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Ozone and oxygen atom reactions with dimethylsulfide and methanethiol in argon matrices

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Ground state oxygen atoms, generated by visible photolysis of ozone, have been reacted with CH_3SCH_3 and CH_3SH in argon matrices. For CH_3SCH_3 , a stepwise addition to form DMSO and dimethylsulfone was observed. Methanethiol reactions with O atoms were more complex, leading to production of CH_3SOH , CH_3OSH , $CH_3S(O)H$, and possibly CH_3-SO_2-H . These results are compared to the $O + H_2S$ reaction. The matrix results are also compared to gas phase studies where more extensive fragmentation has been observed, and inferences are drawn concerning the relative matrix deactivation rates of the highly energetic sulfide-oxygen-atom precursor complex.

I. INTRODUCTION

The mechanism of the oxidation of organic sulfur compounds is becoming increasingly important because of the continued use of large amounts of sulfur-containing fossil fuels for energy production. However, few investigations of gas phase reactions of oxygen atoms with various organosulfur compounds have been reported, 1-4 most notably the work of Slagle and coworkers¹ who have identified free radical reaction intermediates via photoionization mass spectroscopy studies in a flow system at low pressures. Those workers reported results which suggest the formation of triplet activated complex upon initial attack of ground state oxygen atoms $[O(^{3}P)]$ on CH₃SH, C₂H₅SH, or CH_3SCH_3 .¹ It has been proposed that the highly energetic complex deactivates by collision with other atoms or molecules or fragments by C-S or S-H bond scission. Observation of CH₃O and CH₃S radicals in the $O + CH_3SCH_3$ reaction supported a possible migration mechanism which may also occur before deactivation. Kakimoto and co-workers have recently reported the observation of the mirocwave spectrum of HSO radicals following oxygen atom reactions with methanethiol.² Other studies were performed to measure the rate of the $O + CH_3SCH_3$ reaction by monitoring the disappearance of oxygen atoms.^{3,4}

In previous work from this laboratory, Smardzewski and Lin^5 showed that ground state oxygen atoms react with H₂S at 10 K to produce HSOH, which was thought to arise by initial sulfoxide formation since the alternative abstraction reaction has a 3 or 4 kcal/mole activation energy barrier⁶⁻⁸ and would not be expected to compete at 10 K. The present work was performed in order to understand the analogous matrix chemistry occurring when oxygen atoms react with CH₃SCH₃ or CH₃SH in a pseudo-high-pressure-gas environment and to draw comparisons to the low pressure gas results.

II. EXPERIMENTAL

Methanethiol (Matheson, 99.5%) was frozen in a Pyrex finger at 164 K and degassed twice in order to remove

traces of methane which was found to be the only impurity in initial experiments. After degassing, the first fraction to evaporate after removal of the low temperature bath (ethanol-liquid nitrogen slush) was used for the experiments. No other impurities were detected in the infrared. Dimethyl sulfide (hereafter, DMS) was degassed at 77 K prior to use. No impurities were observed in its infrared spectrum. Dimethylsulfoxide (certified ACS Reagent grade, 99.95%) was used as received after several freeze-pump-thaw degassing cycles.

Ozone was prepared as before by the high voltage discharge of ${}^{16}O_2$ (Matheson ultrahigh purity), ${}^{18}O_2$ (Miles Laboratories, 99 at. % O-18) in a Pyrex U-tube at 77 K. ⁹ Partially oxygen-18-enriched ozone was prepared by discharging a mixture of ${}^{16}O_2$ and ${}^{18}O_2$. The ozone was degassed at 77 K to remove residual O_2 prior to sample preparation. The first fraction to vaporize after removing the liquid nitrogen bath was used in order to minimize CO₂ contamination. All reactant gas samples were diluted with argon (Matheson, prepurified) prior to deposition. The ozone and sulfide gas samples were kept in separate manifolds on a stainless steel-Teflon vacuum line precluding contact prior to codeposition onto the cryogenic infrared window (CsI) from separate inlet orifices.

