PHOTOLYSIS OF ALLENE-OZONE MIXTURES AT 647 nm IN CRYOGENIC MATRICES Part 1. Formation of allene oxide*

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ABSTRACT

Matrix studies of the photolytic reaction at 647 nm between allene and ozone were carried out at 12 K. Primary photoproducts include carbon monoxide, acrolein (*cis* and *trans*), cyclopropanone, ketene, ethylene, allene oxide and formaldehyde. In Ar and Kr matrices both acrolein and cyclopropanone are produced in high yields, whereas in Xe matrices cyclopropanone is the major product. Infrared spectra for cyclopropanone and its oxygen-18 and deuterium substitutes are reported. The carbonyl stretch for cyclopropanone is observed at 1815 cm⁻¹ in an Ar matrix. Also reported is the first synthesis of allene oxide. The carbon-carbon double bond stretch is observed at 1823.4 cm⁻¹ and it exhibits a small oxygen-18 shift.

The change in product distribution is discussed in terms of heavy atom spin-orbit enhancement of singlet-triplet excitation, so that in xenon reaction takes place on a triplet surface, whereas in argon it occurs on a singlet surface.

INTRODUCTION

In 1974 Havel [1] proposed a general mechanism for the reaction between ground state atomic oxygen (³P) and allene involving oxygen atom addition to both the central and the terminal carbon atoms. Each resultant diradical was pictured to lead to all of the final observed products, CO, C_3H_4 , and acrolein as well as the same metastable intermediates, cyclopropanone and allene oxide. Terminal addition followed by hydrogen migration appears to be a more direct route to acrolein whereas central carbon addition furnishes a straightforward path to CO and ethylene, via cyclopropanone. Havel studied the $O(^{3}P)$ + allene reaction in the gas phase but was unable to detect either cyclopropanone or allene oxide. Additional work with substituted allenes added evidence that cyclopropanone intermediates were involved. Furthermore, the possibility that allene oxide is another nonradical intermediate is kept alive by

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^{*}Dedicated to Professor K.S. Pitzer on the occasion of his 75th birthday.

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the observation that some substituted allene oxides can isomerize to cyclopropanone [2].

Cyclopropanone was first synthesized in 1966 [3]. It has been the subject of several theoretical studies [4] and postulated as an intermediate in several reactions [5]. Unfortunately its reactivity has caused some difficulties in obtaining a reliable infared spectrum [3,6]. An absorption observed at 1815 cm^{-1} has been attributed to the carbonyl stretch, but in 1973 van Tilborg concluded that this band was due to an impurity, cyclobutanone. More recently Rodriguez et al. [7] obtained a spectrum of cyclopropanone that included the 1815 cm^{-1} band. Based on some preliminary perdeuterocyclopropanone work, they suggested that the carbonyl stretch was involved in a Fermi resonance.

Allene oxide has not been observed, although some t-butyl substituted allene oxides have been synthesized [2,8]. Liberles, Greenberg and Lesk performed Hartree Fock calculations that predict that allene oxide is 21 kcal mol^{-1} higher in energy than its isomer, cyclopropanone [9].

We present here a matrix isolation study of the reaction between allene and ozone initiated photolytically with the red lines of krypton-ion laser. Gas phase ozone is known to dissociate into ground state oxygen atoms and molecular oxygen with red light [10]. Hawkins and Andrews [11] have recently studied the photolytic reaction between ethylene and ozone in an argon matrix using a high pressure mercury lamp. Their products are best explained by matrix photodissociation of ozone although at the shorter wavelengths their photolysis source also produces excited states of both the oxygen atom and molecular oxygen.

EXPERIMENTAL

Mixtures of allene/argon (M/R=100) and ozone /argon (M/R=25) were codeposited through two separate jets at a combined flow rate of one mmol h⁻¹ onto a cold CsI window to give a final matrix composition $Ar/O_3/C_3H_4=200/4/1$. The window was cooled at 12 K by an Air Products two stage closed cycle helium refrigerator (Model CSA-202). All deposition and photolysis were carried out at 12 K. Deposition rates were slower for Xe and Kr matrices (approximately 0.5 mmol h⁻¹). Infrared spectra were recorded at 12 K by a Nicolet 7199 FT-IR spectrometer at a resolution of 0.50 cm⁻¹(200 scans) with a frequency accuracy of ± 0.1 cm⁻¹. A germanium flat (OCLI) transmitting $500 < \lambda < 5000$ cm⁻¹ was placed in the spectrometer's optical path to prevent photolysis by the reference HeNe laser of the FT-IR.

Photolysis sources were a General Electric medium pressure mercury arc lamp (AH4) with envelope removed and a Krypton-ion Coherent laser (model CR-750K) emitting two red lines, 647.1 nm (85%) and 676.4 nm (15%). Laser powers at the cryostat ranged from 0.18 to 0.36 W. The beam, which was not

focused, had an area of about 0.60 cm² at the cold window. All mercury lamp photolysis was carried out through the CsI cold window ($\lambda > 240$ nm).

Ozone was prepared by a static electric discharge (Tesla coil) of oxygen (Matheson 99.99%) and collected in a Pyrex tube at 77 K. Excess oxygen was removed by pumping. Diluted ozone samples were stored in a passivated stainless steel vacuum system and used within a few hours.

Allene (Matheson 98%) samples were prepared by dilution of the middle of three fractions of condensed gas. Upon thawing, the first third was removed and the second third used for sample preparation. Allene- d_4 was purchased from Merck, Sharp and Dome (98% D) and ${}^{18}O_2$ was obtained from Cambridge Isotope Laboratories (98% ${}^{18}O$). Cyclobutanone (Aldrich 99%) and acrolein (Kodak 97%) were degassed by freeze-thaw cycles and pumping at 77 K before matrix samples were prepared.

RESULTS

Samples of allene (M/R=100) and ozone (M/R=25) were codeposited for 2 to 3 h at 12 K. In the spectrum obtained after deposition all bands could be attributed to the allene/ozone sample except an absorption at 2344 $\rm cm^{-1}$ due to carbon dioxide, a common impurity in the ozone samples. Exposure of this matrix to globar radiation $(5000-500 \text{ cm}^{-1})$ for 24 h revealed no infrared induced reaction [12]. After a deposition spectrum had been recorded the matrix was photolyzed with the red lines of a Kr-ion laser and spectra were recorded intermittently throughout the photolysis to observe product growth. In the xenon matrices, 50–60% of the total allene deposited is consumed in the photolytic reaction (as monitored by following the 1949.3 $\rm cm^{-1}$ band of allene). Two-thirds of that loss occurs in the first 5 min of the photolysis (laser power at window 0.26 W). In the krypton matrices around 45–55% of the allene disappears during photolysis, but it took 20 min to remove two-thirds of that amount (laser power at window 0.26 W). For argon matrices 30-45% of the allene is consumed and it took 40 min to lose two-thirds (laser power at window 0.30 W). Since O_2 is a common impurity in the ozone samples, allene/ O_2 /Ar (1:4:200) and allene/O₂ matrices were photolyzed with the Kr-ion laser and reaction was not observed. An allene/O₂/Ar (1:100:100) matrix was also photolyzed with a tungsten lamp and reaction was not detected.

