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Photopolymerization of Carbon Disulfide Yields the High-Pressure-Phase $(CS_2)_x$

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Abstract: Irradiation of carbon disulfide vapor at 313 nm produces a solid aerosol of nanosized particles, which slowly aggregate and settle. Elemental analysis shows the composition of the solid is $CS_{1.98}$, and the density is 1.92 ± 0.03 g/cm^3. Physical properties of this material were found to be nearly identical to Bridgman's black carbon disulfide, which is prepared from liquid CS_2 at pressures above 40 kbar and temperatures around 150 °C. The IR spectrum of $(CS_2)_x$ includes features at 1410 (s, br), 1298 (ms), 1250 (m), 1067 (vs), 891 (w), 854 (vw), 821 (w), 550 (w), 507 (w), 471 (m), and 447 cm^{-1} (m). The $(CS_2)_x$ polymer undergoes photooxidation ($\lambda \leq 500$ nm) in the presence of molecular oxygen to produce CO, OCS, SO_2, CS_2, sulfur, and a partially oxidized polymer. The relative amounts of these products vary widely with the specific experimental conditions employed. Vibrational spectroscopic studies of $(^{13}CS_2)_x$, and the material prepared by irradiating a 50/50 mixture of $^{13}CS_2/^{12}CS_2$, suggest that it predominantly consists of highly S−S cross-linked chains of $(CS_2)_x$. This provides a convenient low-pressure route to an unusual phase of CS_2 and helps elucidate the primary process in the photolysis of CS_2 vapor.

Introduction

P. W. Bridgman first synthesized a black polymeric form of carbon disulfide in 1941. He described: "...a permanent solid form of carbon disulfide ... produced at pressures around 40,000 (bar) and temperatures around 150 °C."[1] This result has been reproduced,[2,3] and Whalley first published the IR spectrum of $(CS_2)_x$ in 1960.[4] Chan and Jonscher investigated its structural and electrical properties in 1969.[3] It was found to have a dc resistivity of 10^{13} Ω cm (300 K) with an activation energy of 0.7 eV. They concluded: "it has a highly conjugated polymeric chain structure with little or no long range order."

The long-wavelength ($\lambda > 280$ nm) photolysis of carbon disulfide vapor has been a topic of disagreement since it was first investigated by de Sorgo and co-workers in 1965.[5−7] Irradiation of gaseous CS_2 at 313 nm was said to produce CS, S_2, and a brown solid.[6,8] There is disagreement about the origin of the CS and S_2, as well as the composition of the solid. Early investigators suggested that the solid consists of the polymer $(CS)_x$[6], possibly formed by wall reactions.[9] Later it was shown that the solid forms in the body of the cell as an aerosol.[10] It is now known that the loss of gas-phase CS at room temperature is not accompanied by formation of a solid $(CS)_x$ polymer. The principal loss reaction without oxygen was shown to be a heterogeneous wall reaction that produced carbon disulfide and a carbon-rich wall deposit.[11] Most recently, the aerosol produced on photolysis of CS_2 has been described as a mixture of $(C)_x$ and $(S)_x$.[12] Carbon disulfide is also thought to undergo multi-photon dissociation on laser excitation in the 313 nm absorption system to produce CS + S. Sulfur is then thought to react with additional carbon disulfide to produce CS + S_2.[13]

The short-wavelength ($\lambda < 240$ nm) photolysis of CS_2 has also been examined. Photofragment dynamics, dissociative photoionization of CS_2, and the reactions within van der Waals clusters (formed in low pressure molecular beams) are current topics of study.[14,15]

Carbon disulfide is a natural component of the troposphere, and it has been observed at elevated levels in the polluted troposphere.[16] Oxidation of CS_2 may produce carbonyl sulfide (OCS), which has a half-life of several years.[17] Convective and diffusive transport make OCS an important source of stratospheric sulfur. Carbon disulfide is known to undergo photooxidation at actinic wavelengths. Photolysis at 313 nm with added oxygen produces CO, OCS, SO_2, and a yellow solid.[6] A quantum yield of only 0.03 would allow this pathway to compete favorably with the hydroxyl radical initiated oxidation in parts of the troposphere.[18,19] The mechanism of this photooxidation remains unknown, and its quantum yield remains controversial.

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Therefore it is important to investigate the primary processes involved in the photolysis of CS_2 and CS_2-O_2 mixtures at actinic wavelengths.

Experimental Section

FTIR Measurements. Gas-phase reactants and products were analyzed with the use of a Nicolet 510 FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector that was optimized for the 800−4000 cm^{-1} spectral region. The signal-to-noise ratio was further enhanced by averaging 100 scans for each spectrum. The sample chamber was purged with N_2 to remove atmospheric H_2O and CO_2. Calibration curves for CS_2 (Fisher ACS grade, dried over P_2O_5, freeze−pump−thaw degassed, and then vacuum distilled from −5 to −90 °C), OCS (Matheson), CO (Union Carbide Corp. Linde Division), and SO_2 (Matheson) were constructed. A manometer was used to measure pressures over 20 Torr. For pressures below 20 Torr, volume ratio techniques were employed. At least two small volumes were used for each calibration curve. All gases showed pressure broadening, and therefore the calibration curves and quantitative measurements were carried out at a constant total pressure of 720 Torr. The balances of the gas mixtures were made up by N_2 (Parsons), O_2 (99.6% Aldrich), a 21% O_2 + 79% N_2 mixture (Matheson), or ambient air. Infrared measurements between 300 and 600 cm^{-1} were carried out with the use of a Nicolet Magna-IR 550 spectrometer. FTIR spectra of solid materials were obtained in KBr pellets.

Photochemical Studies. A KRATOS Analytical Instruments LH150 arc lamp, fitted with a 200-W high-pressure Hg−Xe bulb, was used as a light source in conjunction with a KRATOS LPS 251HR 200-W power supply. Several experiments employed a 1000W Oriel Hg−Xe arc lamp as the radiation source. A 10-cm quartz water filter was used in both cases to remove IR radiation. The sun was also used as a photon source. Intensity scaling of the 1000W lamp output was achieved with Oriel fused silica metallic neutral density filters. The 313-nm mercury line was isolated with an Oriel 3651, 312.6-nm interference filter. Alternatively, a 1 cm path length quartz filter filled with benzene was used to exclude wavelengths less than 280 nm. Colored glass filters (KOPP Glass Inc.) 3-70 and 3-75 were also employed as cutoff filters (approximately 480 and 370 nm, respectively).

