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Photochemistry of Argon Matrices Containing Nitric Oxide and Carbonyl Sulfide. 1. The Photolysis of the Nitric Oxide Dimer, *cis*-N₂O₂

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Irradiation at $\lambda = 220\text{--}320$ nm causes the *cis* isomer of the nitric oxide dimer isolated in an argon matrix at 13–20 K to photodissociate to N₂O and oxygen atoms. The photochemical behavior is interpreted in terms of the structure and bonding of *cis*-[NO]₂ and comparisons are made with predictions based on *ab initio* CI and CNDO/S calculations. The oxygen atoms are observed to react with CO, OCS, NO, and *cis*-[NO]₂ under these conditions and there is evidence for two conformers of the product *sym*-N₂O₃. Concurrent photolysis of OCS in Ar/OCS/NO matrices leads to products characteristic of sulfur atom transfer including SO₂ and regenerated OCS. The use of isotopic enrichment to identify products has yielded direct evidence in support of the cage-recombination mechanism for the matrix reaction of sulfur atoms with O₂.

I. Introduction

In contrast to the many examples of oxygen-atom-transfer reactions known to take place in low-temperature matrices,¹ there are few reports of analogous reactions involving sulfur atoms. The reactions of sulfur atoms, generated by the ultraviolet photolysis of gaseous carbonyl sulfide, OCS, with organic substrates are well documented,² but the only matrix reactions to be investigated to date are those with sulfur and oxygen atoms or dioxygen molecules.³ While sulfur dioxide is readily identified by its phosphorescence as the major product of the sulfur atom–dioxygen reaction, the mechanism of its formation is uncertain.⁴ The present research was undertaken with two principal ambitions: (i) to explore the scope for synthesis of matrix reactions involving sulfur atoms and (ii) to distinguish between the possible mechanisms of product formation.

Our interest in the chemistry of sulfur–nitrogen compounds prompted us to carry out experiments designed to synthesize thio analogues of nitrogen oxides by addition of sulfur atoms to nitric oxide. The identification and characterization of the molecules SNO and SN₂O₂ form the subject of a subsequent paper.⁵ It soon became apparent from our experiments, however, that the complex photochemistry of argon matrices containing carbonyl sulfide and nitric oxide hinged on the presence of the nitric oxide dimer, *cis*-[NO]₂. Although there is some disagreement concerning the visible absorption spectrum of the dimer,^{6–8} *cis*-[NO]₂ exhibits in both the gaseous⁹ and condensed^{6,7} phases an intense ultraviolet absorption at wavelengths shorter than 240 nm. This paper describes the photolysis of *cis*-[NO]₂ by irradiation of the ultraviolet band system and presents evidence for the mechanisms by which many of the secondary photoproducts are formed.

II. Experimental Section

Apparatus. Matrices were deposited on a CsI window cooled to 13–20 K by means of a Displex refrigerator (Air Products, Model CS 202). Temperatures were measured with a chromel vs. iron-doped gold thermocouple or with a hydrogen vapor bulb and were varied by adjusting the voltage applied to a 20-W heater wound around the second stage of the refrigerator. Surrounding the cold station of the refrigerator was a shroud which was evacuated to a pressure less than 10^{−7} torr.

Infrared spectra were recorded by using either a Perkin-Elmer Model 225 or a Perkin-Elmer Model 580 spectrophotometer. With the internal calibration available on the Model 580 instrument, wavenumbers were reproducible to better than 0.4 cm^{−1}, and the resolution was invariably better than 0.5 cm^{−1} in measurements involving precise wavenumber determination.

A Philips HPK 125 W medium-pressure mercury arc was used for photolysis of samples. A 2- or 4-cm water filter reduced the amount of infrared radiation incident upon the matrix during

photolysis, and a Pyrex filter removed short-wavelength ultraviolet light ($\lambda < 300$ nm).

Chemicals. All noncondensable gases—Ar (grade “X”, 99.995%), O₂ (grade “X”, 99.97%), and CO (grade “X”, 99.97%)—were used as received from the British Oxygen Co. Carbonyl sulfide and nitric oxide, as supplied by Matheson, were purified by fractionation *in vacuo*. Isotopically enriched samples of ¹⁵NO (99.1% ¹⁵N), ¹³CO (97% ¹³C), and ¹⁸O₂ (99% ¹⁸O) were used as supplied by Prochem. A sample of nitric oxide enriched in ¹⁸O (44%) was prepared by the reaction of NO with ¹⁸O₂ followed by reduction of the product, ¹⁶ON¹⁸O, with elemental selenium at 30 °C.¹⁰

Procedure. The matrix sample was premixed to give a matrix ratio (matrix gas:guest species) in the order of 100:1 using standard manometric techniques. The matrix was usually deposited at 20 K for 2 h at a rate of 0.7 mmol/h. Better isolation was invariably achieved with deposition at the lower temperature of 13 K but the desire for weakly scattering, transparent matrices necessitated a reduction in the deposition rate to 0.2 mmol/h with a correspondingly longer deposition time of up to 24 h. The matrix was irradiated either during or after deposition, the former technique generally giving higher yields of photoproducts.

III. Results

This paper is concerned with the mechanisms of photoinduced reactions occurring in argon matrices containing carbonyl sulfide and nitric oxide. The photoproducts of immediate interest are all well-characterized species and therefore only those vibrational data directly relevant to the mechanistic details will be presented here.

The infrared spectrum of an argon matrix containing carbonyl sulfide and nitric oxide (Ar:OCS:NO = 100:1:1) deposited at 13–14 K is shown in Figure 1. The matrix had been irradiated with full Hg-arc emission during deposition. Band assignments to the molecule nitrogen oxide sulfide, SNO, are discussed fully in a later paper;⁵ the remaining products are conveniently divided into three groups: (i) oxides of nitrogen, (ii) oxides of carbon, and (iii) oxides of sulfur. Experiments were performed to identify the precursors to each of the three product types and these are treated separately.

(i) **Nitrogen Oxides.** The infrared spectrum of an argon matrix containing carbonyl sulfide and the nitric oxide isotopomers N¹⁶O

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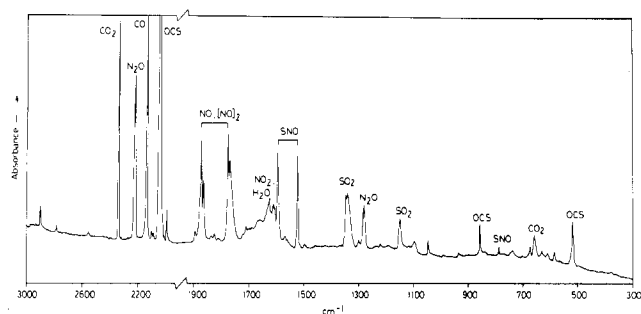


Figure 1. Infrared spectrum of an Ar matrix deposited at 13–14 K and containing 1% OCS and 1% $^{14}\text{N}^{16}\text{O}$; irradiation was carried out during deposition with the unfiltered emission of a medium-pressure Hg arc.

