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Submitted to the
Journal of Physical Chemistry

UCRL-18060
Preprint

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ABSTRACT

S_2Cl_2 was photolyzed in various inert matrices at 20°K for the purpose of identifying the primary photolysis products and studying the nature of the disulfide bond. UV and IR spectroscopy were used to determine the products in Ar, Kr, Xe, CH_4, CO and N_2. In each case, S_2 was found to be formed. The S_2 yield depends on the rigidity of the matrix. CO and N_2 are shown to yield third products. Solute-solute and solute-solvent interactions are excluded from being responsible for the observed results. A plausible mechanism based on the diffusion of photolysis fragments is discussed.

* Part of this work was presented at the 155th National Meeting of The American Chemical Society, San Francisco, Calif., April 1968.

INTRODUCTION

To date the primary photolysis products of S_2Cl_2 are not conclusively known. Snowden and Davidson[1] reported the observation of a new UV absorption at 2370Å when S_2Cl_2 was photolyzed at 77°K in a hydrocarbon glass of 5:1 isopentane-3 methylpentane. They suggested that the absorption might possibly be due to SCl. McGrath[2] reported that S_2 is produced in the flash photolysis of S_2Cl_2. He also listed several new, unanalyzed gas phase absorption bands in the region 3900-4400Å which he attributed to S_2Cl. These bands were only observed when nitrogen was present in S_2Cl_2 to N_2 ratios of 1:100. Thermal decomposition was observed[3] to give sulfur and chlorine as products. The decomposition was proposed to involve breakage of the S-Cl bond to give S_2 and Cl_2 initially.

We have utilized the matrix isolation technique to study the photolysis of S_2Cl_2 because our conditions allow stabilization of reactive intermediates in the photolytic process.

EXPERIMENTAL

The liquid hydrogen cryostat used for most of the matrix experiments has been described earlier.[4] In some of the experiments a Cryo-tip model AC-2L (Air Products and Chemical Company) refrigerator operated with hydrogen was utilized. Experiments at 33°K were performed on the Cryo-tip by operating at the critical temperature of hydrogen. Sapphire or CsBr targets and sapphire or CsI windows, were employed depending on the nature of the experiments.

S_2Cl_2 was premixed with the appropriate amount of matrix gas prior to decomposition. A fixed 5 ml volume was charged with 7 Torr, the room temperature vapor pressure of S_2Cl_2, corresponding to 2 micromoles of material. The S_2Cl_2 was then expanded into a 300 ml volume bulb. Matrix gas was bled into this volume until the desired matrix to S_2Cl_2 ratio (M/R) was obtained, normally 12 cm gas for an M/R = 500. M/R's varied from 200 to 3000.

After equilibration, the mixture was deposited on the target at 20°K. A Delmar greaseless stopcock was used to regulate the flow at approximately 2 millimoles of gas per hour. Pressure in the cryostat during deposition was maintained at 10^{-5} Torr or below.

Eastman practical grade S_2Cl_2 was purified by multiple fractional condensations at -45°C. Linde and Matheson research grade argon, krypton, xenon, methane, and carbon monoxide were used without further purification.

The photolysis source was a General Electric AH-6 high pressure mercury lamp. The lamp was equipped with interchangeable pyrex or

quartz jackets. The wavelength region of photolysis was determined by using a Kodak No. 39 filter with a bandpass of 3100-4800Å and a Corning filter No. 3-73, with bandpass >4000Å. Photolysis times ranged from 5 min. to 3 hours. The lamp to target distance was about 9 in.

Photolysis during deposition was accomplished by passing the mixture of S_2Cl_2 and matrix gas through a 1 in. diameter, 12 in. long externally silvered tube while simultaneously irradiating along the length of the tube.

UV, and visible spectra were recorded using an 0.7 meter Jarrell-Ash Czerny-Turner f/6.3 spectrograph equipped with gratings blazed for 3000Å, 5000Å, and 7500Å, giving dispersions of 5, 10, and 20Å/mm respectively. A xenon high-pressure arc served as the continuum source for photographing absorptions. Spectra were recorded on Polaroid Type 57 film and Kodak type 103a-0 spectroscopic plates.