The experimental procedures used in the present work have been detailed in previous accounts from this laboratory.^{9,10} Briefly, when the system was evacuated to near 10⁻⁶ Torr, the Displex closed cycle helium refrigerator was activated, and the substrate window was cooled to ~10 K as measured with a calibrated carbon resistance thermometer. After cooldown, 10 mM each of the diluted gas samples, ozone and either methanethiol or DMS, were codeposited. High resolution infrared spectra were obtained before and after ozone photolysis. Sample irradiation was performed either with the 514.5 nm line of a defocused argon ion laser (Spectra Physics), or the emissions from a Pyrex-filtered high pressure mercury arc (Philips HPK 125W) in some of the methanethiol reactions. Spectra were recorded on a Beckman IR-12 infrared spectrophotometer which had

been calibrated by standard techniques. Frequency accuracy is believed to be within 0.5 cm⁻¹. One ${}^{18}O_3$ -CH₃SH experiment was performed using a Digilab FTS-15 Fourier transform infrared spectrometer with a 0.25 cm⁻¹ resolution.

III. RESULTS AND DISCUSSION

A. Blank experiments

1. Ozone

Single-deposition blank experiments were performed with the pure reactants diluted in argon matrices (M/R)= 100) before commencement of double-deposition reactions. The infrared spectra of ozone and its oxygen-18-enriched counterparts in solid argon have been previously reported by Andrews and Spiker.¹¹ We observed CO₂ as the only impurity in the blank ozone experiments. The relative amount of CO_2 was markedly decreased by fractional distillation of the ozone. All of the CO₂ impurity could not be eliminated, however, and it is thought that the reaction of ozone with the stainless steel walls of the gas manifold and containers gradually produces CO_2 . Reactions of copper atoms with ozone¹² from the same sample container used in the present work led to no observable Cu-O₂ reactions, ¹³ indicating that ozone decomposition to form O₂ is negligible.

In prolonged deposition experiments, we find infrared features of ozone in an argon matrix sample containing 50% oxygen-18-enriched ozone at 1061.1, 1090.3, 1994.0, 2024.1, 2049.7, 2050.9, 2087.7, and 2110.5 cm⁻¹. The first two bands were observed by Andrews and Spiker in Raman experiments and assigned to ν_1 of the 18-18-16 and 16-16-18 ozone isotopic molecules, respectively.¹¹ In the present work and in an earlier report by Andrews and co-workers, ¹⁴ it was found that these bands are many times stronger than the ν_1 bands of the other four ozone isotopic molecules. This results from a Fermi resonance interaction with the nearby ν_3 modes of the unsymmetrical (non- $C_{2\nu}$) ozone molecules. The higher frequency bands in the 1990-2115 cm⁻¹ region are assigned to the $v_1 + v_3$ combination bands of the six possible ozone isotopic molecules: 18-18-18, 18-18-16, 16-18-16, 18-16-18, 16-16-18, and 16-16-16, respectively. The difference between the ν_1 plus ν_3 sum and the observed frequencies for the four symmetric molecules (X_{13}) is 33.4±0.7 cm⁻¹, while X_{13} for the two less symmetrical isotopic species was 29.2 ± 0.3 cm⁻¹. The better accuracy for the latter value only represents the higher infrared frequency measurement precision as compared to Raman measurements. The two different X_{13} values are most likely a result of the Fermi resonance interaction between ν_1 and ν_3 of the less symmetrical molecules.

2. Dimethylsulfide

The frequencies and relative intensities of bands observed following deposition of an $Ar/CH_3SCH_3 = 100/1$ sample at 10 K are shown in Table I. The agreement between our spectrum and that of gas phase CH₃SCH₃ (Ref. 15) is excellent. With the exceptions of a pair of weak bands in the C-H stretching region at 2867 and

TABLE I. Frequencies (cm⁻¹) and relative intensities (100 \times o.d.) of infrared absorptions observed following 10 K condensation of (a) argon: dimethylsulfide (DMS) = 100:1, (b) argon: dimethylsulfoxide (DMSO) $\simeq 500:1$, and (c) the codeposition of argon: DMS=100:1 and argon: ozone=100:1 with intensities shown before and after 514.5 nm photolysis.