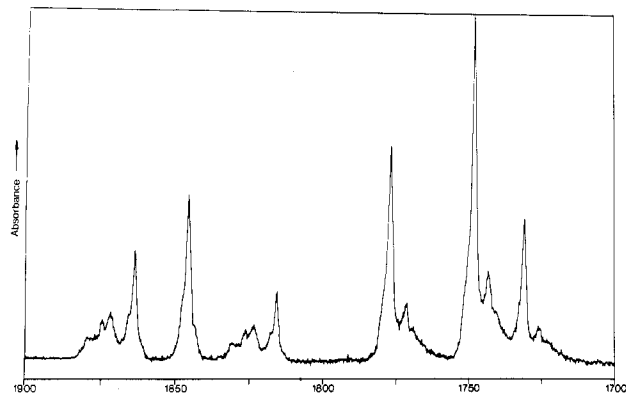


Figure 2. Region 1700–1900 cm^{-1} in the infrared spectrum of an Ar matrix having the composition $\text{Ar}:\text{OCS}:^{14}\text{N}^{16}\text{O}:^{14}\text{N}^{18}\text{O} = 200:2:1.2:1$ deposited at 18–20 K.

and N^{18}O ($\text{Ar}:\text{OCS}:\text{N}^{16}\text{O}:\text{N}^{18}\text{O} = 200:2:1.2:1$) deposited at 18–20 K is shown in Figure 2. The spectrum in the region 1700–1900 cm^{-1} was found to be identical with that of a matrix similar in composition except that it contained no carbonyl sulfide. The band positions, relative intensities, and assignments are summarized in Table I. Two intense asymmetric triplets at 1863.3, 1845.3, and 1817.8 cm^{-1} and 1776.4, 1747.2, and 1730.2 cm^{-1} are readily identified with the $^{16}\text{O}/^{18}\text{O}$ isotopomers of *cis*-[NO] $_2$ by comparison with previous results for these species trapped in a variety of matrices.¹¹ Weak bands on the low-frequency flank of the absorptions originating in the antisymmetric N=O stretching modes of *cis*-[NO] $_2$ are attributed to *cis*-[NO] $_2$ aggregates and *trans*-[NO] $_2$, again by analogy with previous results.¹¹ On deposition at 20 K of an argon matrix containing 1% nitric oxide, the absorption associated with monomeric NO at 1871.3 cm^{-1} appeared only as a weak shoulder on the *cis*-[NO] $_2$ band at 1863.3 cm^{-1} ; deposition at 17–18 K caused these two features to be of similar intensity; deposition at 13–14 K caused the monomer absorption to be twice as intense as the dimer absorption.

Irradiation of an argon matrix containing only nitric oxide with the full emission of the Hg arc reduced the intensity of all bands except those associated with monomeric NO. In addition to the bands at 1871.3, 1838.5, and 1823.0 cm^{-1} attributable to the molecules $^{14}\text{N}^{16}\text{O}$, $^{15}\text{N}^{16}\text{O}$, and $^{14}\text{N}^{18}\text{O}$, respectively, we noted weaker satellites at 1879.0, 1846.0, and 1830.3 cm^{-1} whose locations and insensitivity to photolysis suggest that they too originate in monomeric NO. Presumably therefore the occupancy of a different matrix environment accounts for the blue shift of 7.3–7.7 cm^{-1} with respect to the primary bands. By contrast, irradiation of the matrix with Pyrex-filtered Hg-arc emission ($\lambda > 320 \text{ nm}$) induced no change in the spectrum.

An argon matrix containing nitric oxide ($\text{Ar}:\text{NO} = 100:1$) was deposited at 20 K and photolyzed for 163 min with the unfiltered output of an Hg arc (Figure 3A,B). During irradiation, the

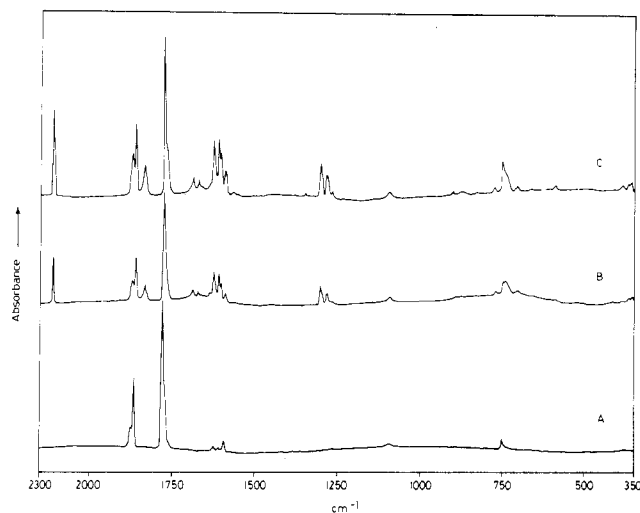


Figure 3. Infrared spectrum of an Ar matrix containing 1% $^{14}\text{N}^{16}\text{O}$: (A) after deposition of 13 μmol of NO at 20 K; (B) after 163-min irradiation with an unfiltered Hg arc; and (C) after deposition of a further 13 μmol of NO with concurrent Hg-arc irradiation.

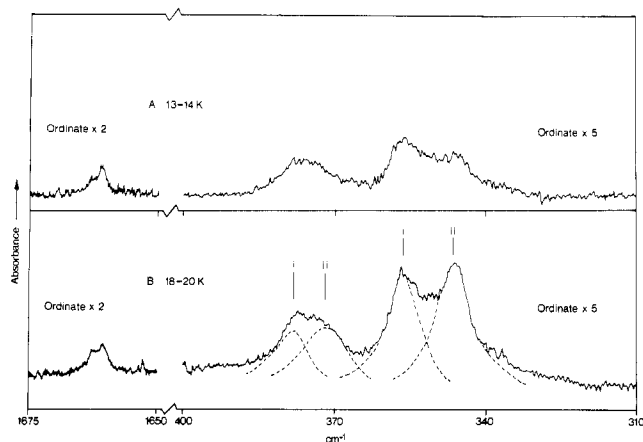


Figure 4. Temperature dependence of the infrared spectrum of *sym*- N_2O_3 formed during photolysis of an Ar matrix containing 1% ^{15}NO . The matrix was exposed to the unfiltered emission of an Hg arc while being maintained at (A) 13–14 or (B) 18–20 K.

absorptions characteristic of *cis*-[NO] $_2$ were reduced by 40% while absorptions characteristic of the following molecules appeared and grew: NO_2 (1612.0/1606.5 cm^{-1}),¹² N_2O (2227.0, 1283.7, and 586.9 cm^{-1}),¹² and both symmetric N_2O_3 (ON–O–NO) and asymmetric N_2O_3 (O_2N –NO).¹³ The spectrum was confused in the region near 750 cm^{-1} by the presence of a weak band which grew, broadened, and split with photolysis. Although the final absorption pattern may reflect in part the formation of N_2O_4 ,¹² the contour showed no discernible change in shape or position when ^{15}NO replaced ^{14}NO . Unfortunately we have not been able to identify the origin of the prephotolysis band but its appearance in almost all our experiments—even those with undoped argon matrices—points to an impurity.