UV−vis spectra were taken with the use of either an IBM 9420 UV−vis spectrophotometer or a Hewlett Packard 8452A diode array spectrometer. A Beer's law plot for freshly sublimed S_8 (UPS sulfur sublimed, Fisher Scientific) in acetonitrile yielded $\lambda_{max} = 262$ nm and $\epsilon_{max} = 6545$ M^{-1} cm^{-1}.

Synthesis of $(CS_2)_x$. Samples were synthesized by continuous photolysis of pure CS_2 vapor, or $CS_{2(g)}$−nitrogen mixtures. The gas mixtures were placed in a 10 cm path length IR cell with CaF_2 windows and irradiated with the isolated 312.6-nm line of a 200-W mercury−xenon arc lamp. Within seconds, aerosol particles were observed (through scattering of visible radiation) forming in the body of the cell. Eventually settling occurs through gravity-driven deposition. Microscope slides were placed on the bottom of the gas cell to collect the deposited material for photolysis and SEM studies. Bulk samples were obtained by filling a 2-L quartz schlenk-tube with a CS_2−nitrogen mixture. In a typical experiment, the tube was filled with 760 Torr of a 25% CS_2/N_2 mixture and exposed to sunlight (at 32° N latitude) for a few days. The solid deposit could be collected directly from the bottom of the flask or suspended in a liquid (hexane or acetone) and recovered by centrifugation. Samples were heated ($T < 100$ °C) for several hours to remove adsorbed CS_2. Polymer yields were typically 60−80 mg, which corresponds to a 4−5% conversion. The $(CS_2)_x$ polymer was stable indefinitely if light or oxygen were excluded. It has no significant vapor pressure at room temperature. A ^{13}C enriched polymer was produced using 97−99% $^{13}CS_2$ (Cambridge Isotope Laboratories). A sample was also produced from a 50:50 mix of $^{12}CS_{2(g)}$ and $^{13}CS_{2(g)}$. Elemental analyses were performed by Desert Analytics.

The irradiation of liquid CS_2 (degassed) was also explored. This yielded a yellow solution. A very small amount of a brown solid film deposited on the vessel wall at the site of irradiation. One week of irradiation produced only a few micrograms of solid. The IR spectrum of this material showed one strong sharp absorption at 1385 cm^{-1}. Evaporation of the yellow solution yielded a few micrograms of a dark solid which showed IR absorptions at 1260, 1094, 1024, and 801 cm^{-1}. Extracting this material with acetonitrile showed only traces of S_8. A paper which appeared after the submission of our manuscript also examined the photolysis of liquid CS_2 and claims that the brown film, which forms on the irradiated surface of the reaction vessel, contains some $(CS_2)_x$.[20]

Electron microscopy studies employed 10-keV electrons in the secondary electron imaging mode, with the use of a Cambridge Model 360 electron microscope. Samples of $(CS_2)_x$ aerosol were deposited on a microscope slide and sputter coated with gold. The $(CS_2)_x$ aerosol clusters seemed to shrink away from the electron beam on prolonged exposure, which suggests that decomposition or further cross-linking is occurring.

Results

Characterization of $(CS_2)_x$. Polymeric $(CS_2)_x$ was synthesized by irradiating CS_2 vapor at 313 nm. At CS_2 pressures above about 1 Torr, the aerosol can be visually detected as it forms in the body of the cell. At pressures above 10 Torr, the aerosol particles appear within a few seconds. After 30 min, deposition of $(CS_2)_x$ begins. Elemental analysis of the deposited solid gave a composition of 15.88% C and 84.12% S. This compares very closely to the theoretical values expected for $(CS_2)_x$: 15.78% C and 84.22% S. The material exhibits a broad diffuse powder X-ray diffraction pattern, indicative of an amorphous solid. A magnetic susceptibility measurement was performed with a Guoy balance, using $CuSO_4 \cdot 5H_2O$ as a standard ($\chi = 0.00146$ cm^3/mol). The material behaves as a weak diamagnetic compound ($\chi \approx -0.00008$ cm^3/mol).

The $(CS_2)_x$ polymer did not dissolve in acetonitrile, acetone, carbon tetrachloride, methylene chloride, methanol, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide, hexane, diethyl ether, or carbon tetrabromide. The polymer was not degraded by concentrated acids (hydrochloric, fuming sulfuric, nitric, and aqua regia) or base (10 M NaOH), even after extended soaking and agitation (months). The insolubility of $(CS_2)_x$ is consistent with it being a highly cross-linked polymer.

The density of $(CS_2)_x$ was estimated by adding small amounts of the finely divided polymer to carbon tetrabromide−methanol mixtures and observing if the particles floated or sunk. The experiment was carried out in a graduated cylinder and so by weighing the cylinder between methanol additions it was possible to determine the density of the solution directly, as well as through the tabulated densities[21] for carbon tetrabromide (2.477 g/cm^3) and methanol (0.792 g/cm^3). The density of the polymer was found to be 1.92 g/cm^3 (1.91 g/cm^3 from tabulated densities), and the error in the measurement was estimated as 1.5%.

Scanning electron micrographs (Figure 1) of the deposited $(CS_2)_x$ aerosols reveal aggregates of roughly spherical particles, which range in size from about 200 nm up to 800 nm in diameter. This morphology is consistent with a cluster−cluster aggregation (CCA) mechanism[22] . The spherical shape of the component particles in the deposited material is consistent with their gas-phase nucleation and growth. These particles appear to grow independently in the body of the cell until they reach the 200−800 nm size range. When the particle density reaches a critical value they cluster to form aggregates, which are removed by gravity-driven deposition. In a few cases, at P_{CS_2}

