absorption centered at 413.0 cm^{-1} for the d_0 molecule. This band, which exhibits no observable ^{13}C shift, cannot reasonably be attributed to either a CH deformation or a C=C—O bending mode. Since any ^{18}O shift is barely detectable and the corresponding absorption in vinyl-d_4 alcohol is observed more than 100 cm^{-1} lower at 310.0 cm^{-1}, its assignment to the out-of-plane COH deformation or OH torsion τ(OH) must be considered. The frequency of 413.0 cm^{-1}, falling as it does between the OH torsional frequencies for saturated alcohols and carboxylic acids (Table IV), is entirely reasonable for this mode of vibration. The torsion frequency for vinyl alcohol is greater than that for saturated alcohols because delocalization of electron density from the lone pairs of the hydroxyl group imparts partial π character to the C–O bond. The extent of this delocalization is expected to be greater for carboxylic acids by virtue of excess negative charge residing at the more electronegative carbonyl oxygen atom. The appearance of a doublet of absorptions in experiments involving CH_2CD_2 shifted from the d_0 and d_4 values supports this assignment, partially deuterated formic or acetic acid exhibiting the same pattern of bands. Furthermore the ratio τ(OH)/τ(OD) for the d_0 and perdeutero isotopomers of vinyl alcohol falls between those of methanol and acetic or formic acid (Table IV), and the change in torsional frequency on hydrogenation of vinyl alcohol [τ[OH-(CH_2CH–OH)]/τ[OH(Et–OH)] = 1.96] is similar to that observed on hydrogenation of methyl vinyl ether [τ[OMe(CH_2CH–OMe)]/τ OMe(Et–OMe) = 2.03].[26]

Mikawa observed that the vibrational spectra of vinyl ethers exhibited two bands in the region 1600–1700 cm^{-1},[24] an intense band between 1610 and 1620 cm^{-1} assigned to the C=C stretching mode (Table III) in Fermi resonance with a slightly less intense band to higher frequency assigned to the overtone of the out-of-plane CH_2 wag. The spectrum of vinyl-d_0 alcohol in this region contains four bands at 1624.5, 1631.0, 1662.0, and 1667.5 cm^{-1} (Figure 2b). Although coincident with a water absorption, the band at 1624.5 cm^{-1} is considered real since, in other experiments in this laboratory, the water absorption is not affected by Hg arc irradiation while irradiated C_2H_4/O_3 samples show a growth in this band. Two of the bands, at 1662.0 and 1631.0 cm^{-1}, are generally sharper than the second pair although without reliable measurements of the integrated absorbances for the four bands, it is not possible to determine which of the components of the lower frequency doublet is associated with those of the higher. Whether

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(26) Kitagawa, T.; Ohno, K.; Sugeta, H.; Miyazawa, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 969. Sakakibara, M.; Inagaki, F.; Harada, I.; Shimanouchi, T. *Ibid.* **1976**, *49*, 46.

the doublet nature of these and other absorptions is a result of trapping (i) the two most stable conformers **1** and **2** or (ii) a single conformer in two different matrix sites is not certain. It would be reasonable to suppose that the vibrational spectra of conformers **1** and **2** differ most in the modes involving the OH group, that is the O–H stretch and the two COH deformations. However only one band around 3600 cm^{-1} can be reasonably assigned to vinyl alcohol while both the C=C stretch and out-of-plane CH_2 wag show doublet structure. The components of the torsion band at 413.0 cm^{-1} are separated by less than 10 cm^{-1}; this spacing is less than half the difference observed for the torsional frequencies of gaseous trans (209 cm^{-1}) and gauche (234 cm^{-1}) propan-2-ol.[27] Furthermore conformational changes in methyl vinyl ether are predicted to change the CH_2CH–OMe torsional frequency by ca. 75 cm^{-1}. Therefore the structure associated with absorptions of vinyl alcohol is considered to arise from isolation of a single conformer, assumed to be the syn conformer **1**, in two or more sites. It appears that Fermi resonance between the C=C stretch and the out-of-plane CH_2 wag also occurs in vinyl alcohol. Estimates of the relative intensities of the four components in resonance favor assignment of the lower doublet to the fundamental. Correction for Fermi resonance by Overends method[28] reveals that the absorption at 1631.0 cm^{-1} lies at 1649.0 or 1643.5 cm^{-1} depending on which of the two components of the doublet at 1662.0 and 1667.5 cm^{-1} is associated with it. The corresponding corrected position of the overtone band is then 1649.0 or 1649.5 cm^{-1}. The corrected frequencies for the overtone and more intense component of the fundamental are therefore taken to be the average of the two cases, 1649.0 and 1646.5 cm^{-1}, respectively.