Irradiation of a matrix with the composition $\text{Ar}:\text{OCS}:^{14}\text{NO}:^{15}\text{NO} = 200:2:1:1$ gave an equiintense quartet of absorptions at 2227.0, 2205.5, 2180.8, and 2156.9 cm^{-1} associated with the four $^{14}\text{N}/^{15}\text{N}$ isotopomers of N_2O . A sample containing N^{16}O and N^{18}O in the proportions 1.3:1 yielded a doublet with components at 1283.7 and 1245.7 cm^{-1} having intensities in the ratio ca. 1.3:1 and arising from the molecules N_2^{16}O and N_2^{18}O , respectively. A nitrogen matrix with the composition $^{14}\text{N}_2:^{15}\text{NO} = 100:1$ displayed after photolysis absorptions attributable only to the isotopomer $^{15}\text{N}_2\text{O}$, with no sign of $^{14}\text{N}_2\text{O}$.

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TABLE I: Wavenumbers of Infrared Absorptions of Ar Matrices Containing Nitric Oxide and Deposited at 18–20 K

wavenumber, ^a cm ⁻¹				intensity ^b	N ₂ matrix wavenumber, ^c cm ⁻¹	absorber ^d
¹⁴ N ¹⁶ O	¹⁵ N ¹⁶ O	¹⁴ N ¹⁶ O + ¹⁵ N ¹⁶ O	¹⁴ N ¹⁶ O + ¹⁴ N ¹⁸ O			
1879.0		1879.0	1879.0	wm		¹⁴ N ¹⁶ O ⁺
1874.2			1874.2	wm	1870	[¹⁴ N ¹⁶ O] ₂ *
1871.3		1871.3	1871.3	m	1876 ^e	¹⁴ N ¹⁶ O ⁺
1863.3		1863.3	1863.3	s	1870	[¹⁴ N ¹⁶ O] ₂
		1849.9		m	1857	[¹⁶ O ¹⁴ N ¹⁵ N ¹⁶ O]
	1846.0			wm		¹⁵ N ¹⁶ O ⁺
			1845.3	s	1851	[¹⁶ O ¹⁴ N ¹⁴ N ¹⁸ O]
			1843.0	w, sh		
	1841.4	1841.4		wm, sh	1835	[¹⁵ N ¹⁶ O] ₂ *
	1838.5	1838.5		m	1842.9 ^e	¹⁵ N ¹⁶ O ⁺
	1830.7	1830.7		s	1837	[¹⁵ N ¹⁶ O] ₂
			1830.3	wm		¹⁴ N ¹⁸ O ⁺
			1826.0	wm		[¹⁴ N ¹⁸ O] ₂ *
			1823.0	m	1827.4 ^e	¹⁴ N ¹⁸ O ⁺
			1817.8	sm		[¹⁴ N ¹⁸ O] ₂
1780.0				w, sh	1785	[¹⁴ N ¹⁶ O] ₂ *
1776.4		1776.4	1776.4	vs	1776	[¹⁴ N ¹⁶ O] ₂
1771.1			1771.1	m		[¹⁴ N ¹⁶ O] ₂ aggregate
1768.3			1768.3	w, sh	1764	<i>trans</i> -[¹⁴ N ¹⁶ O] ₂
		1757.9		s	1756	[¹⁶ O ¹⁴ N ¹⁵ N ¹⁶ O]
	1748.2			m	1752	[¹⁵ N ¹⁶ O] ₂ *
			1747.2	vs	1747	[¹⁶ O ¹⁴ N ¹⁴ N ¹⁸ O]
	1745.1	1745.1		vs	1744	[¹⁵ N ¹⁶ O] ₂
			1742.5	m		[¹⁶ O ¹⁴ N ¹⁴ N ¹⁸ O] aggregate
			1740.0	w, sh		<i>trans</i> -[¹⁶ O ¹⁴ N ¹⁴ N ¹⁸ O]
	1740.0			m		[¹⁵ N ¹⁶ O] ₂ aggregate
	1737.1			vw, sh	1738	<i>trans</i> -[¹⁵ N ¹⁶ O] ₂
			1730.2	s	1738	[¹⁴ N ¹⁸ O] ₂
			1725.0	wm		[¹⁴ N ¹⁸ O] ₂ aggregate

^a Error limits: ± 0.4 cm⁻¹. ^b s, strong; m, medium; w, weak; sh, shoulder; v, very. ^c References 11 and 12. ^d Structure of [NO]₂ is *cis* unless stated otherwise; * denotes less stable form of *cis*-[NO]₂ (see ref 11 and 12); † denotes doublet pattern associated with monomeric NO believed to be due to its existence in more than one environment (see text). ^e Wavenumber for gaseous molecule, ref 12.

Bands characteristic of *sym*-N₂O₃ each took the form of a doublet. The relative intensities of the components of these doublets exhibited a marked temperature dependence, as shown in Figure 4 for *sym*-¹⁵N₂O₃. Photolysis of a matrix with Ar:¹⁵NO = 100:1 at 13–14 K yielded bands at 1660.5, 377.6, and 356.3 cm⁻¹ with weak shoulders at 1662.2, 371.6, and 346.6 cm⁻¹ (Figure 4A). A similar sample photolyzed at 18–20 K gave rise to a spectrum in which the shoulders were relatively more intense than at the lower temperature (Figure 4B). A matrix deposited at 18–20 K and cooled to 13–14 K prior to photolysis yielded an infrared spectrum of *sym*-N₂O₃ similar to that of a matrix deposited and photolyzed at 13–14 K. Subsequent warming of the matrix to 18–20 K had no effect on the relative intensities of the four absorptions between 330 and 400 cm⁻¹. Bands due to *sym*-¹⁴N₂O₃ exhibited the same behavior. The vibrational wavenumbers of *sym*-¹⁴N₂O₃ and *sym*-¹⁵N₂O₃ as formed in argon matrices in these conditions are summarized in Table II.

(ii) *Carbon Oxides*. Irradiation of an argon matrix containing 1% OCS with the unfiltered output of an Hg arc generated new absorptions at 2147.6, 2141.2, and 2137.6 cm⁻¹ associated with CO,¹⁴ and at 2341 and 1526 cm⁻¹ associated with CO₂^{15,16} and CS₂,^{16,17} respectively. The CO₂ and CS₂ absorptions were of comparable intensity. Whenever *cis*-[NO]₂ was also present in the matrix, the yield of CO₂ formed on irradiation with an unfiltered Hg arc was much enhanced.

Two experiments were performed to identify the source of the CO₂ in irradiated Ar/NO/OCS matrices. A sample with Ar: NO:CO = 100:1:1 deposited at 18–20 K to improve the yield of *cis*-[NO]₂ exhibited after 260-min unfiltered Hg-arc irradiation an infrared spectrum in which the absorbance of the CO band at 2137.6 cm⁻¹ was reduced from 0.645 to 0.605; bands associated

TABLE II: Wavenumbers of Infrared Absorptions due to *sym*-N₂O₃ Formed on Photolysis of Ar Matrices Containing Nitric Oxide

wave- number, ^a cm ⁻¹	assignment ^b	N ₂ matrix wave- number, ^c cm ⁻¹
O ¹⁴ N–O– ¹⁴ NO		
1694.8 } 1689.8 }	N=O stretching	1689.7
385.6 } 379.5 }	N–O–N deformation	387.4
363.5 } 354.1 }	antisymmetric O=N–O deformation	365.5
O ¹⁵ N–O– ¹⁵ NO		
1662.2 } 1660.5 }	N=O stretching	1661.6
377.6 } 371.6 }	N–O–N deformation	381.2
356.3 } 346.6 }	antisymmetric O=N–O deformation	359.0

^a Error limits: ± 1.0 cm⁻¹. ^b Taken from ref 12. ^c Taken from ref 13.

with CO₂ and N₂O at ca. 2341 and 2227 cm⁻¹ appeared with an absorbance of ca. 0.18. Secondly, a matrix with Ar:NO:OCS = 100:1:1 was doped with 1% ¹³CO and deposited at 18–20 K. Unfiltered Hg-arc irradiation for 180 min reduced the OCS absorption at 859.1 cm⁻¹ by 27% (Figure 5A,B), increased the O¹³CS absorption at 1996.8 cm⁻¹ by 100%, and produced bands characteristic of ¹³CO₂ at 2275.7 cm⁻¹, ¹²CO₂, ¹²CO, and N₂O. The bands arising from the antisymmetric C=O stretching modes of ¹²CO₂ and ¹³CO₂ in Figure 5B have absorbances roughly in the ratio 1.35:1.