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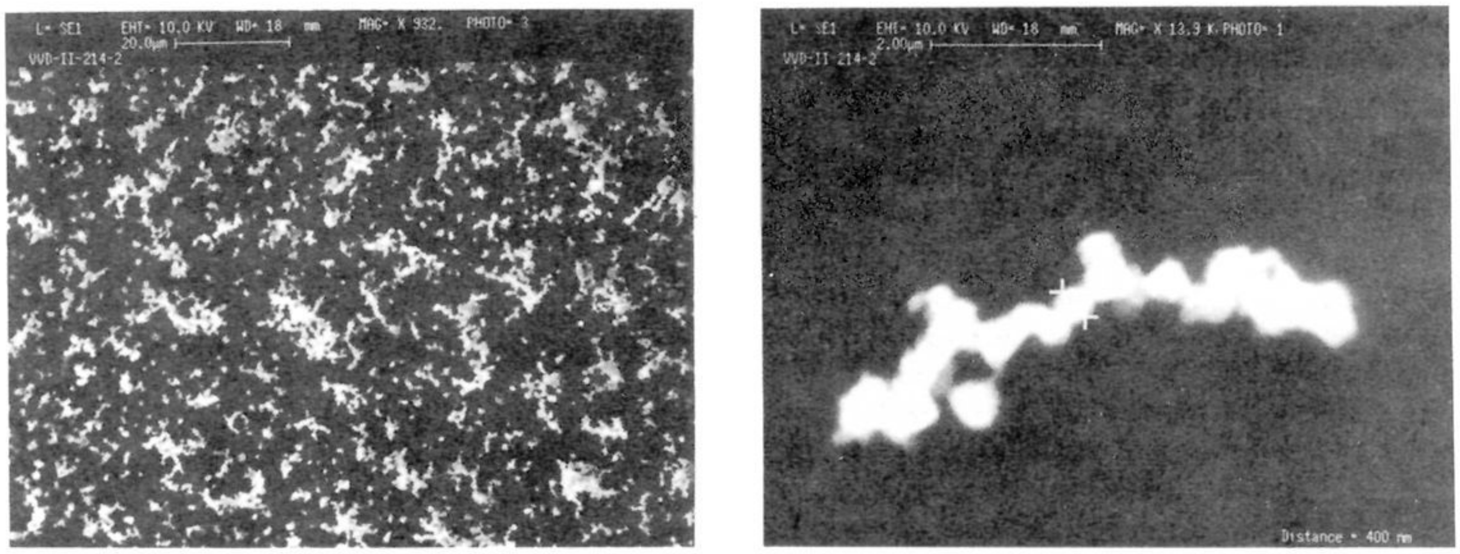


Figure 1. Scanning electron micrographs of $(CS_2)_x$ aerosol (sputter coated with gold), which was deposited by irradiating 120 Torr of $CS_{2(g)}$ at 313 nm. The scale is shown at the top of each panel (20.0 and 2.00 μm for the left and right panels, respectively). The caption in the lower right hand corner (distance = 400 nm) refers to the distance between the two arrowheads.

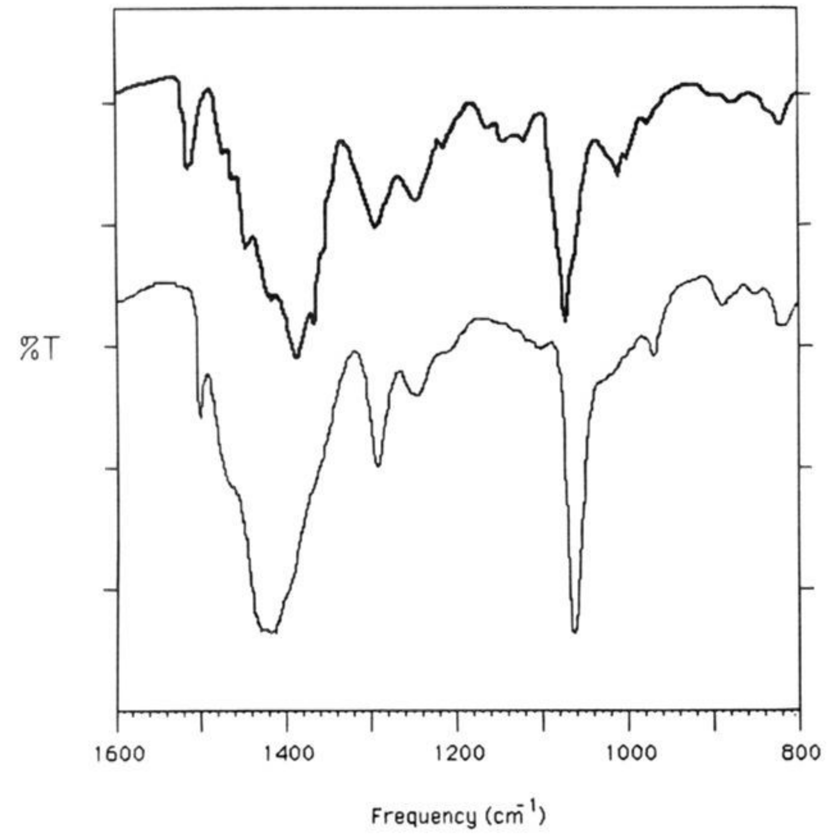
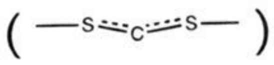


Figure 2. FTIR spectra of $(CS_2)_x$ (bottom) in a KBr pellet and a digitized version of Bridgman's black carbon disulfide from Chan and Jonscher[3] (top). Note that the adsorbed CS_2 was not removed from their spectrum.

above 75 Torr, another morphology was observed. Fibers were seen to nucleate at scratches on the CaF_2 windows. This behavior was also observed by Matsuzaki and Hamada during the laser photolysis of CS_2.[12,23] Some differences should be noted. The nucleation was not reproducible. The IR spectrum of the fiberous material was identical to that of $(CS_2)_x$, in contrast to the results of Matsuzaki and Hamada.

If P_{CS_2} is reduced below a certain critical value, typically below 1 Torr for the geometry employed here, then no scattering of light or deposition is observed. For P_{CS_2} between 1 and 3 Torr aerosol particles can still be seen scattering light in the cell but no deposition is observed on the bottom of the cell. The critical P_{CS_2}'s were also seen to depend on light intensity. Aerosol particles could be observed at lower P_{CS_2} with higher light intensity. This is consistent with a mechanism where photoexcitation produces a species that must be supersaturated, within a region, for nucleation to occur.

Vibrational Spectra. Figure 2 contains the IR spectrum of $(CS_2)_x$ dispersed in a KBr pellet. A digitized spectrum of Bridgman's black carbon disulfide taken from Chan and Jonscher is also displayed.[3] The relative peak intensities are in good agreement. Table 1 lists the peak centers and intensities of the published IR spectra of Bridgman's black carbon disulfide, along with those for the photochemically produced polymer. The slight differences in some peak centers listed in Table 1 are attributed to the differing instruments and resolutions. Additionally, the precise positions of broad peaks are often difficult to estimate. Our interpretation of the spectra agrees with that of Chan and Jonscher.[3] However, we assign the broad absorption centered at 1410 cm^{-1} to asymmetric stretching vibrations



and not symmetric stretching vibrations. A symmetric stretching vibration should occur at a much lower frequency because it primarily involves the motion of the heavy sulfur atoms. For example the symmetric stretch in CS_2 is found at 658 cm^{-1}, and the asymmetric stretch is at 1530 cm^{-1}. The multiple features may arise from the effects of chain length and varied extents of branching within the sample.