Ar:DMS	Ar:DMSO	$Ar: DMS: O_3$	Assignment
	327.0 (5)		DMSO
	376.1 (5)		DMSO
	390.5 (2)		DMSO
		462.5 (0) (1)	$DMSO_2^{a}$
		496.3 (0) (1)	$DMSO_2$
	679.8 (10)	679.9(1)(2)	DMSO
	688 .9 (3)		DMSO
694.6 (10)		694.4 (6) (6)	DMS
		703.7 (6) (3)	O_3
		748.2 (0) (1)	DMSO ₂
	877.0 (3)		DMSO
900.0(3)		899.6 (2) (2)	DMS
	913.8 (9)	913.9 (1) (2)	DMSO
		932.0 (0) (2)	$DMSO_2$
	940.5 (5)	940.4 (0.5) (1)	DMSO
973.1 (26)		972,7 ⁻ (18) (15)	DMS
	1007.3 (16)	1007.0 (3) (4)	DMSO
	1021.1 (2)		DMSO
1030.1 (33)		1032.0 (shoulder)	DMS, O_3
		1040.3 (121) (68)	O_3
	1062.0 (5)		DMSO
	1076.7 (23)	1079 (broad)	DMSO
	1090.8 (78)	1090, 9 (12) (19)	DMSO
		1159.7 (0) (2)	$DMSO_2$
1310.9 (20)		1311,2 (10) (10)	DMS
	1312.6 (5)		DMSO
		1345.8 (0) (4)	$DMSO_2$
	1403.8 (9)	1404.1 (2) (2)	DMSO
	1416.7 (7)	1417.4 (0) (1)	DMSO
1432.3 (57)		1432.6 (29) (30)	DMS
	1437.5 (19)		DMSO
1439.7 (41)		1439.8 (22) (22)	DMS (DMSO?)
1446.0 (14)		1446.1(6)(7)	DMS
2839.4 (13)		2838, 8 (6) (7)	DMS
2858.6 (7)			DMS
2867.4 (11)		2867.4 (5) (5)	DMS
2888,0 (4)		2887.2 (2) (2)	DMS
2926.2 (60)	9095 Q (4)	2926, 5 (32) (33)	DMS
	2925.8 (4)	0.074 = (17) (10)	DMSO
2973.8 (30)		2974.5 (17) (16)	DMS
2990.0 (10)	2006 0 (2)	⊿998, ວ (9) (9)	DMS
	3000.0 (3)		DMSO
	0004.0 (4)		DMSO
	3383,4 (2)		DMSU

^aDimethylsulfone.

Weak DMSO band may be obscured by stronger DMS band in the Ar: DMS: O3 spectrum.

2898 cm⁻¹ observed in our work and a weak band at 2935 cm⁻¹ in the gas phase spectrum, there is an exact correspondence between the two.

3. Dimethylfoxide

The band frequencies and relative intensities of DMSO in solid argon, M/R = 100/1, are also listed in Table I. Again, there is a close correspondence between this matrix spectrum and that of the gaseous species.¹⁶ A careful comparison shows that bands were observed in the gas phase at 926, 898, and 661 cm⁻¹ which were not re-

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TABLE II. Absorption frequencies (cm⁻¹) and relative intensities ($100 \times o. d.$) in parentheses of infrared absorptions observed following 12 K deposition of (a) Ar: CH₃SH:¹⁶O₃ = 200:1:1 and (b) Ar: CH₃SH:¹⁸O₃ = 200:1:1. Absorptions previously observed for CH₃SH isolated in solid argon are listed for comparison. Reactant absorptions, H₂O and isotopic CO₂ absorptions, are identified.