(iii) *Sulfur Oxides*. A sample with Ar:OCS:N¹⁶O:N¹⁸O = 200:2:1.28:1 was deposited at 13–14 K with continuous irradiation using an unfiltered Hg arc. The infrared spectrum in the region

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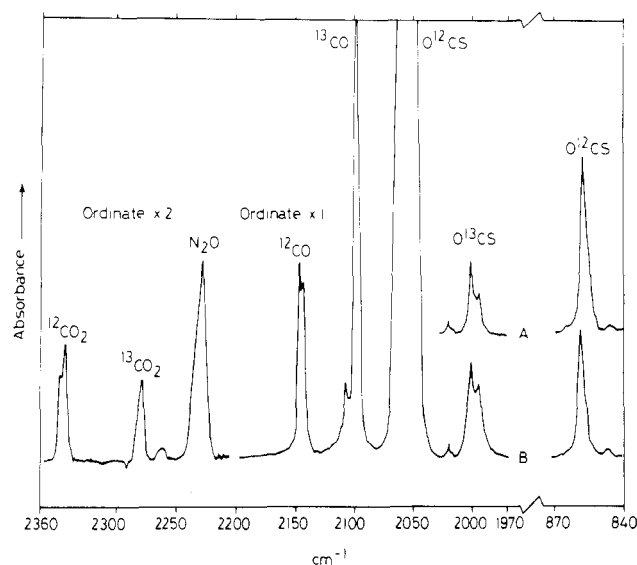


Figure 5. Infrared spectrum of an Ar matrix having the composition Ar:OCS:NO: ^{13}CO = 100:1:1:1 (A) before and (B) after unfiltered Hg-arc irradiation for 180 min.

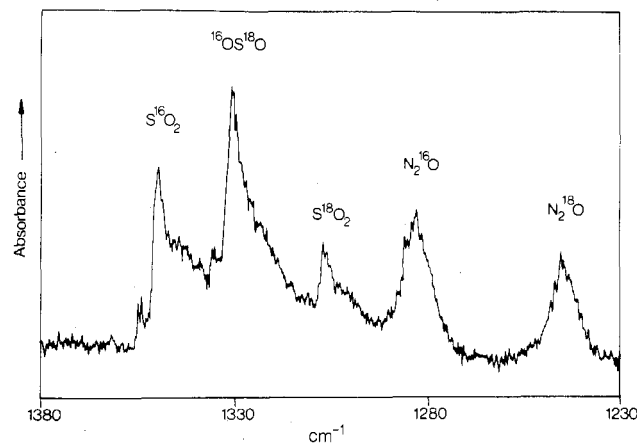


Figure 6. Infrared spectrum of an Ar matrix having the composition Ar:OCS: N^{16}O : N^{18}O = 200:2:1.28:1 after deposition at 13–14 K with concurrent unfiltered Hg-arc irradiation.

1230–1380 cm^{-1} (Figure 6) exhibited an unsymmetrical triplet of absorptions at 1307.5, 1331.5, and 1350.7 cm^{-1} the origin of which must be monomeric S^{16}O_2 , $^{16}\text{OS}^{18}\text{O}$, and S^{16}O_2 , respectively.¹⁸ The approximate relative intensities of these bands, as measured by the peak heights, were 1.70:2.48:1.00 while the calculated values appropriate to a random distribution of oxygen isotopes with $^{16}\text{O}:^{18}\text{O}$ = 1.28:1 are 1.64:2.56:1.00. Each monomer absorption exhibited a broad shoulder on its low-frequency flank with an intensity about half that of the primary feature.

To examine the mechanism of SO_2 formation in argon matrices, a sample with Ar:OCS: $^{16}\text{O}_2$: $^{18}\text{O}_2$ = 200:2:1:1 was deposited at 15 K and photolyzed with the unfiltered emission from an Hg arc. Figure 7 illustrates three regions of the infrared spectrum and the absorption wavenumbers are listed in Table III. Both C^{16}O_2 and $^{18}\text{OC}^{16}\text{O}$ were generated in the same proportions as were S^{16}O_2 and S^{18}O_2 characterized by the absorptions at 1351.0 and 1150.1 cm^{-1} and 1307.5 and 1099.7 cm^{-1} , respectively. A weak, broad absorption was also observed at ca. 1321 cm^{-1} and this increased in intensity as the photolysis proceeded (Figure 7A,B). Annealing the matrix to 40 K for 5 min gave rise, however, to a disproportionate accretion of the 1321- cm^{-1} absorption compared with the features due to S^{16}O_2 and S^{18}O_2 , as well as producing an additional band attributable to C^{18}O_2 (Figure 7C). With suc-

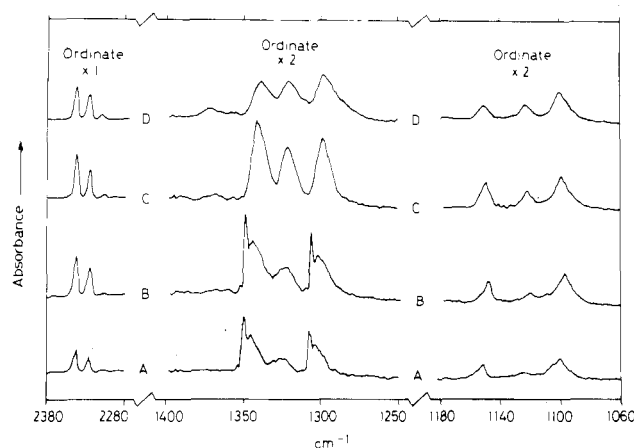


Figure 7. Infrared spectrum of an Ar matrix having the composition Ar:OCS: $^{16}\text{O}_2$: $^{18}\text{O}_2$ = 200:2:1:1: (A) after 30-min unfiltered Hg-arc irradiation at 15 K; (B) after a further 44-min irradiation; (C) after annealing to 40 K for 5 min; and (D) after irradiation of a similar matrix at 20 K followed by annealing to 40 K for 5 min.