Tables 1, 2 and 3 list the photolysis product band frequencies and absorption intensities (peak heights) for Xe, Kr and Ar matrices, respectively. Difference spectra for these are illustrated in Fig. 1. In these spectra products appear as positive peaks while reactants are negative peaks. It is immediately apparent that the product band intensities obtained in the Xe matrices differ from those obtained in Ar and Kr matrices. In the Ar matrices the strongest band is 1708.4 cm⁻¹, followed by 1815.1, 2143.5 and 2137.5 cm⁻¹. The Kr matrix spectra show the same pattern. In contrast, in Xe the most intense product band is at 1817.3

$C_3H_4 + O_3$	A ^c	$C_3H_4 + {}^{18}O_3$	Ac	$C_3D_4 + O_3$	Ac	$C_3D_4 + {}^{18}O_3$	A¢	Assign- ment ^d
a		-		2252.0	0.015	2245	0.011	?
3092*	w	_		2196.4	0.015	2194	0.018	\mathbf{CP}^{d}
-		_b		1856.2	0.036	-		CP^d
2136.4	\mathbf{sh}	2109.6	0.033	2107	_p	2083.6	0.059	К
2133.7	0.070	2082.6	0.031	2133.4	0.026	2083.6	0.059	CO
_ ^b		_b		1935.6	0.010	1933.8	0.006	CP
_ ^b		_b		1794.1	0.007	1792.1	0.012	CP
1979.1	0.037	_p		1760	0.012	1756	0.022	CP
1901.3, 1890.6	0.069	1892.7, 1890.6	0.029	-		-		CP
1867.8	0.024	1860.0	0.015	-		-		CP
1819.9, 1817.3	0.133, 0.118	1798.7, 1796.4	0.182	1837.7	0.097	1815.1	0.198	CP
		1817	0.008	1760.9	0.012	1756.4	0.021	AO
1732.1	0.015	1699	0.024	1721.7	0.009	1695	0.007	F
1708.3, 1705.2	0.037, 0.025	1678	0.017	1685.8	0.024	1641.9	0.029	A, A′
1613	w	-		-		-		A'
1493.8	w	1483	0.008	1088.9	0.012	1074.4	0.018	F
1445.2	0.010	-		-		-		Р
1434.0	0.010	1434.1	0.007	-		-		Е
1402	w			-		-		Α′
1371.9	0.043	1371.6	0.044	-		1038.0	0.072	CP,K
1345.3	0.009	1345.0	0.008	-		-		acetaldehyde
1157	0.019	w		-		-		A, P
1107	w	w		-		-		AO
_b		_b		981.3	0.010	-		CP
1043	_b	1042	0.039	953.7	0.046	952.7	0.036	CP
965.2, 958.6	0.076, 0.065	963, 956	0.037	808.3	0.028	804.6	0.033	CP
947	w	-		-		-		Е
928.9, 931.2	0.070	929.4	0.069	814.8	0.055	813.9	0.066	CP
880.6	0.011	865	w	-		-		AO
868.1	0.020	_ ^b		-		-		EO
790.1	0.020	790.0	0.012	626.0	0.020	621.0	0.020	AO

Product band frequencies (in cm⁻¹) for the Kr-ion laser photolysis of a $C_3H_4/O_3/Xe$ matrix (1:4:200)

^aC-H stretching region assignments are tentative owing to scatter.

 $^{\rm b}{\rm Obscured}$ by ozone, allene or ${\rm CO}_2$.

^cPeak absorbances.

^dA, trans-acrolein; A' cis-acrolein; K, ketene; F, formaldehyde; E, ethylene; P, propadienol; CP, cyclopropanone.

cm⁻¹ and the 1708.3 cm⁻¹ feature is quite weak. This indicates that the 1817.3 and 1708.3 cm⁻¹ bands correspond to different products and that Xe matrices change the product distribution. The growth behavior of these two features are illustrated in Fig. 2. More dilute matrices $(M/O_3 = M/allene = 100)$ revealed the same product bands.

Isotopic substitutions were carried out to help in the identification of the photoproducts. The ¹⁸O composition was 94% (¹⁸O₃), 4% ¹⁶O¹⁸O¹⁸O and 2% ¹⁸O¹⁶O¹⁸O. The deutero-allene composition was 92% C₃D₄ and 7.5% C₃D₃H. The product band frequencies are included in Tables 1 and 3, and the key spectral region (1950–1600 cm⁻¹) is shown in Fig. 3.

TABLE 1

TABL	\mathbf{E}	2
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ν (cm ⁻¹)	Aª	$Assignment^{b}$	ν (cm ⁻¹)	Aª	$Assignment^{b}$
2836.8	0.012	A, A'	1402.8	0.022	A'
2808.2	0.100	Α	1376.3	0.019	CP
2141.4	0.057	K	1359.0	w	Α
2135.2	0.052	CO	1273.8	w	Α
1983	w	CP	1162.7	w	Р
1901.1, 1904.7	0.038	CP	1155.4	0.011	Α
1872.0	0.012	CP	1107.3	0.017	AO
1820.4	0.084	CP, AO	966.7	0.036	A'
1811.8	0.086	CP	960.9	0.029	A, CP
1733.5, 1735.9	0.019	F	956.4	0.033	A, CP
1712.7	0.045	Α′	944.1	w	E
1705.1	0.112	А	931.5, 929.7	0.054	CP
1613.3	0.010	A′	914.2	w	A'
1495.4	w	F	908.2	0.015	Α
1447.6	w	Р	879.4	0.020	AO
1437.2	0.009	Ε	793.6	0.015	AO
1416.7	0.017	Α			

Product band frequencies for the Kr-ion laser photolysis of a $C_3H_4/O_3/Kr$ matrix (1:4:200)

^aPeak absorbances, ^bFor assignment notation see bottom of Table 1. ^cObs, obscured.