The sharp peak at 1507 cm^{-1} in $(CS_2)_x$ was of variable intensity and could be removed entirely from the spectra by gently heating (<100 °C) the sample under vacuum for a few minutes. This absorption decreases slowly with time for samples stored under ambient conditions. The 1507-cm^{-1} peak is assigned to adsorbed $CS_{2(ads)}$. The IR spectrum of $(CS_2)_x$

Table 1. Comparison of Frequency Data[a] (cm^{-1})

Walley's data[4]	Chan's data[3]	$(CS_2)_x$
1502 ± 5 v	1509 v	1506 v
	1480−1363 v, s	1514−1323 s
1286 ± 5 w	1290 ms	1298 ms
1250 ± 5 w	1245 m	1250 m
1220 ± 5 w	1215 w	1220 w (sh)
1144 ± 5 w	1160, 1132, 1115	1176, 1137, 1117 w (v)
1063 ± 5 vs	1069 s	1067 vs
	1010, 990 m, w	1012−988 w (sh)
	975 w	973 w
870 ± 10 vw	875 vw	890 w
		854 vw
806 ± 10 w	820 w	821 w
	780 vw	764 vw
		739 vw
	700 w	700 vw

[a] v = variable intensity, w = weak, m = medium, ms = medium strong, s = strong, vs = very strong, sh = shoulder, vw = very weak.

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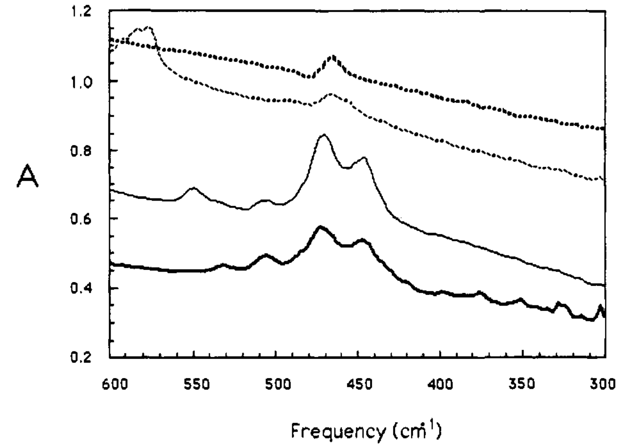

Figure 3. FTIR spectra of 4% w/w mixtures of $(CS_2)_x$ (light solid line), $(^{13}CS_2)_x$ (heavy solid line), sulfur (heavy dashed line), and the photoxidized polymer (light dashed line) in KBr.

displayed in Figure 2 has had most of the adsorbed CS_2 removed. The IR spectrum of $(^{13}CS_2)_x$ shown in Figure 4 has not had the adsorbed $^{13}CS_2$ (1459 cm^{-1}) removed.

Three absorptions were sometimes observed near 1140 cm^{-1}. They were of variable intensity relative to the 1067-cm^{-1} peak and always very weak, but they occurred in similar ratios relative to each other. These absorptions cannot be assigned with confidence. It is possible that they are related to the variable amounts of free sulfur observed in some samples (see below). The photooxidized polymer absorbs strongly within this region.

The absorption centered at 1067 cm^{-1} lies in the C=S symmetric stretching region. Such vibrations are usually intense. This is a highly characteristic absorption for a trithiocarbonate group (1060–1100 cm^{-1}).[24] Ethylene trithiocarbonate, for example, shows an intense feature at 1065 cm^{-1}.[25] Ethylene trithiocarbonate also shows three absorptions which are assigned to C–S–C stretching modes: the symmetric stretch at 503 cm^{-1} and the asymmetric stretches at 882 and 832 cm^{-1}. Therefore we assign the absorption at 550 cm^{-1} (Figure 3) to symmetric C–S–C stretching and the absorptions at 891 and 821 cm^{-1} to asymmetric C–S–C stretching modes of the trithiocarbonate moiety. Some of the other absorptions below 850 cm^{-1} may result from symmetric and asymmetric C–S and S–C–S vibrations.[24,25]

Figure 3 displays IR spectra of 4% w/w mixtures of $(CS_2)_x$, $(^{13}CS_2)_x$, and free sulfur in potassium bromide pellets. The absorptions at 507, 471, and 447 cm^{-1} are attributed to S–S stretching vibrations. The isotopic analysis confirms this, as these absorptions do not shift (see Table 2) in $(^{13}CS_2)_x$. It is unlikely that these arise from free sulfur. A spectrum of the photooxidized polymer, which is known to contain some free sulfur, is also shown for comparison. The absorptions of S–S vibrations in $(CS_2)_x$ are much more intense and shifted in frequency, and they show more structure than the S–S stretch of S_8.

A ^{13}C enriched polymer was synthesized and its IR spectrum recorded (Figure 4). The band energy ratios are listed in Table 2. A harmonic oscillator approximation predicts a fractional shift of 0.961 for a carbon–carbon bond and 0.972 for a carbon–sulfur bond.[26] It is informative to note that the ν_3 absorption of CS_2 vapor (≈1535 cm^{-1}) was seen to shift by

Table 2

frequency, cm^{-1}		$(^{13}CS_2)_n/$	
$(CS_2)_n$	$(^{13}CS_2)_n$	$(CS_2)_n$	intensity[a]
1505	1459.2	0.969	depends on sample
1514.0–1323.4	1470–1272.8	0.967	s (many peaks)
1298.0	1249	0.962	ms
1249.8	1206.7	0.966	m
1220	1182	0.969	w (sh)
1176, 1137, 1117			vw (v)
1066.8	1033.8	0.969	vs
1012–988			w (sh)
973.3	940.2	0.966	w
890.6	863.8	0.970	w
853.7	823.8	0.965	vw
821.3	797.0	0.970	w
764.4	743.2	0.972	vw
738.9	715.7	0.969	vw
700.3			vw
549.6	531.5	0.967	w
506.7	506.7	1.00	w
470.8	470.8	1.00	m
447	447.1	1.00	m

[a] s = strong, m = medium, ms = medium strong, sh = shoulder, w = weak, vw = very weak, vs = very strong.