TABLE III. Wavenumbers of Infrared Absorptions Appearing on Photolysis of Ar Matrices Containing OCS and ^{18}O -Enriched O_2

wave-number, ^a cm^{-1}	intensity ^b	isotopic shift, cm^{-1}	absorber	reported isotopic shift, cm^{-1}
2344.2	sh	15.9	C^{16}O_2 ^c	17.00 ^d
2341.0	s		$^{16}\text{OC}^{18}\text{O}$ ^c	
2327.3	sh		C^{18}O_2	
2325.1	s		S^{16}O_2	
2307.7	vw	17.4	S^{16}O_2	18.19 ^d
1385	vw		S^{16}O_2	
1371.2	w, br		S^{16}O_2	
1358.2	w		S^{16}O_2	
1354.5	w, sh	43.5	S^{16}O_2	43.3, ^e
1351.0	s, sp		$[\text{S}^{16}\text{O}_2]_n$	
1340.2	var		$[\text{S}^{16}\text{O}_2]_n$	
1321.3	var	23.1	$[\text{S}^{16}\text{O}_2]_n$	19.1 ^e
1307.5	s, sp		$[\text{S}^{16}\text{O}_2]_n$	
1298.2	m, br		$[\text{S}^{16}\text{O}_2]_n$	
1150.1	m, br		$[\text{S}^{16}\text{O}_2]_n$	
1122.4	m, br	27.7	S^{16}O_2	28.4 ^e
1099.7	m, br		S^{16}O_2	
1154.2	w, sh	42.9	S_2^{16}O	41.4 ^f
1111.3	w, sh		S_2^{18}O	

^a Error limits: CO_2 , ± 0.8 cm^{-1} ; SO_2 , ± 1.6 cm^{-1} ; otherwise, ± 0.4 cm^{-1} . ^b s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad; sp, sharp; var, variable. ^c Splitting due to occupancy of different matrix sites (cf. ref 15). ^d Relates to gaseous CO_2 molecule. See: Berney, C. V.; Eggers, D. F., Jr. *J. Chem. Phys.* 1964, 40, 990. Chackerian, C., Jr.; Eggers, D. F., Jr. *J. Mol. Spectrosc.* 1968, 27, 59. ^e See ref 18. ^f See ref 19.

cessive periods of photolysis and annealing, the positions of the broad absorptions between 1300 and 1360 cm^{-1} shifted to lower frequency as their intensity increased. Wavenumbers quoted in Table III refer to annealed samples and represent what appeared to be the ultimate values. Deposition and photolysis of the same sample (Ar:OCS: $^{16}\text{O}_2$: $^{18}\text{O}_2$ = 200:2:1:1) at 20 K revealed the same overall features but the band at 1321 cm^{-1} and that associated with C^{18}O_2 were relatively more intense than before at all stages of photolysis and annealing (Figure 7D).

Finally, as illustrated in Figure 7, A and B, weak shoulders could be discerned at 1154.2 and 1111.3 cm^{-1} . These are assigned to S_2^{16}O and S_2^{18}O , respectively, on the basis of their proximity to absorptions associated with S^{16}O_2 and S^{18}O_2 and the $^{18}\text{O}/^{16}\text{O}$ isotopic shift of 42.9 cm^{-1} .¹⁹ There is evidence for the simulta-

(18) Allavena, M.; Rysnik, R.; White, D.; Calder, V.; Mann, D. E. *J. Chem. Phys.* 1969, 50, 3399. Maillard, D.; Allavena, M.; Perchard, J. P. *Spectrochim. Acta, Part A* 1975, 31A, 1523.

(19) Hopkins, A. G.; Daly, F. P.; Brown, C. W. *J. Phys. Chem.* 1975, 79, 1849.

neous growth of a very weak band near 675 cm⁻¹ probably associated with the second stretching fundamental of S₂O but there was no detectable feature near 380 cm⁻¹ corresponding to the bending mode, weakest of the three in infrared absorption. The appearance of the bands at 1154 and 675 cm⁻¹ showed that S₂O is also a minor product in photolyzed Ar/OCS/NO matrices. Prolonged photolysis of such a matrix led to the growth of a very weak absorption at ca. 382 cm⁻¹ which may well arise, at least in part, from the bending mode of S₂O, although the interpretation of the spectrum is clouded by the proximity of bands due to N₂O₃ [see section III(i) and Table II] and by the presence of other potential absorbers in the molecules SNO and SN₂O₂.⁵

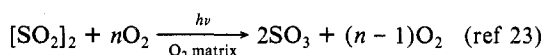
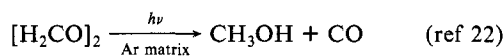
Very weak and broad absorptions at ca. 1371.2 and 1358.2 cm⁻¹ grew during both photolysis and annealing of argon matrices containing OCS together with an equimolar mixture of ¹⁶O₂ and ¹⁸O₂ (Figure 7B-D, Table III); these are presumed to originate in ¹⁶O/¹⁸O isotopomers of SO₃.²⁰

IV. Discussion

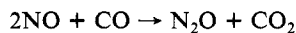
Photolysis of *cis*-[NO]₂. Unfiltered Hg-arc irradiation of *cis*-[NO]₂ isolated in an argon matrix results in the formation of N₂O together with NO₂, *sym*-N₂O₃ (ON-O-NO), and *asym*-N₂O₃ (ON-NO₂). The detection of CO₂ after a similar treatment of Ar/NO/CO samples demonstrates that oxygen atoms may be transferred from *cis*-[NO]₂ to a substrate molecule, in this case CO, during the period of formation of N₂O. Furthermore, in the presence of OCS, irradiation of ¹⁸O-enriched *cis*-[NO]₂ yields SO₂ and N₂O enriched in ¹⁸O to the same extent as the precursor, *cis*-[NO]₂ (Figure 6), demonstrating that OCS provides no oxygen for these products. Since Pyrex-filtered irradiation (λ > 320 nm) has no effect on *cis*-[NO]₂ and the gaseous nitric oxide dimer exhibits a continuous absorption extending from 245 nm to wavelengths less than 200 nm,⁶ we propose that the primary photolytic process involving *cis*-[NO]₂ in argon matrices at 13–20 K is



and that the O atoms so produced react further with matrix dopants. The failure to react with N₂^{1,21} suggests the predominance of O(³P) rather than O(¹D) atoms. The photolability of *cis*-[NO]₂ demonstrates anew the capacity of weak complex formation to influence the photochemistry of a molecule; it may be compared, for example, with the following matrix reactions which have recently come to light:

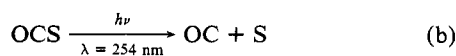


The photodissociation of *cis*-[NO]₂ is the reverse of the matrix reaction used by Guillory and Hunter to show that the stable nitric oxide dimer contains an N-N bond.¹¹ It also invites comparison with the oxygen-transfer reaction



involving NO either coordinated as in [Ir(NO)₂(PPh₃)₂]⁺ or adsorbed on the surface of certain metals and believed to evolve via ONNO moieties.²⁴

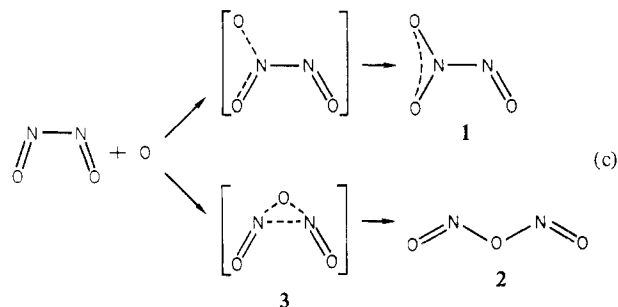
Together with the simultaneous fragmentation of carbonyl sulfide



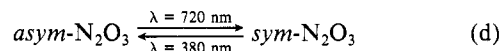
the photolytic formation of oxygen atoms from *cis*-[NO]₂ accounts

for much of the chemistry observed in irradiated Ar/OCS/NO matrices. Discussion of the mechanisms by which photoproducts form is presented according to product type.