In Fig. 3b the most intense features are at 1797.9 and 1679.4 cm⁻¹. From their intensities they are most logically related to the $C_3H_4 + ({}^{16}O)_3$ features at 1815.1 and 1708.5 cm⁻¹, respectively, giving ¹⁸O isotopic shifts of 0.990 and 0.983. These shifts can be compared to the calculated shift of an oxygen atom vibrating against a carbon atom, 0.976. Similar comparison in Fig. 3c and d connect intense doublet features at 1839.1 (1847.8) and 1695.7 (1689.9) cm⁻¹ for $C_3D_4 + ({}^{16}O)_3$ to 1817.8 and 1664.5 cm⁻¹ for $C_3D_4 + ({}^{18}O)_3$. Here the isotopic shifts are, respectively, 0.988 and 0.982, close to those for C_3H_4 .

Comparison of Figs. 3a and c is not quite as straightforward. In Fig. 3c, the intense doublets at 1839.1 (1847.8) and 1695.7 (1689.9) cm⁻¹ are connected, by intensities, to the Fig. 3a features at 1815.1 and 1708.5 cm⁻¹. This connection implies deuterium shifts of 1.013 and 0.993, respectively. The comparison of Fig. 3b and d gives the same anomalous upward shift on deuteration for the higher frequency band, (1817.8/1797.9) = 1.011 and (1664.5/1679.4) = 0.991. Similar results were obtained with Xe matrices. It seems probable that this anomalous behavior is explained by a Fermi resonance, as discussed later.

Important but not so prominent features appear in the C_3D_4 spectra in the 1770–1760 cm⁻¹ region. These absorbances show small ¹⁸O isotopic shifts, 7–8 cm⁻¹. Since there are no counterparts in this spectral region for C_3D_4 , we propose that they are accounted for partially by the structure on the high fre-

	•		•		2			
$C_{3}H_{4} + O_{3}$	Aª	$C_3H_4 + {}^{18}O_3$	A ^a	$C_3D_4 + O_3^c$	Aª	$C_{3}D_{4} + {}^{18}O_{3}$	Aª	Assign- ments ^d
3950 1	0.003	3950 1	0.008					U
120020	0000	1.0040	0,000	I		I		
3106	M	3105.3	0.003	I		1		E
2993.9	0.003	2993.8	q	I		I		Е
2840.7	0.011	2828.3	0.015	2265.8	0.061	2259.3	0.007	Α, Α΄
2813.8	0.00	2807.3	0.021	2078.3	0.069	2075.1	0.808	A
2760	0.006	2757.4	0.009	1		ł		Α
2746.7	0.006	2742.4	0.008	1		1		A'
2702.8	0.004	2696.0	0.004	2053.8	Μ	2047.3	M	А
t		1		1804.7	0.008	1798.9	0.014	CP
2143.5	0.067	2117.2 ^e	0.075	2117.1	0.240	2093.0	0.063	К
2137.5	0.049	2086.3	0.057	2138.0	0.127	2087.4	0.061	CO
1980.2	0.004	I		1762.0	w	1757.4	0.030	CP
1904.7^{e}	0.038	1896.5°	0.024	I		I		CP
1877.4^{e}	0.013	1870.2^{e}	0.012	ι		I		CP
1823.4	0.066	1818.1	0.049	1765.2^{e}	0.058	1761.0	0.053	AO
1815.1°	0.119	1797.9^{e}	0.270	1839.1^{e}	0.333	1817.8	0.170	CP
1735	0.018	1703.8°	0.032	1689.9	0.214	1652.2	0.040	Ľ4
1713.8^{e}	0.031	1687.8^{e}	0.027	1689.9	0.214	1652.2^{e}	0.040	Α'
1708.4	0.192	1678.5	0.141	1695.5	0.342	1664.5	0.171	А
1616.4	0.014	1611.8°	0.035	1589.9^{e}	0.043	1554.0	0.022	A'
1497.0	0.007	1486.9	0.016	1091.9	0.063	1076.3	0.042	н
1440.1	0.011	1440.0	0.016	1074.5	0.034	1075	M	Е
1419.0	0.017	1414.8	0.024	1152.3	0.021	1149.5	0.008	А
1404.9	0.025	1402.9	0.039	1170.6	0.086	1167.1	0.046	A'
1379.9^{e}	0.013	1379.6°	0.023	q		1040.1	0.071	CP
1361.0	0.005	1357.6	0.007	ł		I		А
1275.7	W	1275.7	0.007	I		1		Α

Product hand frequencies (in cm⁻¹) for the Kr-ion laser photolysis of an allene/ozone/argon matrix (1:4:200) at 12 K

TABLE 3

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А	K	2 AO	3 CP	Α	V	Α'	3 CP, A	CP, A	e E	s CP	7 A'	7 A	I AO	3 AO
	0.01	0.012	0.058				0.015		0.035	320.0	0.027	0.01	0.031	0.016
I	922.6	912.7	951.7	I	I	1	809.8	I	729.5	817.0	727.1	727.1	739.6	623.2
M	0.025	0.026	0.071				0.032		0.049	0.150^{b}	sh	sh	0.056	0.095
853.1	923.2	919.9	956.1	ſ	I	I	812.2	I	729.5	818.3	726.7	723.0	748.0	629.2
0.016	0.012	0.021	0.023		q	Ω.		0.055	0.015	0.072	0.023	0.032	0.033	0.028
1155.9	1109.5	1101.9	1044.2	q	970.2	964.2	q	958.4	947.3	930.8°	913.4	909.4	868.5	793.8
0.010	0.017	0.017		0.010	0.022	0.023	W	0.034	0.011	0.051	0.013	0.013	0.023	0.016
1156.8	1109.2	1109.2	q	991.6	973.8	968.2	964.8	958.4	947.5	934.3°	914.9	910.2	881.1	793.8

"Feak absorbances. "Obscured by ozone, allene or CO. "C-D stretch region assignments are tentative. "AO = allene oxide, CP = cyclopropanone, A' = cis-actolein, A = trans-acrolein, E = ethylene, K = ketene, F = tormaldehyde, CO = carbon monoxide. "Accompanied by weaker satellite feature or features.



Fig. 1. Difference spectra for the Kr-ion laser photolysis of $C_3H_4/O_3/M$ (1:4:200) matrices at 12 K. (A) Ar matrix 210 minute photolysis. (B) Kr matrix 210 minute photolysis. (C) Xe matrix 100 minute photolysis.

quency side of the 1815.1 $(C_3H_4 + ({}^{16}O)_3)$ and 1797.9 cm⁻¹ $(C_3H_4 + ({}^{18}O)_3)$ features, at 1823.4 and 1818.1 cm⁻¹, respectively.