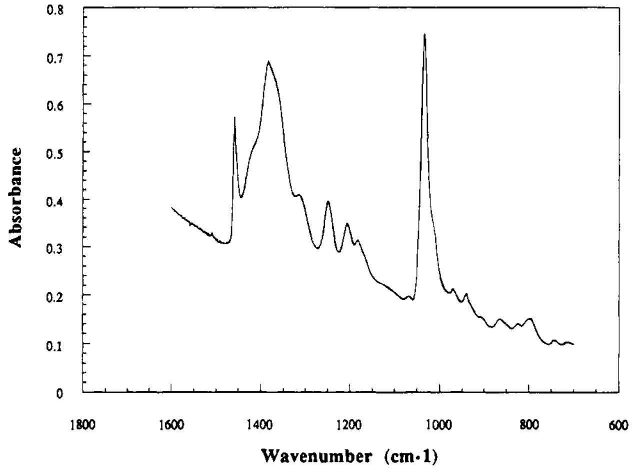

Figure 4. FTIR spectra of $(^{13}CS_2)_x$ in a KBr pellet.

0.967 on isotopic substitution, in agreement with published values.[27] Most of the observed fractional shifts between $(CS_2)_x$ and $(^{13}CS_2)_x$ were also about 0.967. The absorption at 1298 cm^{-1} shifted 0.962. This suggests that it might be a carbon–carbon bond; but the frequency is too low to be a double bond (typically 1625–1675 cm^{-1}) and a bit too high to be a carbon–carbon single bond (typically 900–950 cm^{-1}).[26] Carbon–carbon single bond vibrations are very rarely seen in IR spectra because of the small dipole moment change involved. The intensity of this peak is not enhanced in the mixed isotope sample and it only appears to split into two peaks (see below). For these reasons we are uncertain about the assignment of the absorption at 1298 cm^{-1}.

A $^{12}C/^{13}C$ mixed polymer was synthesized from an approximately 50% $^{12}CS_2$/50% $^{13}CS_2$ mixture. Its IR spectrum (Figure 5) confirms that the absorption at 1067 cm^{-1} (in the $(^{12}CS_2)_x$ spectrum) is indeed a C=S absorption. There are only two peaks in the mixed polymer, one corresponding to $S_2{}^{12}C{=}S$ and one to $S_2{}^{13}C{=}S$. If this absorption were due to a carbon–

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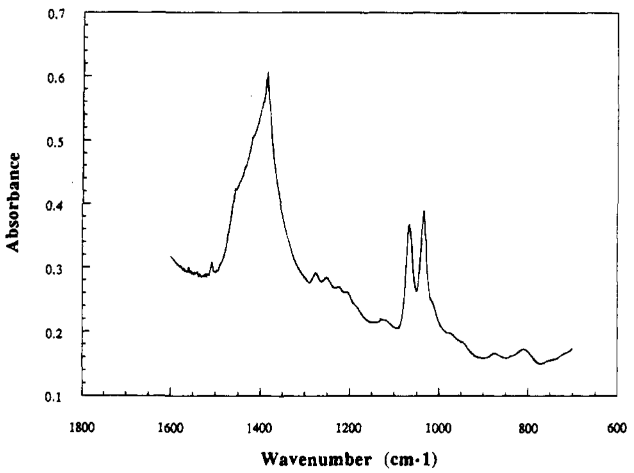

Figure 5. FTIR spectra of $(^{12}CS_2/^{13}CS_2)_x$ in a KBr pellet.

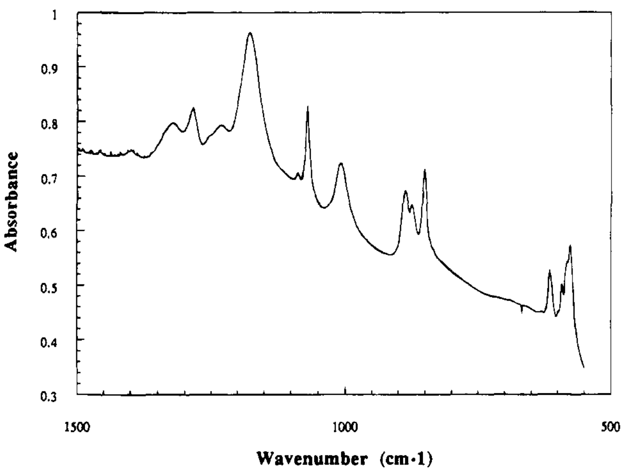

Figure 6. FTIR spectra of the photooxidized polymer in a KBr pellet.

carbon stretch, there would have been three peaks ($^{12}C-^{12}C$, $^{12}C-^{13}C$, and $^{13}C-^{13}C$) or one broad absorption. The absorptions of adsorbed $^{12}CS_2$ and $^{13}CS_2$ were observed in their proper positions (1505 cm^{-1} and 1459 cm^{-1}, respectively) and were removed by heating the sample at 110 °C in an oven overnight. The shape and size (relative to the peaks at 1067 and 1034 cm^{-1}) of the large absorption centered at 1410 cm^{-1} is roughly a sum of the $(^{12}CS_2)_x$ and $(^{13}CS_2)_x$ absorptions in this region. There were no features to suggest a new absorption from the presence of a $^{12}C-^{13}C$ stretch. Because the $^{12}C-^{13}C$ group lacks approximate inversion symmetry, it would be expected to enhance the IR intensity of any C−C or C=C stretching vibrations present. The 1298-cm^{-1} absorption failed to show any enhancement in its intensity, and it did not appear to split into three peaks which would be expected for a C−C stretch. This does not completely rule out the possibility of C−C bonding in the polymer; however, it does suggest that none of the major IR absorption features arise from such vibrations.

Thermal Decomposition of $(CS_2)_x$. The presence of elemental sulfur was diagnostic of $(CS_2)_x$ decomposition. Only minute amounts of S_8 could be extracted from freshly prepared $(CS_2)_x$ with acetonitrile (UV analysis), or benzene (sohxlet extraction and gravimetric analysis). The amount was variable, always amounting to less than 0.4% weight of the initial sample. Sulfur could not be detected in some samples.

Sulfur did not sublime from $(CS_2)_x$, with a temperature gradient of 135 °C/22 °C, in 2 h. In contrast, 6 mg of S_8 sublimed in about 12 min from elemental sulfur under identical conditions. When the sublimation temperature of $(CS_2)_x$ was increased to 175 °C, a small amount of an orange solid deposited on the cold finger over 5 days. This amounted to less than 1% of the initial polymer weight. Infrared analysis of the sublimate shows multiple weak absorptions between 300 and 1600 cm^{-1}, with the strongest feature at 1064 cm^{-1}. This absorption is consistent with $S_2C{=}S$ stretching. Extraction of this sublimate with acetonitrile, followed by UV analysis, also revealed traces of S_8. These results are consistent with mass spectral experiments, which show that both CS and S_2 begin evolving from the polymer at 155 °C.