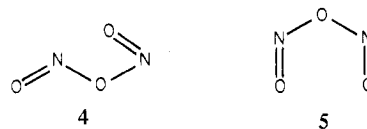
Mechanisms of Product Formation. (i) **Nitrogen Oxides.** Reaction of photoproduct oxygen atoms with NO and *cis*-[NO]₂ leads to the formation of NO₂ and N₂O₃, respectively. Asymmetric N₂O₃ (1) can result from a simple addition mechanism



while the formation of symmetric N₂O₃ (2) requires either (i) a rearrangement of the asymmetric isomer or (ii) oxygen atom insertion into the N-N bond of *cis*-[NO]₂. A photoinduced isomerization of N₂O₃ has been observed by Varetti and Pimentel¹³



In the present experiments, in which unfiltered Hg-arc irradiation was used, this isomerization could occur in both directions. However, our spectra for *sym*-N₂O₃ differ from those of Varetti and Pimentel¹³ in that all three of the observed bands are doublets (1694.8/1689.8, 385.6/379.5, and 363.5/354.1 cm⁻¹). While this could be associated with the change in host matrix from nitrogen to argon, the thermal behavior of components of these bands supports the assignment to two different conformers of *sym*-N₂O₃. The relative intensities of the doublet components are independent of the temperature of deposition but dependent on the temperature at which *sym*-N₂O₃ is formed, i.e., the photolysis temperature. Matrix site occupancy is more likely to be influenced by the thermal history of the lattice while the nature of the products will depend on the energy available during their formation. Further support for the assignment to two conformers is provided by the vibrational spectrum. The conformers 2, 4, and 5 are expected



to differ most in the deformation motions of the N-O-N and O=N-O subunits and values of Δν/ν = 2.95 × 10⁻³, 15.8 × 10⁻³, and 25.9 × 10⁻³ for the pairs of absorptions at 1694.8/1689.8, 385.6/379.5, and 363.5/354.1 cm⁻¹, respectively, are consistent with this property. According to Varetti and Pimentel,¹³ normal-coordinate analysis suggests that the trans-trans conformer 2 is present in nitrogen matrices. Details of these calculations have not appeared in the literature, however, and it is uncertain whether the same conformational preferences prevail in argon matrices.

The highest occupied molecular orbital of *cis*-[NO]₂ is of a₁ symmetry and thus located in the plane of the molecule.⁸ Interaction of the N-N bond with an oxygen atom in the molecular plane will be least hindered in the direction which results in the activated complex 3 since the dimer is nearly rectangular in both the gas²⁵ and solid²⁶ phases. The structure of complex 3 resembles most nearly that of 5, the *cis*-*cis* conformer, while reorientation of a single N=O group results in 4. Thus, the species i and ii of Figure 4 are most likely 5 and 4, respectively, with 5 being

(20) Lovejoy, R. W.; Colwell, J. H.; Eggers, D. F., Jr.; Halsey, G. D., Jr. *J. Chem. Phys.* **1962**, *36*, 612. Jones, P. R.; Taube, H. *J. Phys. Chem.* **1973**, *77*, 1007.

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(23) Sodeau, J. R.; Lee, E. K. C. *J. Phys. Chem.* **1980**, *84*, 3358.

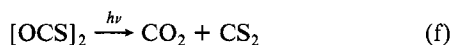
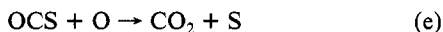
(24) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.

(25) Western, C. M.; Langridge-Smith, P. R. R.; Howard, B. J.; Novick, S. E. *Mol. Phys.* **1981**, *44*, 145.

(26) Lipscomb, W. N.; Wang, F. E.; May, W. R.; Lippert, E. L., Jr. *Acta Crystallogr.* **1961**, *14*, 1100.

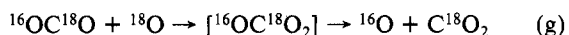
preferred at the lower temperatures of 13–14 K when the matrix is more rigid. Furthermore, any weak interaction between the terminal oxygen atoms, such as occurs in *cis*-[NO]₂,⁷ will stabilize 5 relative to 2 and 4. The possibility that conformer ii is 2 cannot be ruled out, however, since the relative ease of formation of 2 and 4 from 3 must depend on the detailed mechanism of reorientation in the matrix.

(ii) *Carbon Oxides*. Since both ground-state O(³P) and excited O(¹S) atoms react with CO to yield CO₂,²⁷ the formation of CO₂ in the present experiments gives no clue to the electronic state of the oxygen atoms ejected from *cis*-[NO]₂ during photolysis. The observation of similar quantities of ¹²CO₂ and ¹³CO₂ after irradiation of Ar/OCS/NO/¹³CO matrices demonstrates, however, that OCS itself is a source of CO₂. This can occur in two ways, viz.



The latter reaction occurs to a small extent in Ar/OCS matrices but yields a quantity of CO₂ which is negligible in comparison with that implied by the results illustrated in Figure 5. That matrix contained 1% of both OCS and ¹³CO and 27% of the OCS was dissociated on irradiation. On the assumptions that the yield of CO₂ via reaction between oxygen atoms and CO is proportional to the concentration of CO and that CO is the sole source of CO₂, the maximum ratio ¹²CO₂:¹³CO₂ is expected to be 0.27. The observed ratio of 1.35 shows that more than 80% of the ¹²CO₂ is formed via reaction e at this stage of photolysis. No evidence was found for SCO₂, which is a likely intermediate in the reaction. Hence, we believe that the reactions of oxygen atoms (i) with OCS and (ii) with CO afford respectively the primary and secondary sources of the CO₂ generated in these conditions.

Irradiation of an Ar/OCS matrix containing equimolar proportions of ¹⁶O₂ and ¹⁸O₂ yields C¹⁶O₂ and ¹⁶OC¹⁸O in similar proportions. That there is present also a small amount of C¹⁸O₂, which is augmented by annealing, argues for an intermediate with three equivalent oxygen atoms at some stage of the reaction. In keeping with the results of previous studies involving, for example, the photolysis of solid CO₂,²⁸ this intermediate is most plausibly identified with the molecule CO₃ (reaction g). Such a change



parallels reaction e, in which CO₂ is formed by the attack of oxygen atoms on OCS. Of CO₃ itself there was no direct evidence, the spectra revealing no hint of absorption near 972 cm⁻¹ corresponding to the most intense feature of the molecule as formed in solid CO₂.²⁸ However, this does not invalidate its intermediacy in the reaction between oxygen atoms and CO₂: the C¹⁸O₂ absorption was relatively weak even after annealing and it is doubtful whether CO₃ would be formed in concentrations sufficient to be detected by its IR spectrum; added to this, the results of previous studies²⁸ lead us to anticipate destruction of CO₃ by Hg-arc irradiation.