Ar/CH ₃ SH ^a	Ar/CH ₃ SH/ ¹⁶ O ₃	Ar/CH ₃ SH/ ¹⁸ O ₃	Assignment
	325.2 ^b	318.2 ^b	Reference c
	363.5 ^b	362.6 ^b	
	529,0 ^b	506.4 ^b	
	662.2	660.8	CO_2
		644.9 (12)	¹⁸ O ₃
704.0	704.5 (20)	704.8 (9)	CH_3SH , ${}^{16}O_3$
	716.5 ^b (3)	693.5 ^b (4)	0 0
	732.5 ^b (5)	707.7 ^b (10)	
	767.4 ^b (14)	743.5 ^b (20)	
799.8	800.7 (6)	800.3 (5)	CH ₃ SH
	806.4 ^b (9)	792.7 ^b (6)	
	835.3 ^b (5)	Reference c	
	920.3 ^b (5)	917.8 ^b (6)	
		949.8 ^b (6)	
954.8	955.0 (16)	955.4 (12)	CH ₃ SH
		982.9 (>200)	¹⁸ O ₃
	997.5 ^b (3)	997.1 ^b (2)	
	1022.6 ^b (3)		
	1033.4 (sh)		¹⁶ O ₃
	1040.2 (>200)		¹⁶ O ₃
		1044,4 (2)	¹⁸ O ₃
1067.9	1068.9 (25)	1069, 5 (23)	CH ₃ SH
	1084.0 ^b (15)	1056.3 ^b (43)	
	1096.4 ^b (15)	1056, 3 ^b (43)	
		1131, 6 ^b (8)	
		1135,0 ^b (7)	
	1139.7 ⁶ (2)		
		1151.5 ^b (7)	
	1152.00 (2)	.	
		1159.00(7)	
	1162.0 [°] (5)		
	1197.8° (11)	i	
		1300.0" (8)	
		$1311.5^{\circ}(4)$	
1326.0	1326.9	1327.2 (18)	CH ₃ SH
	1344.03 (10)	1050 ob (0.10)	
		$1350.2^{\circ}(0.13)$	
	1004 10 (7)	1362.8° (7)	
	1364, 1° (7)	1074 00 (0)	
	1007 00 (0)	1374, 8° (2)	
1405 0	1397.6" (9)	1496 6 (90)	CH CH
1435.3	1430, 0 (24)	1430.0 (20)	CH ₃ SH
1445.4	1440.0 (23)	1440, 8 (21)	¹⁸ 0
	9110 0	1994.0 (13)	16O
	4110.0	2309 0 (15)	C ¹⁸ C
		2303.0 (13)	$C^{16}O^{18}O$
	2245 5 (42)	2345 0 (15)	C ¹⁶ O
	2513 5 (3)	2513 0 (4)	(CH.SH) 2
(2552)	2552 0 (2)	2552 5	(CH ₃ SH) _x
2603 2	2601 5 (1)	1001.0	CHASH
2000.2	2853 5 (7)	2853 0 (9)	(CH.SH) ?
	2879 0 (2)	2000,0 (0)	?
	2937.0 (15)	2937.0 (20)	(CH ₂ SH)
2948.1	2948.5 (36)	2948.0 (42)	CHASH
3007.0	3007.0 (19)	3007.5 (24)	CH ₃ SH
3011.0	3012.0 (15)	3011.5 (21)	CH ₃ SH
	3551.0 (3)	3551.5(4)	CH ₃ SH
	3586.8 ^b (4)	3575.6 ^b (4)	U U
	3595.4 ^b (5)	3584.6 ^b (5)	
	3709.6 (3)		H ₂ O

^aFrequencies taken from Ref. 16.

^bBand intensity increases with photolysis.