A melting point determination showed significant decomposition of the polymer above 200 °C. A ring of sulfur condensed near the top of the melting point tube and a black deposit remained. TGA (Thermal Gravitational Analysis) performed under nitrogen showed that the decomposition to volatile products was very slow at 200 °C; only 4% weight loss was observed in 5 h. Ramping up the temperature at 20 °C/min showed 25% weight loss over the next 6 min ($T_{5h,6min}$ = 320 °C). Decomposition, indicated by weight loss, was essentially complete before the temperature reached 950 °C, and a black residue remained in the sample holder.

Direct port injection mass spectrometry was also carried out with the polymer. Samples were typically heated to a target temperature (such as 155 °C) and held there for 5 min. Then the temperature was ramped at 25 °C/min up to 255 °C and held there until decomposition subsided. Carbon monosulfide, carbon disulfide, and S_2 could be observed evolving from $(CS_2)_x$ at temperatures as low as 155 °C, albeit in very small amounts. At temperatures near 200 °C the predominant peaks observed included CS and S_2. Smaller amounts of CS_2 and longer chain sulfur species (S_3-S_8) were also detected. Signals associated with C_xS_y peaks appeared slightly above the background noise. A spectrum of $CS_{2(g)}$ taken under identical conditions showed predominantly a parent ion peak at 76 amu (CS_2^+). Two peaks were also observed at 44 amu (CS^+) and 32 amu (S^+) that were about 0.1× and 0.07× the intensity of the parent peak, respectively. A peak at 64 amu (due to S_2) was detected just above the background noise. The ratio of the parent CS_2 peak to its daughters shows that the primary thermal decomposition products, CS and S_2, are not simply produced by fragmentation of CS_2 in the mass spectrum.

Photooxidation of the Polymer. Exposing the $(CS_2)_x$ polymer to 313-nm radiation, or ambient sun light at 32° N latitude, under an oxygen containing atmosphere initiates a heterogeneous photooxidation reaction. For all photooxidation studies, polymer samples free of adsorbed CS_2 were used. The products detected were CO, OCS, SO_2, CS_2, free sulfur, and a partially photooxidized polymer. The relative amounts of the products depend on the partial pressure of oxygen, as well as the light intensity and duration. The photooxidized polymer shows a distinct IR spectrum (Figure 6). The spectrum of the material produced from $^{13}CS_2$ is indistinguishable from that produced with $^{12}CS_2$. If complete photooxidation is carried out under an atmosphere of pure oxygen (250 W light source and a benzene cutoff filter), then all the sulfur not accounted for as OCS shows up as SO_2 (Figure 7). The stochiometry of complete photooxidation approximates eq 1.

$$(CS_2)_x + 13O_2 \rightarrow 4CO + 2OCS + 10SO_2 + (CS_2)_{x-6} \quad (1)$$

The observed product distribution is not consistent with oxidation of CS as an intermediate. The reaction between CS and O_2 yields OCS and CO in a ratio of at least 10:1.[28,29] In our

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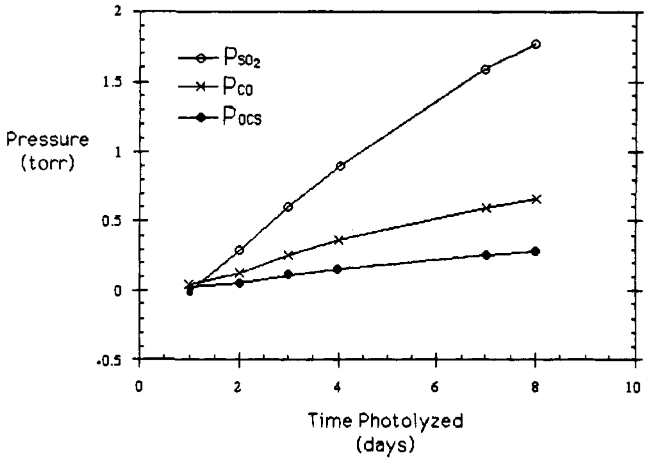


Figure 7. Product distribution during the photolysis of $(CS_2)_x$ under an atmosphere of oxygen as determined by FTIR measurements.

experiments, the OCS:CO ratios observed were almost always less than 1:1.

Attempts to press optically transparent KBr disks containing the $(CS_2)_x$ polymer were unsuccessful because scattering dominated the spectra. Diffuse reflectance spectra between 300 and 800 nm show that $(CS_2)_x$ absorbs throughout the visible spectrum. A region of relatively low absorption is seen around 800 nm. From 740 to about 500 nm, there is an approximately linear increase in absorbance. Between 380 and 500 nm, there is a plateau with a maximum near 460 nm. Below 380 nm the absorption decreases slightly. This is consistent with the observed red-brown to black color of the polymer.

Three cutoff filters were employed to see if photooxidation of $(CS_2)_x$ could be initiated by visible radiation. One day of photolysis was carried out under O_2, using the benzene filter ($\lambda > 280$ nm), the 3-75 filter ($\lambda > 375$), or the 3-70 filter ($\lambda > 480$) and the 200 W arc lamp. Photolyses were carried out under identical conditions. Carbon monoxide and carbonyl sulfide were detected as products in all cases. After correcting for the total output of the lamp in each region, both the benzene and the 3-75 filters produced similar amounts of products per unit time. The rate with the 3-70 filter was only a bit slower, about $^3/_4$ that with the other filters. This shows that the polymer absorbs light and undergoes photooxidation for $\lambda < 480$ nm.

Discussion

Evidence that photopolymerized CS_2 is the same phase as Bridgman's black carbon disulfide includes its IR spectrum, elemental analysis, density, insolubility, and thermal decomposition behavior. All IR peaks in the published spectra of Bridgman's black carbon disulfide were present in photopolymerized $(CS_2)_x$ samples in the appropriate height ratios.[3,4] The density of Bridgman's black carbon disulfide was determined by Butcher as 1.89 g/cm^3.[2] This is within the error of our measurement (1.92 ± 0.03 g/cm^3). These values differ from the density of graphitic carbon (2−2.2 g/cm^3) and yellow sulfur (1.95−2.05 g/cm^3).[21] Butcher also reports: "It is insoluble in all the normal laboratory solvents."[2] Both Butcher and Chan describe attempts to form Bridgman's black carbon disulfide at temperatures above 200 °C, which produces a different material. It lacks the characteristic IR features of Bridgman's black, and contains large amounts of free elemental sulfur.[3,30] Whalley and Bridgman agree that "When heated to about 200 °C at normal pressure it decomposed to carbon and sulfur."[4,31]

Butcher estimates the decomposition temperature at 170 °C.[2] Our mass spectral results suggest that decomposition just begins at 155 °C. Chan and Jonscher published an EPR spectrum of $(CS_2)_x$.[3] Since the bulk solid is diamagnetic, this must have resulted from small amounts of free radicals. This may result from "dangling bond" end groups that a free radical polymerization process would be expected to generate.