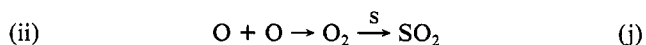
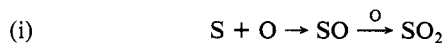
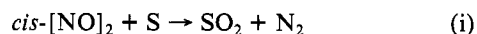
No evidence has previously been found for the recombination of sulfur atoms and CO in matrix-isolation or other experiments in the condensed phases.²⁹ The twofold increase in intensity of the O¹³CS absorption at 1996.8 cm⁻¹ after irradiation of an Ar/OCS/NO/¹³CO matrix demonstrates that reaction h does



occur. About 4–5% of photogenerated sulfur atoms react in this way, as determined by the change in intensity of bands associated with O¹²CS and O¹³CS. The proportion of recombination of S/CO pairs after photodissociation of OCS may well be much higher on account of their proximity in the matrix and this estimate

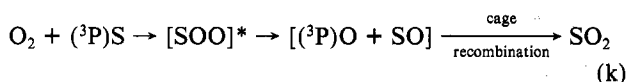
should therefore be regarded as a lower limit.

(iii) *Sulfur Oxides*. Photolysis of a matrix with the composition Ar:OCS:N¹⁶O:N¹⁸O = 200:2:1.28:1 results in a triplet of absorptions between 1300 and 1360 cm⁻¹ associated with the molecules S¹⁶O_x¹⁸O_{2-x} (x = 0–2);¹⁸ the relative intensities of the bands show that *cis*-[NO]₂ is the sole source of oxygen. Sulfur dioxide may be produced in one of two ways:



The present experiments cannot distinguish between these processes, although it is possible to predict which is more likely to occur. Reaction i entails interaction between one photoproduct (S atoms) and one relatively abundant precursor (*cis*-[NO]₂) in a bimolecular reaction: reactions j each involve no less than three photoproducts (O and S atoms) in what are essentially termolecular processes. Furthermore, for every molecule of SO₂ formed, reaction i requires the destruction of just one *cis*-[NO]₂ molecule, compared with two such molecules as required by reactions j. No oxygen atoms are available until *cis*-[NO]₂ has been formed and photolyzed: Figure 3 reveals that, at most, 50% of the available *cis*-[NO]₂ dissociates photolytically and the oxygen atom photoproduct is also consumed in reactions yielding CO₂, NO₂, and N₂O₃. On the balance of probabilities, therefore, we favor reaction i as the major source of SO₂ in Ar/NO/OCS matrices.

The reaction between O₂ and sulfur atoms has been observed by monitoring the $\bar{a}^3\text{B}_1\text{-}\bar{X}^1\text{A}_1$ phosphorescence of SO₂ or its infrared spectrum between 1100 and 1400 cm⁻¹.³ Smardzewski has suggested a mechanism for this matrix reaction, summarized in eq k, on the basis of kinetic studies in the gas phase,⁴ but no direct



evidence has yet been offered on the basis of matrix experiments.

The possibility that the reaction occurs on photolysis of Ar/OCS/NO matrices prompted an investigation of the photochemistry of Ar/OCS matrices including equimolar proportions of ¹⁶O₂ and ¹⁸O₂ which were irradiated at, and annealed to, various temperatures. Although there was no hint of any absorption near 1100 cm⁻¹ attributable to SO,³⁰ our results are entirely consistent with Smardzewski's proposed mechanism, as illustrated by several features. If cage recombination of (³P)O and SO were 100% efficient, no absorptions characteristic of ¹⁶OS¹⁸O would be observed. In the extreme case that all (³P)O/SO pairs diffuse apart, each of the regions 1090–1160 and 1300–1360 cm⁻¹ should exhibit a 1:2:1 triplet of absorptions corresponding to scrambled S¹⁶O_x¹⁸O_{2-x} (x = 0–2) isotopomers. Traces A and B of Figure 7 show that at the lowest temperature employed (15 K), when the matrix is most rigid, little ¹⁶OS¹⁸O is produced. Furthermore, the diffuseness of the absorption is indicative of aggregation resulting from its formation by a diffusion-controlled process. Annealing the matrix to 40 K allows further reaction of sulfur atoms trapped in the lattice at 15 K and, although both S¹⁶O₂ and S¹⁸O₂ monomer bands have now disappeared, the growth in all other absorptions due to SO₂ molecules is much closer to that expected for a free diffusion process. Thus, at 40 K few of the (³P)O/SO pairs recombine. Irradiation of a similar sample at 20 K followed by annealing (Figure 7D) leads to a similar spectrum except for a slight increase in the intensity of the ¹⁶OS¹⁸O absorptions relative to the S¹⁶O₂ and S¹⁸O₂ absorptions consistent with a greater degree of diffusion during the initial photolysis.

The formation of C¹⁶O₂ and ¹⁶OC¹⁸O in similar quantities noted in the preceding section testifies independently to the intermediacy of oxygen atoms in this system. The mechanism proposed by Smardzewski for the formation of SO₂ from sulfur atoms and O₂ (eq k)⁴ gives a ready explanation for the formation of these oxygen

(27) Fournier, J.; Deson, J.; Vermeil, C.; Pimentel, G. C. *J. Chem. Phys.* **1979**, *70*, 5726.

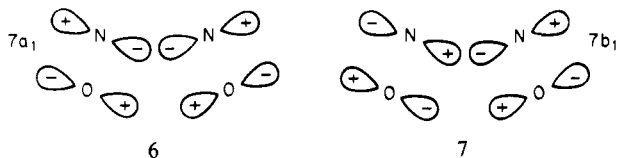
(28) Moll, N. G.; Clutter, D. R.; Thompson, W. E. *J. Chem. Phys.* **1966**, *45*, 4469. Jacox, M. E.; Milligan, D. E. *Ibid.* **1971**, *54*, 919.

(29) Gollnick, K.; Leppin, E. *J. Am. Chem. Soc.* **1970**, *92*, 2217.

(30) Hopkins, A. G.; Brown, C. W. *J. Chem. Phys.* **1975**, *62*, 2511.

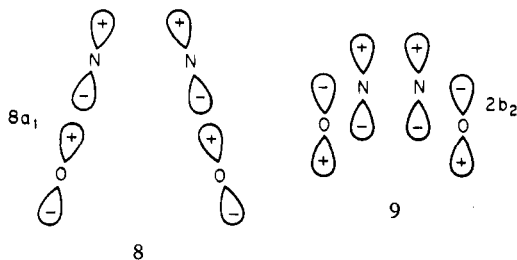
atoms without recourse to photodecomposition of either SO₂ or O₂, each a potential source of oxygen atoms in its own right. Thus, Sodeau and Lee have reported that photolysis of [SO₂]₂ in an oxygen matrix yields, among other products, SO₃ and O₃ (see Discussion); however, they failed to procure any such change with [SO₂]₂ in an argon matrix doped with O₂, even on irradiation of the sample with the output of a 1000-W Hg arc.²³ High-energy photolysis ($\lambda < 254$ nm) of O₂ under the conditions of our experiments cannot be discounted but the facility of the oxidation of CO to CO₂ makes it much more likely that the oxygen atoms are derived from the reaction of sulfur atoms with O₂.