On this basis most of the features of the isotopically enriched spectra can be rationalized. Resonance persists in ^{18}O-enriched vinyl alcohol since the out-of-plane CH_2 wag at 818.5 cm^{-1} exhibits no ^{18}O shift and the C=C stretch only a 1.5-cm^{-1} shift (Figure 2c). A shift of 17 cm^{-1} expected for the $\gamma(CH_2)$ overtone in vinyl-$^{13}C_2$ alcohol is, however, much smaller than the 54.5-cm^{-1} shift for the C=C mode, and Fermi resonance is absent for this isotopomer, as evidenced by the intense band at 1592.0 cm^{-1} (Figure 2d,e). The shift of 54.5 cm^{-1} is smaller than the 64.5 cm^{-1} expected for a harmonic C=C oscillator and this, together with the 1.5-cm^{-1} ^{18}O shift for the C=C stretch, suggests a weak interaction with the C—O stretch. The C=C mode of CH_2=$^{13}CHOH$ is observed at 1613.0 cm^{-1} with a shoulder at 1606.5 cm^{-1} and Fermi resonance is absent for this isotopomer. For $^{13}CH_2$=CHOH however the C=C stretch lies at 1617.0 cm^{-1} and has been reduced from an estimated value of ca. 1623 cm^{-1} by Fermi resonance; the overtone for this isotopomer is a weak band observed at 1639.0 cm^{-1} (Figure 2e). The bands exhibited by CH_2=CDOD and CD_2=CHOH may be distinguished by the weakness of the Fermi doublet at 1630.0 and 1657.0 cm^{-1} for CH_2=CDOD and the intensity of the C=C mode at 1610.0 cm^{-1} for CD_2=CHOH, a result of the shift in $2\gamma(CH_2)$ to ca. 1300 cm^{-1}. Finally the overtone of the out-of-plane CH_2 wag in vinyl alcohol shows quartic anharmonicity as its frequency is slightly more than twice that of the fundamental. This however has also been observed for the same mode in both methyl and phenyl vinyl ether (Table III), the CH_2 wag in all three ketenes (d_0–d_2) in the gas phase[21] and the CH_2 wag in the halomethyl radicals CH_2X (X = Cl, Br, I).[29]

Mechanism and Intermediates

DeMore has shown that both ^3P and ^1D oxygen atoms react with ethene in liquid argon.[4] In this laboratory, separate argon samples containing N_2 ($Ar/N_2 = 380$) and O_3 ($Ar/O_3 = 300$) were condensed and irradiated by the Hg arc, and a modest yield of N_2O was formed. The reaction $N_2 + O \rightarrow N_2O$ occurs with $O(^1D)$ but not $O(^3P)$ atoms,[30] and in liquid nitrogen the quantum yield is very small (1.3×10^{-2}).[30] It is therefore surprising that any $O(^1D)$ can be detected in a N_2-doped argon matrix at these low concentrations. Consequently, it is possible that $O(^1D)$ reactions play a significant role in the $Ar/C_2H_4/O_3$ system. The $O(^1D)$ reaction would be important for complexes between O_3 and C_2H_4 or near-neighbor pairs in the matrix. Formation of the primary ozonide of ethene at 80 K in Xe matrices containing ethene and ozone suggests that heterodimers are probably formed upon condensation.[31]

Vinyl alcohol may be formed in one of three reactions of oxygen atoms with ethene (i) insertion by $O(^1D)$ into a C–H bond, (ii) H abstraction by either $O(^3P)$ or $O(^1D)$ followed by cage recombination of vinyl and hydroxyl radicals so formed, and (iii) addition of an O atom to the carbon–carbon double bond to give the biradical **4** followed by a 1,2 hydrogen rearrangement. The present experiments cannot distinguish between these possibilities or between these and rearrangement of electronically or vibrationally excited acetaldehyde and ethylene oxide. The more likely reaction pathways can be outlined however.