Secondary photolysis with the AH-4 lamp provides additional information about the identities of the product bands in Tables 1, 2 and 3. Hence, after photolysis with the Kr-ion laser, some matrices were further photolyzed with the medium pressure lamp through the CsI window. A typical difference spectrum, that of $C_3H_4 + ({}^{18}O)_3$ in a Xe matrix, is shown in Fig. 4. A Xe matrix was used because it exhibited less interferences. The spectrum illustrated in Fig. 4 was used because the product bands after the mercury lamp photolysis were best illustrated (Xe matrices deposited at 12 K scatter greatly). Upon photolysis of a $C_3H_4 + ({}^{16}O)_3$ matrix in Xe, ten of the most intense features observed after Kr-ion laser photolysis decreased in intensity: 1901.3, 1867.8, 1819.9,



Fig. 2. Product growth curves for the Kr-ion laser photolysis of $C_3H_4/O_3/M$ matrices (1:4:200) at 12 K.

Fig. 3. Product bands for the Kr-ion laser photolysis of (A) allene/ozone/Ar 210 min; (B) allene/ $^{18}O_3/Ar$ 280 min; (C) allene-d_4/ozone/Ar 120 min; (D) allene-d_4/^{18}O_3/Ar 80 min; (E) allene/ozone/Xe 100 min.



Fig. 4. Difference spectra of a $C_3H_4/{}^{18}O_3/Xe$ (1:4:200) matrix (A) after 90 minutes of Kr-ion laser photolysis; (B) 102 minute mercury lamp photolysis *after* the 90 minute Kr-ion laser photolysis.



Fig. 5. (A) Kr-ion laser photolysis of an allene/ozone/Ar matrix (1:4:200) at 12 K for 280 min. (B) Mercury lamp photolysis (110 min) of matrix (A).

TABLE 4

ν (cm ⁻¹)	Relative intensity	Assignment
3107.1	w	ethylene
3078.4	w	ethylene
2111.0ª	s, br	ketene
2082.3ª	S	СО
1724.6	w	acetaldehyde
1702ª	m	formaldehyde
1443.9	w	propadienol
1434.0	S	ethylene
1345.1ª	W	acetaldehyde
1148.9	m	propadienol
947.4	S	ethylene

Product band frequencies for the mercury lamp photolysis of a $C_3H_4/{\rm ^{18}O_3}/Xe$ matrix (1:4:200) previously photolyzed with the Kr-ion laser

^aPresent in Table 1 (col.3).

1817.3, 1371.9, 965.2, 958.6, 933.6, 931.2 and 928.9 cm⁻¹. The ¹⁸O counterparts of these bands are observed as negative peaks in Fig. 4b. The bands observed growing in Fig. 4b are listed in Table 4.

When the above experiment was carried out in an Ar matrix similar results were obtained. In the $C_3H_4 + ({}^{18}O)_3$ experiment, a notable behavior was displayed by the 1818.1 cm⁻¹ band. As shown in Fig. 5, while 80% of the intensity of the nearby 1797.9 cm⁻¹ feature was lost under mercury lamp photolysis, 1818.1 cm⁻¹ did not change at all (note the ordinate scale change between Fig. 5a and 5b). Thus 1818.1 cm⁻¹ and its counterparts (-H, $-^{16}O$ 1823.4 cm⁻¹; -D, $-^{16}O$ 1765.2, 1768.2 cm⁻¹; -D, $-^{18}O$ 1761.0 cm⁻¹) are identified as absorptions due to a primary photolysis product that is neither lost nor produced during mercury lamp photolysis. Isotopic shifts for deuterium are 0.970 ($-^{16}O$), and 0.968 ($-^{18}O$), and for oxygen 0.997 (C_3H_4) and 0.996 (C_3D_4).

To help in the identification of the products, the matrix spectra were recorded of some of the molecules observed in the gas phase reaction. Acrolein in Ar at M/R = 250 showed its strongest peak at 1708.4 cm⁻¹ and additional peaks, in order of decreasing intensity, at: 958.0, 910.3, 1421.4, 1157.1, 2814.9, 991.7, 1359.4, 2761.2 and 564.8 cm⁻¹. All these absorptions, except 564.8, are close in frequency and relative intensity to product features listed in Table 3 (differing on the average by 0.8 cm^{-1}). These bands are designated A in Tables 1,2 and 3. Photolysis of this matrix with the AH-4 lamp through a CsI window caused the above bands to decrease in intensity and a new set of absorptions to appear at: 1715.3, 1616.6, 1405.3, 914.4, 993.1, 970.0, 2839.7 and 2747.4 cm⁻¹. The four most intense bands correspond to product features in Table 3, both in frequency (average difference 0.3 cm^{-1}) and in relative intensity. These features are labeled A' in Tables 1, 2 and 3.

In a final experiment with acrolein, a matrix of $acrolein/O_3/Ar$ (1:4:200) was photolyzed for three hours with the red lines of the Kr-ion laser. Photolysis products were observed with absorptions at (decreasing intensity): 1745.5 (1757.4, 1726.9), 1132.9, 2148.0 and 2139.9 cm⁻¹.

Matrix spectra of other possible products are already in the literature with most intense features as follows: ethylene (Ar) absorbs at 948 and 1441.0 cm⁻¹ [13]; CO at 2138.4 cm⁻¹ [14]; formaldehyde (N₂) at 1740.3 and 1499.7 cm⁻¹ [15]; and ethylene oxide (Ar) at 879.0 cm⁻¹ [11].

If ethylene is produced in the reaction it is possible for it to undergo photolytic reaction with ozone [11]. So as to detect whether this reaction would interfere with the allene reaction, matrix samples of $C_2H_4/O_3/Ar$ (1:4:200) were photolyzed with the red lines of the Kr-ion laser. The strongest bands, in order of decreasing intensity, are: 876.5, 1352.7(1348.8), 1742.2(1738.4), 2147.9(2142.2), 1430.9(1426.0) and 1119.7 cm⁻¹. With the assistance of Hawkins and Andrews' work most of the bands were assigned [11]. Similar experiments were also performed in Xe and Kr matrices. It was observed that in all three matrices the product distribution, i.e., the relative intensities of the bands, remained constant for all three matrix materials.

Because of disagreements in the literature about the carbonyl stretching frequency of cyclopropanone and cyclobutanone an infrared spectrum was recorded for cyclobutanone in an Ar matrix (M/R=100) [6]. The strongest spectral feature was at 1795.5 cm⁻¹, with other strong absorptions at 2980.0, 1396.0, 1207.0 and 1070.2 cm⁻¹. None of these frequencies were observed in the allene experiments.

DISCUSSION

Tables 1 and 3 show that the most intense product absorption in an argon matrix, at 1708.4 cm⁻¹, is only a minor feature in the xenon matrix spectra. Furthermore, photolytic decomposition of the allene/ozone samples in xenon is eight times faster than in argon (Fig. 2). Identification of the products is the first step toward understanding these differences.