Structure, Bonding, and Photochemistry of *cis*-[NO]₂. The wavenumbers of the N=O stretching vibrations of matrix-isolated *cis*-[NO]₂ fall between those reported for the gaseous and solid nitric oxide dimer.¹² This suggests that a planar molecule with $\angle\text{ONN} = \text{ca. } 98^\circ$ and $r(\text{N-N}) = \text{ca. } 2.25 \text{ \AA}$ exists in an argon matrix, to judge by its structure in the vapor²⁵ and solid²⁶ phases. Calculations based on the structure of the solid predict a ¹A₁ ground state for *cis*-[NO]₂.^{7,8} Furthermore, the N-N bond is of σ symmetry and weak interaction between the terminal oxygen atoms adds stability to the almost rectangular structure. CNDO/S calculations⁷ predict a strong absorption at 250 nm corresponding to a transition to a B₁ state which is σ -antibonding with respect to the N-N bond. In this approximation, the ¹B₁ and ³B₁ states are degenerate. Excitation of an electron from the 7a₁ orbital 6 to the lowest unoccupied b₁ orbital 7 satisfies the symmetry



requirements for this transition. Ab initio configuration-interaction calculations support the earlier CNDO/S analysis with regard to the nature of the N-N bonding but conclude that for $r(\text{N-N}) \approx 2.2 \text{ \AA}$ the ¹A₁ ground state is an admixture of the configurations in which 7a₁ and 7b₁ are doubly occupied. Furthermore, the singlet and triplet manifolds are no longer degenerate and the ¹B₁ transition is much increased in energy with a strong absorption at 123 nm. These calculations predict no singlet spin-allowed transitions between 701 (¹A₂) and 123 (¹B₁) nm but two spin-forbidden transitions to ³A₂ and ³B₂ states at 344 and 274 nm, respectively.

Although the CNDO/S calculations appear to offer a more inviting basis for interpretation of the present results, the observed matrix photochemistry of *cis*-[NO]₂ is at odds with the character of the 250-nm transition predicted by these calculations.⁷ For a single-photon process the photoproducts, N₂O and an O atom, imply increased electron density between the nitrogen atoms at the expense of the electron density between the nitrogen and oxygen atoms. Only two combinations of the 2p orbitals achieve this, the in-plane 8a₁ (8) and out-of-plane 2b₂ (9) orbitals. The



first ¹A₁ transition was not included in the calculation whereas the ¹B₂ transition is at 1286 nm, a wavelength inconsistent with the observed photolysis at $\lambda < 320$ nm.

The disparity between the results of the calculations and the experimental findings may be reconciled in one of three ways.

(i) Irradiation into the ultraviolet absorption may effect the transition to the ¹B₁ state described by the CNDO/S study. Dissociation to N₂O and oxygen atoms then occurs via crossing to a repulsive state which correlates with N₂O (¹ Σ^+) and either O(¹D) or O(³P).

(ii) Matrix-isolated *cis*-[NO]₂ may be distorted such that C_{2v} symmetry is maintained but $\angle\text{NNO}$ is increased. In the limit of D_{∞h} symmetry, the ground state is a triplet with π_u orbitals doubly occupied. Since π_u (D_{∞h}) correlates with a₁ + b₂ (C_{2v}), distortion of *cis*-[NO]₂ toward a linear form could result in a ³B₂ ground state for *cis*-[NO]₂ in an argon matrix. Transitions to perturbed ³A₂ and ³B₁ states then become spin allowed but the 2a₂ orbital is π^* with respect to the N-N bond and the ³B₁ ← ³B₂ transition is symmetry forbidden. Perhaps more significant, however, is the expected stabilization of the 8a₁ orbital as a result of any distortion of *cis*-[NO]₂ toward the linear form. This orbital (8) is strongly N=O antibonding and, in the linear molecule, strongly N-N bonding. Excitation to a configuration involving population of 8 would be consistent with the photochemistry of *cis*-[NO]₂.

(iii) The photolysis of *cis*-[NO]₂ may occur in a two-photon process. The water filter transmits only 10% of incident radiation near 1286 nm and therefore absorption of an ultraviolet photon would necessarily be the first step. Internal conversion or intersystem crossing to a singlet or triplet state having a relatively long lifetime, followed by absorption of a second photon, could provide access to high-energy states involving some occupancy of the 8a₁ molecular orbital 8.

V. Conclusions

Irradiation of *cis*-[NO]₂ isolated in an argon matrix at 13–20 K with 220–320-nm emission from an Hg arc photodissociates the dimer to N₂O and oxygen atoms. The photochemical behavior is discussed in terms of the structure and bonding of *cis*-[NO]₂ and invites comparison with predictions based on CNDO/S⁷ and ab initio CI⁸ calculations. Orbital considerations imply an A₁ or B₂ upper state for the transition leading to dissociation, although the ultraviolet absorption at 250 nm implied by the CNDO/S study⁷ corresponds to a B₁ upper state. This discrepancy is rationalized in one of three ways: (i) internal conversion of the initial excited state, (ii) distortion of *cis*-[NO]₂ to produce a more nearly linear geometry in an argon matrix, or (iii) a two-photon mechanism.

Photogenerated oxygen atoms react with both NO and *cis*-[NO]₂ to yield NO₂, *asym*-N₂O₃ and *sym*-N₂O₃. Evidence is presented for the isolation of two conformers of *sym*-N₂O₃. Oxygen atoms also react with both CO and OCS in an argon matrix to form CO₂, the reaction with OCS being evidently the more efficient. Photolysis of *cis*-[NO]₂ is always accompanied by photodissociation of OCS in Ar/NO/OCS matrices and products characteristic of sulfur atom reactions are observed. In addition to the products SNO and SN₂O₂ to be discussed elsewhere,⁵ SO₂ and regenerated OCS have been identified. Reaction of sulfur atoms with *cis*-[NO]₂ is proposed as the source of SO₂ in Ar/OCS/NO samples. On the other hand, a study of the photochemistry of Ar/OCS/O₂ matrices lends support to Smardzewski's cage-recombination mechanism⁴ for the S/O₂ reaction. Small amounts of SO₃ and S₂O are also formed.

Acknowledgment. We thank SERC both for a grant to assist the purchase of equipment and for the award of a studentship (to M.H.). To Professor C. Trindle and Dr. R. N. Perutz we are also grateful for helpful discussions.

Registry No. Ar, 7440-37-1; OCS, 463-58-1; O¹³CS, 6142-96-7; *cis*-[NO]₂, 16824-89-8; N₂O, 10024-97-2; N₂¹⁸O, 21296-89-9; NO, 10102-43-9; ¹⁵NO, 15917-77-8; N¹⁸O, 15917-78-9; NO₂, 10102-44-0; *sym*-N₂O₃, 10544-73-7; *sym*-¹⁵N₂O₃, 24341-05-7; CO, 630-08-0; ¹³CO, 1641-69-6; CO₂, 124-38-9; ¹³CO₂, 1111-72-4; OC¹⁸O, 18983-82-9; C¹⁸O₂, 2537-69-1; S₂O, 20901-21-7; S₂¹⁸O, 56629-60-8; SO₂, 7446-09-5; OS¹⁸O, 14899-63-9; S¹⁸O₂, 24262-77-9; SO₃, 7446-11-9; SNO, 56971-19-8; O₂, 7782-44-7; ¹⁸O₂, 32767-18-3; O, 17778-80-2; H₂O, 7732-18-5.