Both insertion and abstraction reactions are expected to be unique to excited $O(^1D)$ atoms in a matrix. In liquid argon, $O(^1D)$ appears to react with the C–H bonds of ethene and methane or ethane at similar rates which indicates that the activation energy for these processes are similar (ca. 7 kcal/mol).[32] Ground-state $O(^3P)$ should have little excess energy to overcome such an activation energy barrier. Indeed in liquid-argon formation of C_2H_2 was observed only for reaction of $O(^1D)$ with ethene, and the C_2H_2 produced was only 1–3% of the total reaction product in a system scavanged almost completely of $O(^3P)$ atoms.[4] It must be pointed out, however, that C_2H_2 may not be the exclusive decomposition product of the vinyl radical. In any event the abstraction or insertion reactions of $O(^1D)$ should enhance the yield of vinyl alcohol compared with acetaldehyde and ethylene oxide.

Reaction of $O(^1D)$ with the carbon–carbon double bond of ethene in liquid argon is 5 times faster than that with the C–H bond,[4] and the activation energy for addition of $O(^3P)$ to ethene under similar conditions is 0.6 kcal/mol.[3] Since both $O(^3P)$ and $O(^1D)$ react in this way, **4** and **5** are expected to be major initial intermediates. Rearrangement by 1,2 H shifts provides routes to either acetaldehyde or vinyl alcohol, while ring closure of the biradical **4** and formation of C–O bonds in the complex **5** yield ethylene oxide. The formation of acetaldehyde by rearrangement is supported by the larger yield of CD_2HCHO than CH_2DCDO as determined by the relative intensities of their C—C=O deformation absorptions in CH_2CD_2/O_3 samples. This reflects the relative rate of the H and D shift. Formation of vinyl alcohol in this way may well be limited because of the competition between the two modes of H shift. All three products are expected to be formed vibrationally or electronically excited and may rearrange further before being quenched by the matrix. With use of standard tables of bond enthalpies[33] it is estimated that the biradical **4** formed from $O(^3P)$ and ethene will contain ca. 12 kcal/mol excess energy. That from $O(^1D)$ will be 57 kcal/mol above its ground state. Either product probably has sufficient energy to rearrange, but neither is sufficiently excited to decompose via H-atom loss. With the assumption that the biradical is completely quenched by the matrix before decomposition, the products acetaldehyde, vinyl alcohol, and ethylene oxide will have excess energies of ca. 90, 77, and 67 kcal/mol respectively.

Neither excited acetaldehyde nor ethylene oxide have, to our knowledge, been observed to yield ketene. We have also found that no ketene is formed during UV and visible irradiation of these molecules isolated in argon matrices. Excited states of these molecules attained by irradiation however may differ from those formed by the O + C_2H_4 reaction and have a different energy distribution. Both vinyl alcohol and the biradical **4** when excited may, however, provide the source of this species in irradiated

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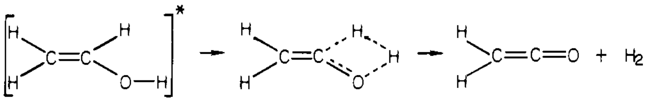
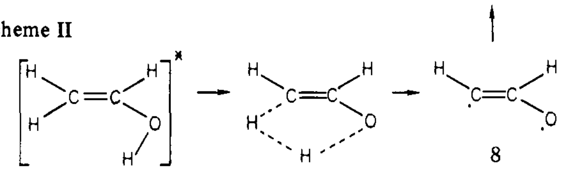
Scheme I



Scheme II



C_2H_4/O_3 samples in argon matrices. Concerted four- and three-center elimination of H_2 from vinyl alcohol (Scheme I) and **4**, respectively, would provide a low-energy pathway for decomposition. Elimination of H_2 from excited vinyl alcohol in the syn conformation **1** would also lead to ketene, via the intermediate **8** that may be responsible for the same product in O + C_2H_2 reactions (Scheme II). The lack of C_2H_2 photoproduct in irradiated C_2H_4/O_3 samples however favors α rather than β elimination of H_2 from vinyl alcohol.