Identification of products

Acrolein

Acrolein was identified by recording its spectrum in argon(Ar/acrolein=250/l) and xenon (Xe/acrolein=110/l). The nine most intense absorptions of acrolein correspond, with an average frequency discrepancy of 0.8 cm^{-1} and with the same relative intensity, to nine product features in Table 3. The tenth most intense absorption, at 564.8 cm⁻¹ was not observed, undoubtedly

because of the high noise level near the end of the Ge optical window. Five additional, weaker features appeared in both the reference spectrum and in the first column of Table 3 and are also assigned to acrolein.

Thus acrolein is surely the compound that is prominent among the argon matrix products and a minor product in xenon matrices. In Table 1, it is seen that absorption at 1708.3 cm⁻¹ has an optical density of only 0.04 and the second most intense acrolein absorption, near 958 cm^{-1} , is obscured by a product band clearly too intense to be from acrolein. None of the still weaker features of acrolein could be positively identified.

Carbon monoxide

In both xenon and argon matrices, Kr-ion laser photolysis produces two prominent absorptions in the spectral range where CO is known to absorb: in xenon, at 2136.4 and 2133.7 cm⁻¹ and in argon, at 2143.5 and 2137.5 cm⁻¹. Hallam lists the frequencies of CO isolated in Xe as 2141.0 cm^{-1} and isolated in Ar as 2149.4 cm⁻¹ [16]. For 1:500 ratios of CO/M the band is observed at 2138.0 cm^{-1} for Ar and for Xe, at 2133.1 cm^{-1} . Yet, identification is not immediately obvious because nearest neighbor shifts of several wavenumbers are known to occur. All ambiguity is removed, however, by our ¹⁸O experiments, since a diatomic should display almost exact agreement with the calculated shift. The calculated ${}^{16}O/{}^{18}O$ shift for CO predicts that the two xenon features. if both are due to CO, would shift to 2084.9 and 2082.3 cm⁻¹. Our product spectra with ${}^{18}O_2$ in xenon show features at 2109.6 and 2082.3 cm⁻¹ (see Table 1). The agreement between calculated and observed shifts show that in xenon, 2133.7 cm^{-1} is ascribable to CO and 2136.4 cm^{-1} is not. Accord is equally definitive in the argon matrix spectra where calculated ¹⁸O frequencies fall at 2091.8 and 2086.0 cm^{-1} . The observed product features at 2117.2, 2110.3 and 2086.3 cm⁻¹ (see Table 3) show that 2137.5 cm⁻¹ is due to CO and 2143.5 cm^{-1} is not.

Ketene

Ketene offers a possible explanation for the remaining products feature near 2140 cm^{-1} , even though it is not expected as a product in the Havel mechanism [1]. The spectrum of ketene in Ar matrices has been carefully studied by Moore and Pimentel [17]. In an Ar matrix they found a dideutero shift of 29 cm⁻¹. Tables 1 and 3 show that our observed dideutero shifts are 29.4 cm⁻¹ in xenon and 26.4 cm⁻¹ in argon. Our corresponding shifts due to ¹⁸O substitution are almost the same, 26.8 and 26.3 cm⁻¹, respectively. The second most intense absorption of ketene in Ar occurs at 1381 cm⁻¹ and it shifts to 1225 cm⁻¹ upon deuteration. We find product absorptions in this spectral region (1379.9 and 1378.2 cm⁻¹ in Ar) but with too high an intensity to be due to ketene alone. Nevertheless, the observed isotopic shifts identify ketene as a minor product.

Ethylene

Four product absorptions are found in Table 3 that show deuterium shifts but no ¹⁸O shifts. In order of decreasing intensity, these are 947.5, 1440.1, 2993.9 and 3106 cm⁻¹. These match well, both in frequency and relative intensity the absorptions of ethylene isolated in nitrogen; 947.1, 1437.7, 2989.6 and 3107.1 cm⁻¹ [18]. The absorptions of ethylene isolated in argon are listed by Rytter and Green [13]: 948, 1441.0, 2997.0 and 3114.0 cm⁻¹. Slight variations in frequency are expected since the ethylene must have other reaction products as neighbors and is thus not isolated. The identification of ethylene is made definitive by isotopic shifts with deuteration (1440.1/1074.5=1.340 and 947.5/729.5=1.300: see Table 3 and complete absence of ¹⁸O shift.

Further product identification was substantially aided by photolysis with a mercury arc ($\lambda > 237$ nm with CsI filter).

Acrolein

When a matrix of acrolein in argon (1:250) was irradiated with the Kr-ion laser no change was observed. Irradiation with the mercury lamp, however, caused the loss of the absorptions due to acrolein and growth of absorptions at 1713.8, 1405.3 and 914.4 cm⁻¹. All three of these features are present, in the same relative intensity, among the product bands listed in Table 3. Furthermore, each is within 5-6 cm^{-1} of a parent acrolein band which points to the identity of the product as the *cis*-rotameric form of acrolein (A'). At room temperature most of the acrolein is in the *trans* form thus trapped at 12 K. Upon photolysis the *trans* is converted to *cis* by rotation through the carboncarbon single bond. Vibrational frequencies for *cis*-acrolein determined from vibrational contours of the near UV bands that appear in the gas phase fluorescence of acrolein [19] are in good agreement with the frequencies obtained in this work. Approximately 30% of the trans-acrolein isomerizes to cis-acrolein upon mercury lamp photolysis. Recently Gebicki and Krantz reported that they had been able to induce rotation of matrix isolated acrolein through UV photolysis, but they have yet to publish their results [20].

Cyclopropanone

When products of the Kr-ion laser photolysis were photolyzed with a mercury lamp, a group of bands decreased in intensity, the strongest of these being the 1815 cm⁻¹ feature in Ar or the 1817.3 cm⁻¹ in Xe. Ethylene and CO are detected as photolysis products. This group of bands exhibit similar intensity ordering in Xe and Ar matrices and are thus assigned to the same product, cyclopropanone. The vibrational frequencies and relative intensities obtained here are in good agreement with the most recent gas phase spectrum reported for cyclopropanone (Table 5) [7]. This assignment is supported by the mercury lamp photolysis work. Cyclopropanone exhibits an electronic absorption

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TABLE

Cyclopropanone bands in a xenon matrix (frequencies in cm^{-1})

C ₃ H ₄ O	C ₃ H ₄ O ⁻¹⁸ O	C ₃ D ₄ O	C ₃ D ₄ O- ¹⁸ O	Lit. values ^c	Assignment
3092a _b b	م م	2196.4 1856.2, 1854.9, 1852.9	2194 - 1033 8	3086	C-H comb. (1038+815) comb (953+981)
۱ ^۵ ۱	، ^م	1794.1	1792.1		comb. (980s + 814)
1979.1	۹- ٦	1760s	1756	1980	comb. (1040 + 930)
1901.3	1892.7, 1890.6	ł	I	1905	comb. (960s + 950s)
1867.8	1860.0	1	ł	1868	over. (930×2)
1819.9, 1817.3	1798,7, 1796.4	1843.4, 1837, 7, 1831.8	1815.1	1818	C=0
1371.9	1371.6	٩	1038.0		CH_2
٩	٩	981.3	٩ ٦	1050	C-C
٩٦	1042	953.7	952.7	1028	C-C
965.2, 958.6	963, 956	808.3	804.6	980, 949	CH_2
933.6, 931.2, 928.6	929.4	814.8	813.9	920	CH_2

^aTentative. ^bObscured by ozone, allene or CO_2 . ^cRef. 47.