The IR assignments are consistent with a polymer dominated by linear $(CS_2)_x$ chains that are extensively cross-linked (Chart 1). The (−SCS−) moiety (group A) is believed responsible for the absorption centered at 1410 cm^{-1}. Group B (a trithiocarbonate group) is believed to be responsible for the absorptions at 1067, 890, 821, and 550 cm^{-1}, and group C (the disulfide bridges) for the three peaks at 507, 471, and 447 cm^{-1}. Yang et al. synthesized the compound C_6S_{10}, which contains some of the structures (Chart 2) thought to be present in $(CS_2)_x$[32].

Chart 1

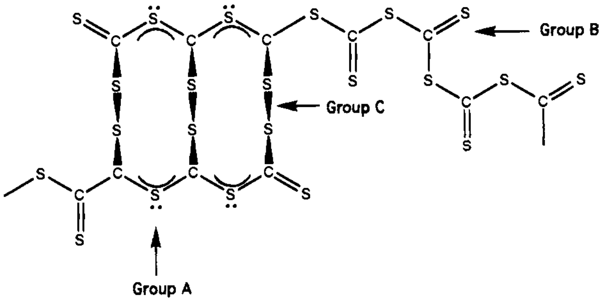
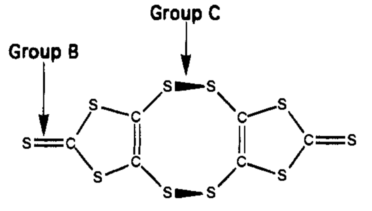


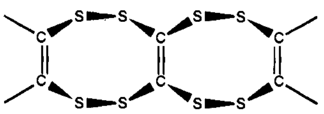
Chart 2



The compound shows a simple IR spectrum with: "a weak $\nu_{C=C}$ (1504 cm^{-1}), strong $\nu_{C=S}$ (1056 cm^{-1}), and a moderately intense ν_{S-S} (505, 467, and 447 cm^{-1})." No other bands were reported. The three absorptions assigned as ν_{S-S} for disulfide bridging carbon atoms in a ring structure are very similar to those in $(CS_2)_x$ (Table 1). The S−S assignment for these absorptions in $(CS_2)_x$ has been confirmed by isotopic analysis. The thiocarbonate (group B) is seen within its characteristic frequency range.

We also considered a structural motif of the type shown in Chart 3. This does not seem to be a major structural element in $(CS_2)_x$ for the following reasons. First, no trithiocarbonate moiety is seen in this structure, yet the 1067-cm^{-1} absorption for group B in $(CS_2)_x$ dominates the spectrum. Second, the mixed $^{12}C/^{13}C$ polymer shows no evidence for any $\nu_{^{12}C=^{13}C}$ vibrations. An intensity enhancement is expected for any $^{12}C-^{13}C$ absorptions present. Furthermore, the absorption centered at 1410 cm^{-1} is too low in frequency for $\nu_{C=C}$, which are

Chart 3



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typically found between 1625 and 1675 cm^{-1}.[24] The high intensity of the 1410-absorption also suggests that it is not a C=C stretch. Such vibrations are typically weak or medium in intensity.[25]

The evolution of CO, OCS, and CS_2 from the polymer during the initial stages of photooxidation supports the notion that the polymer is built from $(CS_2)_x$ fragments. Irradiation of the partially photooxidized polymer under vacuum evolves predominantly CO and CS_2, along with a smaller amount of OCS. This shows that oxygen is incorporated into the polymer during photooxidation and that these products do not merely arise by gas-phase photooxidation of CS_2. Changes in the IR spectrum of the solid support this view. The absorption at 1175 cm^{-1} for the photooxidized polymer may be due to S=O vibrations, which typically are seen in the region 1050−1250 cm^{-1}.[24] Other absorptions may be assigned to other S=O type vibrations or O=S=O stretches. The indistinguishable spectra of the photooxidized $(^{12}CS_2)_x$ and $(^{13}CS_2)_x$ polymers suggest that S=O vibrational modes dominate the IR spectra. Irradiation of the $(CS_2)_x$ polymer (with adsorbed CS_2 removed) without molecular oxygen present produces no IR active gases, including CS_2. The polymer appears photostable (λ > 280 nm) in the absence of oxygen.

The continuous photolysis of carbon disulfide has been studied by several groups.[6,10,23,33,34] A consensus has not been reached about the composition of the aerosol particle. Ernst and Hoffman postulated that the particles consist of $(CS)_x$ formed through reaction of CS.[10] This was inferred from published work, which shows CS and S_2 formation during flash photolysis of CS_2.[6,35] Matsuzaki proposed that the aerosol particle is an amorphous mixture of carbon and sulfur polymers.[23,34] They based this on an observed IR spectrum that agrees quite well with ours. However, they state that "Neither the intense band of C−S nor the C=S stretching vibration is observed in these spectra." They assign the strongest feature of their spectrum at 1070 cm^{-1} to "vibrational modes characteristic of carbon materials." In the far-IR (200 to 450 cm^{-1}) they see one strong absorption centered near 390 cm^{-1}, which is not present in our samples of $(CS_2)_x$ photoproduct. The reason for this difference is not known. A resonance Raman spectrum of $(CS_2)_x$ obtained between 300 and 1600 cm^{-1} does agree with the published spectrum showing absorptions at 1444, 1255, and 497 cm^{-1}.[34]

Matsuzaki and co-workers[34] also published a mass spectrum of their material after heating to 200 °C. The spectrum shows mostly sulfur polymers, CS_2, and CS. This is consistent with the thermal stability discussed here. The mass spectrum recorded by us at 200 °C showed less prominent peaks from the higher weight sulfur ions and more prominent CS and S_2 peaks than reported by Matsuzaki et al. This may arise from different inlet and ionization conditions. It may also result from partial *in situ* thermal decomposition of the aerosol polymer, which was previously prepared[34] with an intense light source (nitrogen laser). The observation of CS and S_2 as the major thermal decomposition products is consistent with a highly S−S cross-linked structure for $(CS_2)_x$.