The distribution of products in the C_2H_4/O system cannot distinguish between the intermediates **4** and **5**. If these intermediates are an important source of ketene, however, the biradical **4** would probably be favored. It is difficult to predict the pathway for the complex **5** to decompose to ketene involving, as it does, elimination of two hydrogen atoms from the same carbon atom. The study of the formation of ketene in this and other systems is being continued in an attempt to elucidate details of this mechanism.

Conclusion

The photolysis of O_3 in argon matrices containing ethene leads to the formation of acetaldehyde, ethylene oxide, ketene, and vinyl alcohol as primary products. There is some evidence for the participation of excited $O(^1D)$ atoms, in addition to $O(^3P)$, which may increase the relative yields of vinyl alcohol via H-atom abstraction or insertion mechanisms. Ketene is considered to be formed primarily by H_2 elimination from either vinyl alcohol or the initial addition product, a biradical, although the decomposition or arrangement of "hot" acetaldehyde and ethylene oxide cannot be ruled out.

The vibrational spectrum of vinyl alcohol exhibits several characteristics of alkyl vinyl ethers. Fermi resonance between the overtone of the out-of-plane CH_2 wag and the C=C stretch is relieved on ^{13}C or deuterium enrichment. Evidence for slight π character in the C–OH bond is found in the torsional frequency of the OH group which lies between that for saturated alcohols and carboxylic acids. Extensive interaction between the C–O stretch and in-plane COH and CH′ deformations leads to reduced ^{18}O and ^{13}C shifts and a large deuterium shift for the former vibrational mode. Finally the similarity between the infrared spectra of vinyl alcohol and the vinyl halides and ethers does not reflect the observed instability of vinyl alcohol. That samples can be kept at room temperature suggests that vinyl alcohol is indeed a stable if reactive molecule.

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Role of Higher Triplet States in the Anthracene-Sensitized Photoisomerization of Stilbene and 2,4-Hexadiene[1]

Jack Saltiel,* David E. Townsend, and Alan Sykes

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306.
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Abstract: Irradiation of benzene solutions of anthracene (A) in the presence of varying amounts of *trans,trans*-2,4-hexadiene (tt) leads to trans → cis photoisomerization of the diene. Ratios of tc/cc are close to those expected for a high triplet energy donor. The anthracene-sensitized diene photoisomerization is not quenched significantly by *cis*-stilbene, though pronounced c → t stilbene photoisomerization is observed. Conversely, the diene quenches the anthracene-sensitized *cis*-stilbene photoisomerization. In air-saturated solutions where the lowest triplet of anthracene, $^3A^*$, is quenched by oxygen and is thus unavailable for interactions with the diene, diene photoisomerization to tc is slightly enhanced, as are tc/cc ratios. The upper limit for the rate constant of $^3A^*$ quenching in benzene by tt, determined by flash-kinetic spectroscopy at room temperature, is $1.2_5 \times 10^3$ M^{-1} s^{-1}. When reported values for the interaction of A excited singlets, $^1A^*$, with the diene and A are used, kinetic analysis of the isomerization quantum yields leads to the conclusion that triplet excitation transfer to the diene is almost exclusively from a higher A triplet, $^3A^{**}$, while $^3A^*$ is responsible for stilbene photoisomerization. The data require that formation of the two triplets from $^1A^*$ be mainly sequential: $^1A^* \rightarrow {}^3A^{**} \rightarrow {}^3A^*$. The estimated effective lifetime of $^3A^{**}$ is ~30 ps. The effect of oxygen on the formation of cc suggests that quenching of $^1A^*$ by oxygen leads in part to adiabatic formation of $^3A^{**}$. This pathway may account for the inefficiency in singlet oxygen formation associated with $^1A^*$ quenching.

It is well established that the chemical response of acceptor molecules in triplet-sensitized photoreactions often depends on the energy of the triplet state of the donor (sensitizer) that transfers the excitation.[2] Commonly, the active state is the lowest triplet state of the donor, T_1, but in a series of elegant papers, Liu and co-workers showed that when anthracenes are employed as sensitizers, triplet–triplet energy transfer from a higher triplet state, T_2, becomes the dominant sensitization process.[3] At one stroke these experiments explained why product ratios from the acceptor molecules were consistent with excitation transfer from a high

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