^cUnassigned bands are attributed to CH₃SH-O₃ reaction products.

produced in the matrix spectrum. These results suggest that the latter bands are in fact due to the rotational envelopes of Q branches located at 915 and 674 cm⁻¹, respectively, in the gas phase. Several new bands were observed in the matrix spectrum at 1021, 1062, and 1071 cm⁻¹ which are undoubtedly obscured by strong bands in the gas phase spectrum. Weak features in the combination region were observed at 3363 and 3383 cm⁻¹ only in the matrix spectrum.

4. Methanethiol

The infrared spectrum of methanethiol in solid argon had been previously reported.¹⁷ The frequencies observed in the present work are in good agreement with those of Barnes *et al.*¹⁷ and are listed in Table II along with the relative intensity of each band. The only impurity band in the blank experiment occurred at 1305 cm⁻¹ and is due to CH₄. Subsequent experiments were performed using CH₃SH purified by degassing at 164 K prior to sample preparation. No CH₄ was observed when this procedure was employed.

B. Codeposition experiments

1. $CH_3SCH_3 + O_3$

Codeposition of $Ar/CH_3SCH_3 = 100$ and $Ar/O_3 = 100$ samples produced new bands at 680, 914, 940, 1007, 1091, and 1404 cm^{-1} in addition to the bands previously detailed for unreacted CH₃SCH₃ as well as features of O_3 at 704, 1032, 1040, and 2110 cm⁻¹. By comparison (Table I) with the Ar/DMSO spectrum, it is obvious that the new bands are all assignable to DMSO, formed by the reaction of CH_3SCH_3 with O_3 upon deposition. Sixty minutes of 514.5 nm photolysis (1.5 W) caused the DMSO bands to experience a moderate increase, while the ozone features decreased by about 50% and the CH₃SCH₃ bands remained essentially unchanged. Additionally, a new set of weak bands at 462, 496, 748, 932, 1160, and 1340 cm⁻¹ was observed to grow after 514.5 nm photolysis. These latter bands are in good accord with the gas phase infrared spectrum of dimethylsulfone^{18,19}

and are consequently assigned to that species. Moreover, the only features in the spectrum other than very weak bands of atmospheric CO_2 and H_2O impurities were those assigned to either O_3 , DMS, DMSO, or dimethylsulfone. Survey spectra of argon matrices containing only DMS (a) and DMS and ozone (b) before and (c) after 514.5 nm photolysis are depicted in Fig. 1.

2. $CH_3SH + O_3$

When $Ar/CH_3SH = 100$ and $Ar/O_3 = 100$ samples were codeposited, many new bands were observed, as in the case of the CH_3SCH_3 -ozone reaction. As in the DMS reactions, photolysis of methanethiol-ozone matrices increased the product yield. This conclusion is sup-

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500

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FIG. 1. Survey infrared spectra observed following 10 K deposition of (top) dimethylsulfide (DMS) in excess argon, (middle) codeposition of DMS and ozone from separate orifices each diluted with excess argon, and (bottom) the same matrix shown in the middle trace following 1 h of 514.5 nm (1.5 W) laser photolysis. Asterisks in middle trace denote absorptions of dimethylsulfoxide. Arrows in lower trace denote absorptions of dimethylsulfone.



1500

1000

WAVENUMBER

Ar:DMS = 100:1

Ar:DMS:0 3 = 200:1:1

after photolysis

1900

1

TRANSMISSION

CH₃SH was deposited in argon, with an argon $-{}^{16}O_3$ sample, and with an argon $-{}^{18}O_3$ sample. There are three spectral regions of particular interest in these experiments which will now be discussed in detail.

a. O-H region. The pair of product bands observed at 3595 and 3587 cm⁻¹ in the ${}^{16}O_3$ experiments are indicative of an O-H stretching vibration in the product. The 10.8 and 11.2 cm⁻¹ red shifts observed upon oxygen-18 substitution are in good agreement with the calculated isotopic shift for a harmonic diatomic O-H stretching vibration (viz., 11.8 cm⁻¹) in this spectral region. Spectra are shown in Fig. 2. It is inferred from this observation that the O-H stretch arises from insertion of an oxygen atom into the S-H bond of CH_3SH rather than into one of the three equivalent C-H bonds. This assumption seems plausible for two reasons. First, there was no evidence for C-H bond oxidation in reactions of CH₃SCH₃ with ground state oxygen atoms, second, the activation energy for the gas phase hydrogen atom abstraction from methane by ground state oxygen atoms is $10 \pm 1 \text{ kcal/mole}^{20,21}$ and thus is precluded in the 10 K matrix environment.