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band that extends from 380 to 260 nm. Gas phase photolysis in this region leads to ethylene and CO.

Band assignments for cyclopropanone were determined by comparison to similar molecules. For example, methylenecyclopropanone exhibits a CH_2 inplane motion for the ring groups at 1410 and 1353 cm⁻¹ [21]. Cyclopropanone shows an absorption at 1378 cm⁻¹, that exhibits a large deuterium shift, which we have assigned to CH_2 . Absorptions assigned to the C–C stretches are lower in frequency than the stretches for similar three membered cyclic compounds. This is most likely due to the longer C–C bond length associated with the stretch opposite to the carbonyl, as determined by microwave work [6b].

Some bands are assigned to overtones and combinations. The 1980.2 cm⁻¹ absorption in argon is probably a combination mode of the 934.3 and 1040s cm⁻¹ bands. Upon deuteration these two bands shift to 987.4 and 812.2 cm⁻¹: the combination band can be found at 1795 cm⁻¹. The 1867.9 cm⁻¹ feature in Xe is due to twice the 931.2 cm⁻¹ band. A deuterated counterpart could not be found.

However, these combinations and overtones are unusually intense. For example, the 1901.3 cm⁻¹ band in Xe is of similar intensity to the bands to which it has been related. (In Xe $A_{1901,3}=0.069$, $A_{965,2}=0.076$ and $A_{931,2}=0.070$.) This anomalous behavior leads to the suspicion that mixing is occurring with the strong carbonyl stretch. The carbonyl stretch at 1817 cm^{-1} also exhibits unexpected behavior. A rather modest shift of 20 cm⁻¹ is observed with ¹⁸O substitution. Upon deuteration instead of shifting to lower frequency, the stretch increases in frequency by approximately 20 cm^{-1} . This behavior corroborates the observation that mixing is occurring between the carbonyl and one or more of the overtones or combinations. The extent of mixing appears to be greater for non-isotopic cyclopropanone. For cyclopropanone-¹⁸O the combination and overtone bands become weaker $(A_{1901,3}:A_{1817,3}$ in Xe goes from 1:3 to 1:10 from CP to CP-¹⁸O). For cyclopropanone- d_4 several of the overtone and combination features could not be detected. It would appear that the carbonyl is sharing its intensity with at least three features, 1979.1, 1901.3 and 1867.3 cm^{-1} bands in Xe.

Additional evidence of mixing is supplied by some preliminary work with allene-d₁. An allene-d₁/O₃/Ar (1:4:200) matrix was photolyzed with the Krion laser and then exposed to the mercury lamp. Bands due to cyclopropanone grew in with the Kr-ion laser and decreased with the mercury lamp photolysis. The difficulty of the experiment arises from the fact that there are six possible different molecules of acrolein-d₁ (*trans* and *cis*) as well as two formaldehyde, ketene and allene oxide molecules which complicate the spectra. However it was evident from the experiment that six bands disappeared with mercury lamp photolysis and are thus attributed to cyclopropanone-d₁: they are 1924.9, 1917.3, 1852.6, 1806.5, 953.6, 868.5 cm⁻¹. The 1852.6 and 1806.6 cm⁻¹ bands are of similar intensity. Since there is only one possible structure for cyclopropanone- d_1 , all these bands arise from the same molecule. Two bands in the carbonyl stretching frequency region indicate that the partial deuteration has altered the extent of mixing. In this particular case it would seem that one of the combination or overtone bands is very close in frequency to the carbonyl stretch allowing for a greater degree of mixing which causes the two features to share equally the intensities.

The possibility that a Fermi resonance occurs in cyclopropanone was suggested earlier by Rodriguez et al. [7]. Based on some preliminary unpublished results with cyclopropanone- d_2 and $-d_4$ they speculated that a Fermi resonance was occurring between the carbonyl and an overtone or combination of fundamentals in the 900–1050 cm⁻¹ region. The work presented here supports their interpretation.

Allene oxide

Only four bands with absorbance greater than 0.010 units are left unassigned; these are 1823.4, 1109.2, 881.1 and 793.8 cm^{-1} in an Ar matrix. These four bands did not disappear upon mercury lamp photolysis and are not due to any of the already mentioned photoproducts. They retain the same relative intensity ordering in all three matrices, except for 1107 cm^{-1} in Xe which is partially obscured by a reactant absorption. The 1823.4 cm⁻¹ band exhibits a small but obvious ¹⁸O isotopic shift (5 cm^{-1}) indicating that the molecule contains oxygen, but not in a carbonyl form. The large deuterium shift (55 cm^{-1}) points to a carbon–carbon double bond stretch. Allene oxide is the only expected reaction product which has not been assigned, and it also happens to possess a C=C bond. Using a diatomic model approximation for allene oxide, we can picture the methylenic and epoxide groups, with masses 14 and 42 respectively, moving as a single mass. The expected frequency for the allene oxide-¹⁸O molecule would be 1813.0 cm⁻¹, thus predicting a 10.4 cm⁻¹ shift. A similar calculation for the frequency of the deuterated species leads to a shift of 98.5 $\rm cm^{-1}$. Taking into account the roughness of the approximation this diatomic model supports the conclusion that this band is assigned to a C=C stretch of allene oxide. Comparison with substituted allene oxides adds additional weight to this assignment [2,8]; 1-t-butylallene oxide exhibits a strong infrared absorption at 1815 cm^{-1} in a CCl₄ solution.

The band at 1109.2 cm^{-1} exhibits a 7.3 cm⁻¹ shift with ¹⁸O substitution and a 189.6 cm⁻¹ shift upon deuteration. For ethylene oxide, bands are observed at 1126 and 1154.5 cm⁻¹ in an Ar matrix [11]. Only the 1154.5 cm⁻¹ feature shows an appreciable ¹⁸O shift (5 cm⁻¹) signaling some C-O stretching character. Both bands are attributed to CH₂ motions of oxirane [6b]. Thus the 1109.2 cm⁻¹ absorption exhibits comparable behavior to CH₂ motions of oxirane (ethylene oxide).