Although $(CS_2)_x$ is photostable in the absence of O_2, it appears to undergo thermal decomposition with intense light sources. When a sample is irradiated through the walls of a Pyrex flask with a 1000 W arc lamp (using a benzene UV cutoff filter, water IR filter, and focusing optics) it appeared to undergo thermal decomposition. Free sulfur was easily extracted from the residue. The formation of free sulfur, indicative of thermal decomposition, was not observed when the intensity of the radiation source was reduced with a 1.5 OD (≈3% transmission) fused silica neutral density filter (with 33× the irradiation time, coresponding to an equal number of photons deposited). Since $(CS_2)_x$ is photostable in the absence of O_2, the decomposition in the intense light beam probably results from local heating of the strongly absorbing $(CS_2)_x$ polymer. Mass spectra of the photodecomposed polymer (T = 200 °C) showed dominant peaks from higher weight polysulfur ions. This suggests that secondary thermal decomposition of $(CS_2)_x$ aerosol may complicate photochemical studies of CS_2 that employ intense light sources.

Wen et al. studied photoinduced nucleation in a cloud chamber containing small amounts of CS_2 and found: "...the light intensity required to obtain a constant rate of nucleation is inversely proportional to the CS_2 concentration...". If nucleation were initiated by CS or S_2, one would be forced to conclude that, in order to obtain the same rate of nucleation, the same concentration of CS or S_2 should be required regardless of the concentration of CS_2 in the vapor phase."[36] Therefore, if nucleation was initiated by CS or S_2, then $I[CS_2]^2$ would have to be constant (where I is light intensity) to observe the same rate of nucleation. This line of reasoning is based on the reaction scheme (eq 2) first proposed by De Sorgo et al.,[6] where CS_2^* represents a photoexcited state of CS_2. Wen et al. showed

$$CS_2^* + CS_2 \rightarrow 2CS + S_2 \tag{2}$$

experimentally that $I[CS_2]$ is constant for the same rate of nucleation.[36] This observation is consistent with a mechanism where irradiation produces a species that directly induces nucleation.

Safarik and Strausz published a theoretical paper on the mechanism of the long-wavelength photolysis of CS_2 vapor.[7] They note that the most recent thermochemical data make eq 2 endothermic, and therefore untenable. Furthermore, CS appears before S_2 in temporal studies with flash photolysis. They postulate a reaction series (eqs 3−5),

$$CS_2^* + CS_2 \leftrightarrow (CS_2)_2^* \tag{3}$$

$$(CS_2)_2^* \rightarrow CS_3 + CS \tag{4}$$

$$2CS_3 \rightarrow 2CS_2 + S_2 \tag{5}$$

but do not discuss the polymer, other than noting that it exists. The inclusion of $(CS_2)_2^*$ in their reaction series stems from studies of the pressure dependence of the fluorescence intensity in neat $CS_{2(g)}$.[33] This study invoked "eximer" species to explain deviations from Stern−Volmer quenching behavior of CS_2^*. It is possible that the eximer leads directly to the polymer through addition of CS_2. The species CS_3 has only been observed in an electron impact mass spectrum neutralization−reionization experiment involving the decomposition (at 70 eV) of 4,5-dioxo-2-thioxo-1,3-dithiolan.[37] For CS_3 to undergo a bimolecular reaction with itself (eq 5), it would have to have a long lifetime.

There are no published quantum yields for the formation of CS, S_2, and the aerosol, as far as we are aware. Wood and Heicklen did publish rate constant ratios based on Scheme 1,

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which employs their numbering scheme. They attributed the brown deposit that formed in the absence of oxygen to CS wall reactions.[9] These studies employed photolysis cells "preconditioned" by previous photolyses, and concluded that $k_{4b}/k_{4a} = 0.83$. This was based solely on the observed [CO]/[OCS] ratio following photolysis. Reaction 4 is now known to go predominantly by channel 4a with $k_{4b}/k_{4a} < 0.1$.[29,38] Our finding that secondary photolysis of $(CS_2)_x$ in the presence of oxygen produces predominantly CO helps explain the conflicting results, since it provides a source for CO unrelated to CS oxidation. The ratio $k_{4b}/k_{4a} = 0.83$ was used as part of a kinetic analysis to derive the ratios k_{2a}/k_2, k_{3b}/k_3, and k_3/k_2.[9] These other ratios have been used in many later works on the photochemistry of CS_2[19,36,39] and some of these later conclusions bear reexamination.

Scheme 1

$$CS_2^* + CS_2 \rightarrow 2CS + S_2 \qquad (2a)$$

$$CS_2^* + CS_2 \rightarrow 2CS_2 \qquad (2b)$$

$$CS_2^* + O_2 \rightarrow CS_2 + O_2 \qquad (3a)$$

$$CS_2^* + O_2 \rightarrow CS + SO_2 \qquad (3b)$$

$$CS_2^* + O_2 \rightarrow \text{polymer} \qquad (3c)$$

$$CS + O_2 \rightarrow OCS + O \qquad (4a)$$

$$CS + O_2 \rightarrow CO + SO \qquad (4b)$$

Conclusions

Irradiation of $CS_{2(g)}$ at 313 nm produces a solid aerosol that behaves identically to the high-pressure phase—Bridgman's black carbon disulfide. This polymer's elemental composition is $CS_{1.98}$, and we suggest that it forms by a photoinduced polymerization of $CS_{2(g)}$. A similar reaction does not occur efficiently in the liquid, which suggest that a long-lived excited state of CS_2 is involved. The polymer contains IR absorptions diagnostic of the trithiocarbonate ($S_2C{=}S$) groups expected for the linear polymer; however, the intensity of absorptions in the disulfide stretching region suggests an extensively S−S cross-linked structure.

The CS and S_2 observed in some flash photolysis studies of CS_2 appear to be at odds with the nature of the bulk photoproduct. This may be due to either "energy pooling"[40] or a very low probability mechanism, such as the one proposed by Safarik and Strausz.[7] It is also possible, given the ability of the aerosol to absorb UV and visible light, and to thermally generate CS and S_2, that the CS and S_2 observed during photolysis are produced secondarily through local heating of aerosol particles. This is likely under conditions of high light intensity. Most previous studies of the gas-phase photooxidation of CS_2 failed to account for secondary aerosol photochemistry and often were performed in "preconditioned" cells that contain the photoactive $(CS_2)_x$ polymer and its photodecomposition products. Quantitative studies of the mechanism of the gas-phase photooxidation, and its relevance to tropospheric CS_2 are in progress.

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