Table II summarizes three experiments in which

b. C-O, S=O region. The second critical region

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FIG. 2. High resolution infrared spectra in $3550-3620 \text{ cm}^{-1}$ region following codeposition of isotopic ozone samples and methanethiol (P), each diluted in argon (Ar:O₃: P=200:1:1). Unshifted band near 3550 cm^{-1} is a P absorption. These spectra were recorded after overnight Pyrex-filtered mercury arc irradiation.

occurs between 1040 and 1100 cm⁻¹ and is shown in Fig. 3. This is the region where the C-O (single) and the S=O (double) bond stretching vibrations should occur. For example, the C-O stretch of methanol in argon matrices occurs at 1034 cm⁻¹, ²² and the S=O stretch of DMSO occurs at 1091 cm⁻¹. The top trace of Fig. 3



FIG. 3. High resolution infrared spectra in the 1020-1100 cm⁻¹ spectral region following codeposition of isotopic ozone samples and methanethiol (P), each diluted in argon. These spectra were recorded after overnight Pyrex-filtered mercury arc irradiation.



FIG. 4. Infrared spectrum in the $1050-1060 \text{ cm}^{-1}$ region observed following codeposition of an Ar/CH₃SH/¹⁸O₃ = 400/1/2 sample showing partial resolution of two accidentally degenerate reaction product absorptions. This spectrum was recorded after deposition (no photolysis).

shows two intense reaction product bands appearing at 1096 and 1084 cm⁻¹, along with a parent CH₃SH absorption at 1069 cm⁻¹ and the very strong v_3 band of ozone at 1040 cm⁻¹. The middle trace of Fig. 3 shows the much simplified spectrum observed in this region when ozone-18 was codeposited with CH₃SH. In this spectrum, the intense ν_3 band of ozone is red-shifted to 983 ${\rm cm}^{-1},$ and the two sharp reaction product bands found in the ozone-16 reaction are replaced by a slightly broader new band at 1056 cm⁻¹. We prefer this interpretation over the alternative explanation that the 1096 cm⁻¹ band has shifted under the broader 1069 cm⁻¹ CH₃SH absorption since the intensity ratio of the 1069 to 1327 cm⁻¹ CH₂SH band in the ozone-16 experiment. 1.35, is very close to that found in the ozone-18 run. 1.28. If one of the reaction product bands had shifted to 1069 cm^{-1} in the ozone-18 experiment, this ratio would be expected to increase to well over 2.0. The greatly enhanced intensity of the 1056 cm^{-1} band in the ozone-18 experiment adds supportive evidence for this assignment as well. The scrambled ozone experiment produced no additional features, thereby indicating that all reaction products contain a single oxygen atom.

In an attempt to prove that two bands accidentally overlap in the $^{18}O_3$ experiments, one experiment was performed using higher resolution (0.25 cm⁻¹) FTIR analysis after depositing an Ar/CH₃SH/¹⁸O₃ = 400/1/2 sample. The 1056 cm⁻¹ band produced in that experiment is depicted in Fig. 4 and consists of a poorly resolved doublet with relative maxima at 1056.8 and 1056.2 cm⁻¹. This result confirms that two reaction product bands lie at nearly the same frequency in the $^{18}O_3 + CH_3SH$ argon matrix experiments.