The 881.1 cm⁻¹ feature in Ar matrices is also common for epoxides. In ethylene oxide matrix spectra a feature is observed at 879.0 cm^{-1} , shifting to 854.5 $\rm cm^{-1}$ in oxirane-¹⁸O and to 755.0 cm⁻¹ with deuteration [11]. This absorption is attributed to the ring breathing motion of ethylene oxide. The 881.1 cm⁻¹ band shows a larger deuterium shift (120 vs. 100) and a smaller ¹⁸O shift (13 vs. 22) than ethylene oxide. However the shifts are similar enough to conclude that the 881.1 cm⁻¹ band is due to ring breathing motions of allene oxide. The effect of ¹⁸O substitution is reduced in allene oxide by the additional mass supplied by the ethylenic group to the epoxide ring. The additional hydrogens lead to an increased deuterium effect.

Finally the 793.8 cm⁻¹ band does not shift with ¹⁸O substitution, indicating that it is due to CH_2 motions of the ethylene group. By comparison with literature spectra of substituted allene oxides and qualitative agreement with similar molecules, we conclude that allene oxide has been produced in the photolysis of allene and ozone with red light. This is the first reported synthesis of unsubstituted allene oxide. Vibrational assignments are summarized in Table 6.

In summary, the products of the photolytic reaction of allene with ozone in cryogenic matrices are confidently assigned to allene oxide, cyclopropanone, *cis* and *trans*-acrolein, ethylene, carbon monoxide, ketene and formaldehyde.

Matrix effects

Product distribution

From the spectra (Fig. 1) and product growth curves (Fig. 2) it is apparent that the product distributions and kinetics for the allene-ozone photolytic reaction are strongly dependent on matrix material. A common product to all three matrices, cyclopropanone, reaches half of its total growth after approximately 3 min in a xenon matrix, 10 min in a krypton matrix and 21 min in an argon matrix. Whereas product distributions for argon and krypton matrices are similar, xenon matrices show marked differences. The ratio of areas (not peak heights listed in Tables 1, 2 and 3) of cyclopropanone (1817 cm⁻¹) to

TABLE 6

Frequencies	(cm^{-1})			Assignment
C_3H_4O	C ₃ H ₄ O~ ¹⁸ O	C ₃ D ₄ O	$C_3D_4O^{-18}O$	
1823.4	1818.1	1768.2, 1765.2	1761.0	C=C
1109.2	1101.9	919.9	912.7	$C-O, CH_2$
881.1	868.5	748.0	739.6	ring
793.8	793.8	629.2^{b}	623.2 ^b	CH_2

Allene oxide bands in an argon matrix^a

^aFrequencies from Table 3.

^bTentative assignment.

acrolein (1708 cm^{-1}) is 2.5 times larger for a xenon matrix than it is for an argon matrix. Thus in xenon there is more cyclopropanone and much less acrolein than in argon matrices.

Excited states of ozone

Gaseous ozone exhibits a weak absorption near 647 nm in the long wavelength tail of the Chappuis band. Because of the low extinction coefficient, this absorption has, in the past, been assumed to be due to a transition from a ground state singlet to an excited triplet [22]. Theoretical work leaves much ambiguity about the energies and even the sequence of the expected levels. Of the three most recent calculations [23–25], the two that include configuration interaction probably present the most useful guidance. Jones [23] summarizes the vertical excitation energies in his Table IV. Thunemann et al. [24] found five of these at energies near or below 44 kcal mol⁻¹ (647 nm): ${}^{3}B_{2}$, 27.7; ${}^{3}A_{2}$, ${}^{33.2}$; ${}^{3}B_{1}$, ${}^{36.7}$; ${}^{1}A_{2}$, ${}^{39.7}$; ${}^{1}B_{1}$, ${}^{45.0}$ kcal mol⁻¹. Hay and Dunning [25] place the vertical excitation of only the ${}^{3}B_{2}$ state below 44 kcal mol⁻¹ (at 36.9 kcal mol⁻¹) but the ${}^{3}B_{1}$ and ${}^{3}A_{2}$ states are reasonably close at 46.4 and 48.2 kcal mol⁻¹, respectively. These workers found the vertical excitations to the lowest singlet states, ${}^{1}A_{2}$ and ${}^{1}B_{1}$, to be at 54.0 and 55.6 kcal mol⁻¹.

Levene and coworkers [26] have recently conducted photofragmentation studies of O_3 at nine wavelengths in the range 638 to 560 nm. All of their CARS spectra are interpreted with the premise that excitation of ozone from the ground ${}^{1}A_{1}$ state to the ${}^{1}B_{1}$ state is involved. If this premise is correct, these experiments would show that the ${}^{1}B_{1}$ state has sufficient absorption at 638 nm (44.8 kcal mol⁻¹) for their experiment, in accord with the theoretical calculations of Thunemann et al. [24] and contradicting the placement of this state by Hay and Dunning [25].

It is clear that there are probably three triplet $({}^{3}B_{2}, {}^{3}A_{2}, \text{ and } {}^{3}B_{1})$ and, less confidently, two singlet states of ozone $({}^{1}A_{2} \text{ and } {}^{1}B_{1})$ that might be excited at 647 nm. This provides a basis for interpreting the matrix effect on absorption coefficient and on photolysis rate.

Absorption by ozone in argon and xenon

Figure 6 shows the UV-visible spectra for allene/ozone/argon and for allene/ozone/xenon matrices at 12 K. The absorbance for the xenon matrix is much higher and it is possible that there is a change in the structure of the absorption band. At 647 nm, absorbance is about four times larger in xenon matrix than in argon matrix. This observation correlates with the faster rate of photolysis in xenon, which occurs about eight times more rapidly in xenon than in argon.

Two possible explanations for these observations are considered, both associated with the spin-orbit coupling provided by the xenon environment.

First, if only triplet excitation occurs in argon matrix, then the entire ab-



Fig. 6. UV-vis spectra of (A) allene/ozone/Ar matrix (1:4:200) at 12 K, 3.01 mmol of ozone/Ar (4:100) deposited. (B) allene/ozone/Xe matrix (1:4:200) at 12 K, 2.26 mmol of ozone/Xe (4:100) deposited.

sorption change would be attributed to enhancement of the transition probability for the spin-forbidden singlet-triplet transition. This enhancement would account for half the increased reaction rate. The remainder would have to be attributed to higher reaction quantum yield in xenon, although the spin-orbit perturbation might be expected to lower quantum yield because of increased rate of quenching through internal conversion.