The assignment of the 1084 cm⁻¹ band to a C-O stretching mode is made on the basis of the frequency ratio in the two oxygen isotopic experiments, 1056/1084 = 0.9744. This ratio is close to that expected for a harmonic diatomic C-O oscillator upon oxygen-18 isotopic substitution (viz., 0.9758). The analogous ratio for methanol-O-18/methanol = 0.9750.²² On the other hand, the ratio for the 1096 cm⁻¹ band (1056/1096) is 0.9634, very close to that predicted for a harmonic diatomic S-O oscillator (0.9622), and this absorption is consequently



FIG. 5. High resolution infrared spectra in the 700-800 cm⁻¹ spectral region following codeposition of isotopic ozone samples and methanethiol (MT), each diluted in argon. Small letters denote reaction product absorptions. Primes denote red-shifted absorptions of O-18 isotopic counterparts of bands observed in O-16 experiments. These spectra were recorded after over-night Pyrex-filtered mercury arc photolysis.

assigned to that vibration. These assignments imply -C-O- and



linkages in the reaction product, a condition not possible if only one reaction product is present. This result leads us to postulate at least two reaction products.

c. S-O region. The final spectral region of interest is between 700 and 800 cm⁻¹, the S-O single bond stretching region. The S-O stretch of the HSOH molecule in argon matrices was found at 763 cm^{-1} , ⁵ In the present experiments, three weak bands were found at 767, 732, and 716 cm⁻¹ with appropriate oxygen-18 isotopic shifts for assignment to S-O stretching vibrations. Isotopic spectra in the 700-800 cm⁻¹ region are shown in Fig. 5. Again, this result is supportive of an S-O linkage in the reaction product, but in this case, it is clearly not a terminal oxygen, but rather a bridging oxygen, structure. Linkages consistent with this interpretation are -C-O-S- and -C-S-O-. The former possibility has already been alluded to as being responsible for the C-O band at 1084 cm⁻¹, and the latter is in accord with a molecule having an -O-H moiety (i.e., H₃C-S-O-H structure).

The most plausible explanation of the results at hand

is that there are three distinct $O-atom + CH_3SH$ reaction products which give rise to these spectra, namely,

C. Other absorptions

Several much weaker bands were observed in the 1150– 1200 and 1325–1400 cm⁻¹ spectral regions. These bands were markedly enhanced upon visible light photolysis as opposed to the bands previously detailed which only increased modestly with photolysis. The appearance of these bands in the scrambled ozone isotopic experiment was difficult to ascertain, but it appeared that new intermediate features were present. This result and the comparison to the dimethylsulfone spectrum where two of the most intense bands were found to occur at 1346 and 1160 cm⁻¹ lead us to propose formation of a molecule containing an $-SO_2$ - linkage upon visible light photolysis. Such a molecule might have a structure such as



However, due to the noted complexity and weakness of the bands in the 1100-1400 cm⁻¹ region, this assignment must be regarded as tentative.

There are also several other intense bands clearly assignable to single-oxygen-atom reaction products which have not been discussed, most notably those bands at 325, 363, and 806 cm⁻¹. Of these, only the 363 cm⁻¹ band had too small an oxygen-18 shift to be definitively resolved into a doublet in the scrambled isotopic ozone experiment. Assignment of these bands to a specific vibration or even to a specific molecule is difficult since the isotopic shifts were not recognizable as being caused by simple diatomiclike vibrations. As a result, we can only note their presence and use them as supportive evidence for a one-oxygen-atom reaction product. They are probably due to bending vibrations involving the heavy atoms, i.e., α C-S-O, α C-O-S, or α C-S=O.

D. Comparison of gas phase and matrix chemistry

The initial complex forming when a ground state oxygen atom reacts with RSR', where R is H, CH_3 , or C_2H_5 , in the gas phase, is believed to be a highly energy-rich triplet molecule¹

This sulfoxide intermediate may release its excess energy by two routes: collisional deactivation to produce the stable single sulfoxide or S-R (S-R') bond cleavage to form free radical products RSO+R' or R'SO+R.¹ In support of this mechanism, Slagle and co-workers observed CH₃, CH₃SO, and CH₃SOH signals following oxygen atom reactions with methanethiol.¹ Oxygen atom reactions with DMS produced CH_3 , again supporting their proposed mechanism.¹ DMSO could not be detected in the O+DMS reaction since the starting material had traces of DMSO contamination.¹

The present matrix results are supportive of the gas phase mechanism proposed by Slagle and co-workers; however, we note this major difference: in the matrix reaction of O+DMS, only consecutive addition of oxygen atoms to form DMSO and dimethylsulfone was observed; no C-S bond cleavage was detected. The matrix reaction of O atoms with methanethiol, however, produced evidence for the three products expected on the basis of the previous gas phase results assuming that free radical fragments would recombine because of the matrix cage effect

$$CH_{3}SH + O \rightarrow \begin{bmatrix} O \\ H \\ CH_{3}S - H \end{bmatrix}^{\ddagger} \xrightarrow{O} CH_{3} + S - H \rightarrow CH_{3}OSH$$

$$O \\ O \\ CH_{3}S - H \\ O \\ CH_{3}S - H$$

$$O \\ O \\ CH_{3}S + H \rightarrow CH_{3}SOH$$

Oxygen atom reactions with H_2S in the gas phase are known to produce HSO radicals^{2,23} as might be expected from the earlier gas phase oxygen atom reactions with DMS and methanethiol. Smardzewski and Lin have observed that the HSOH molecule is the predominant matrix product.⁵

The previous results of O atom matrix reactions with H_2S (Ref. 5) and the present results may be understood when the effect of the inert solid matrix is considered. The fragmentation-recombination mechanism is observed in the matrix predominantly for the lighter species (H_2S), while deactivation of the intermediate adduct is predominant for the more complex species (CH_3SCH_3).

The matrix results are consistent with a more rapid deactivation of the complex adducts, presumably because of the greater availability of vibrational (and rotational) deactivation pathways for

$$\begin{array}{c} O \\ \parallel \\ CH_3SCH_3 \ (3N=30) \end{array}$$

as compared to

$$\begin{array}{c} O \\ \parallel \\ CH_3SH \ (3N=21) \end{array}$$

The

$$\bigcup_{\substack{\parallel\\ \text{HSH}}(3N=12)}^{O}$$

species, with even fewer deactivation pathways, yielded the fragmentation-recombination product HSOH predominantly in the earlier matrix work.⁵ Further work to support this deactivation scheme is under way.

A final point in support of the mechanism proposed by Slagle et al. has been invoked for oxygen atom reactions

with substituted ethylenes by Singleton and Cvetanovic.²⁴ In both cases [i.e., O+ substituted ethylenes and O(RSR')], very small or negative activation energies and nonlinear Arrhenius plots have been reported.^{4,7,24} This behavior has been shown to be consistent with a mechanism involving a metastable olefin-oxygen atom (or sulfide-oxygen atom) adduct,²⁴ precisely the intermediate proposed by Slagle *et al.*¹

IV. CONCLUSIONS

Oxygen atoms react with CH₃SCH₃ in argon matrices with no apparent activation barrier to produce DMSO and dimethylsulfone in a stepwise mechanism. Unlike the gas phase reaction, no bond cleavage was observed following the initial oxidation step. Methanethiol reactions with atomic oxygen led to the production of several single-oxygen-atom products. The apparent explanation is that in argon matrices, C-S or S-H bond cleavage of the activated complex is rate competitive with simple deactivation. This trend can be followed on to H₂S reactions with oxygen atoms in which the simple adduct was not observed but only HSOH, apparently formed by recombination of HSO and H fragments in the same matrix cage. The fragmentation mechanism in this reaction is much favored over the competing deactivation pathway although the H-S bond is some 15-20 kcal/mole stronger than the C-S bond.

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