A second more self-consistent argument can be based on the assumption that only (or predominantly) singlet excitation occurs in the argon matrix (as assumed by Levene et al. [26] for gas-phase excitation). Now, the heavy atom environment would relax singlet-triplet selection rules to add absorption into triplet states. This would account for both the increased absorption and the apparent change of absorption contours. Furthermore, the longer lived triplet states now excited might well have higher quantum yields for reaction than the shorter-lived singlet states, providing a plausible explanation for the eightfold increase in reaction rate associated with the fourfold increase in absorption. We will base further discussion on this assumption, that predominantly singlet excitation occurs in argon matrix and that the heavy atom environmert of xenon adds new reaction channels by relaxing spin-selection rules to permit direct access to triplet reaction surfaces.

Reaction symmetry considerations

Gas phase photolysis of ozone results in chemistry attributable to the formation of ground state oxygen atoms $O({}^{3}P)$ and ground state oxygen molecules, $O_{2}({}^{3}\Sigma_{g}^{-})$ [26]. By microscopic reversibility, it is clear that these two states could either originate from a singlet or a triplet excited state of ozone (as well as from a quintet state). Once these two fragments are separated, the gas phase reaction with allene will be entirely due to the reaction of $O(^{3}P)$ with ground state allene, so reaction will occur on a triplet reaction surface to give, in the first instance, a triplet product.

The situation is more interesting if the ozone-allene photochemistry all occurs within a matrix cage and within the spin-correlation time. Now, it matters whether the ozone excitation is nominally to a singlet or to a triplet state, since that fixes the symmetry of the "supermolecule" that begins as reactants held in proximity and ends as products. The significance of this is seen by contrasting the implications for final product Y of initial (nominal) excitation of ozone to its ${}^{1}B_{1}$ vs. its ${}^{3}B_{1}$ state.

$$^{1}[O_{3}(^{1}A_{1}) \cdot C_{3}H_{4}(^{1}A_{1})] + h\nu \rightarrow ^{1}[O_{3}(^{1}B_{1}) \cdot C_{3}H_{4}(^{1}A_{1})]$$

 $\rightarrow {}^{1}[O_{2}({}^{3}\Sigma_{g}^{-})\cdot {}^{3}Y] \quad (1)$

$${}^{1}[O_{3}({}^{1}A_{1}) \cdot C_{3}H_{4}({}^{1}A_{1}] + h\nu \rightarrow {}^{3}[O_{3}({}^{3}B_{1}) \cdot C_{3}H_{4}({}^{1}A_{1})] \rightarrow {}^{3}[O_{2}({}^{3}\Sigma_{g}^{-} \cdot {}^{1,3}Y]$$
(2)

In reaction (1), the overall singlet supermolecule symmetry *requires* that Y be a triplet. Reaction (2), on the other hand, occurs on a triplet surface and the triplet character of $O_2({}^{3}\Sigma_{g}^{-})$ permits Y to be *either* a singlet or triplet.

A proposed model

These considerations lead us to a model which, we believe, is consistent with and suggested by our information.

(a) In argon matrix, excitation of the ozone-allene cage complex is predominantly to a singlet state correlated with the $O_3({}^1B_1)$. In xenon matrix, because of spin-orbit perturbations by the matrix environment, there is additional excitation to an ozone-allene triplet state correlated with one or more of the ozone triplet states ${}^{3}B_2$, ${}^{3}A_2$, and/or ${}^{3}B_1$.

(b) Chemistry proceeds within the cage, retaining the initial symmetry throughout. This leads to a preference in argon matrix for products that can be formed initially in a triplet state whereas in xenon matrix, products that can be formed initially in a singlet state become accessible.

(c) The symmetry considerations in (b) account for the change in the major product from acrolein in argon matrix to cyclopropanone in xenon.

The excited states of the products

Figure 7 shows the energy relationships among reactants and the major products as obtained from heats of formation [7,10,27] and from spectroscopic data [7,19,28]. The shaded boxes indicate estimates of triplet level positions and uncertainty ranges.

According to our model, cyclopropanone is the major product in xenon be-



Fig. 7. Energy level diagram for the Kr-ion laser photolysis of the allene-ozone system.

cause of excitation of ozone triplet states to produce cyclopropanone in an excited singlet state (reaction 2). Figure 7 shows that there is such an excited singlet state, the ${}^{1}A_{2}$ state, perhaps 30–40 kcal below the ozone triplet states.

The situation is less clear for formation of acrolein, which we would attribute to singlet ozone excitation to produce acrolein in an excited triplet state (reaction 1). The energy available after 647 nm light absorption is 153 kcal above the acrolein ground state, an energy at which there are undoubtedly additional acrolein states, both singlet and triplet, which are, as yet, unidentified, hence not shown in Fig. 7.

Mechanistic details

The photochemistry of ozone in the presence of allene results, of course, in oxygen atom transfer. The simplest mechanistic scheme is that transfer to the end atom provides a facile route to acrolein, whereas transfer to the central atom would lead to cyclopropanone. Each of these transfers produces, in the first instance, a biradical. In central atom attack, the biradical formed would have an allyl-like stabilization. This is, no doubt, the ${}^{1}A_{2}$ state of cyclopropanone, formed through π , π^{*} excitation and the allyl stabilization undoubtedly accounts for the relatively low excitation energy of the ${}^{1}A_{2}$ and ${}^{3}A_{2}$ states of cyclopropanone. A comparable argument is not evident for the end atom attack except to note that it leads to acrolein with very high internal energy.

It must be noted that ozone dissociation followed by cage escape of an $O(^{3}P)$ atom furnishes a second mechanistic route to products. That route results exclusively in triplet reaction surface chemistry, so the only difference to be expected between argon and xenon matrices would lie in the different ease of cage-escape and atom migration. It is possible that isolated ozone molecules, which might account for about half of the ozone present, show a greater extent of cage escape in the somewhat larger xenon lattice than in the argon lattice. If so, this could contribute to the larger final percentage of allene consumption in xenon over that observed in argon.

CONCLUSIONS

The matrix photolysis of ozone in the presence of allene meshes well with Havel's earlier studies [1] of the reaction of $O({}^{3}P)$ atoms with allene in the gas phase. Havel postulated a mechanism that led to the expectation of products cyclopropanone and allene oxide, but neither was observed. Both were detected in the present work, allene oxide for the first time by any technique. A number of minor and secondary products were identified, as well: ethylene, carbon monoxide, ketene, and formaldehyde.

Equally interesting was the influence of the matrix on the branching ratio between the major products, acrolein and cyclopropanone. This outcome is explainable in terms of the spin-orbit coupling environment furnished by the xenon matrix, which would favor both direct photolytic excitation to a triplet reaction surface and, then, formation of the final product in an excited singlet state. Thus, this system adds to the list of examples [29,30] of condensed phasexxx photochemistry in which the product distribution can be controlled by the matrix environment.

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