Infra-red spectra were recorded on a Perkin-Elmer No. 421 Infra-red spectrometer covering the region 4000-250 cm^{-1}.

RESULTS

Figure 1 shows a spectrum of 2 micromoles of S_2Cl_2 in 2 millimoles CH_4. After deposition, the S_2Cl_2 spectrum is observed as a broad, structureless band, centered at approximately 2600Å. The absorption reported at 3100Å in the solution spectrum was not observed, probably because of insufficient amounts of S_2Cl_2. After photolysis, the S_2Cl_2 spectrum is much weaker, or disappears entirely, while a progression of bands corresponding to the S_2 $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition appears from 2800Å-3100Å.[4] No other absorbing species were observed in the UV-visible portion of the spectrum.

The observed process takes place in all matrices studied. The formation of S_2 from S_2Cl_2 is most efficient in a xenon matrix and least efficient in nitrogen. Table I lists various matrices, their melting points, and the photolysis times required for producing an absorbance of 20% at 20°K in a sample containing 2 μmoles of S_2.

Since S_2 forms so readily in xenon, this system was used in several experiments to carefully characterize the photolysis. The results showed that photolysis with radiation of λ 3100-4800Å was as efficient as photolysis with unfiltered AH-6 light, with quartz envelope, and that no appreciable photolysis was observed when the excitation wavelength was greater than 4000Å. The photolysis yield of S_2 is equally efficient over a M/R range of 200 to 3000, and no discernible difference in efficiency was observed at 33°K as compared with photolysis at 20°K. Also, photolysis during deposition gave results similar to photolysis after deposition. In all cases a strong S_2 spectrum was the only observed product absorption.

After five minutes photolysis was incomplete as evidenced by the presence of the S_2Cl_2 absorption band. The progress of the photolysis could also be followed by observation of the ν(S-Cl) infra-red absorption (Fig. 2).

No evidence was obtained for the formation of the SCl radical. Furthermore, we did not observe an absorption in the 2400Å region as reported by Snowden and Davidson.[2] No evidence was obtained for the formation of other secondary products and specifically, xenon chloride was not observed. Similarly, argon, krypton and methane failed to react under the conditions of the photolysis. If secondary products were present their amounts were below our detection limits.

Two of the solvents studied showed a different behavior. When nitrogen was used as a matrix, only trace amounts of S_2 were observed. There was, however, a noticeable decrease in the intensity of the (S-Cl) stretch in the infra-red indicating loss of the S-Cl bond. Therefore, photolysis must have led to other products. Accordingly significant amounts of sulfur were found on the target after warmup. The IR spectrum did not show the N-S stretch.

Carbon monoxide has in the past proven to be an immensely useful reactive matrix.[5] We chose it for the purpose of assisting in indentification of the primary photolysis products, since Milligan and Jaycox[5] reported the reaction of chlorine atoms with CO to give ClCO with essentially zero activation energy. If present, this species would indicate the formation of chlorine atoms during photolysis.

Figure 3 shows the IR absorption in CO after 90 minutes of photolysis of S_2Cl_2 with the AH6 source in a quartz envelope and no filter.

The peaks at 2052, 857, and 839 cm^{-1} all disappear early in the warm-up, but not until the CO matrix has vaporized. The peaks at 1770 and 804 cm^{-1} persist for some time thereafter.

The absorptions at 2052, 857 and 839^{-1} are assigned to COS.[6] The absorption at 1770 and 804 cm^{-1} do not correspond accurately to any possible reported species; therefore any assignment remains inconclusive. The peak shown at 875 cm^{-1} might not be due to a product.

Photolysis in the 3100 to 4800Å region with the Kodak No. 39 filter, considerably reduces the amounts of secondary products formed. Photolysis on the target during depositon resulted in larger amounts of these secondary products.

DISCUSSION

As Table I indicates, the time elapsed before appearance of S_2, and hence, the extent of photolysis of S_2Cl_2 closely parallels the melting points of the matrix gases. It is a linear function of melting point for the gases CH_4, Ar, CO and N_2. The close correlation with melting points suggests that rigidity is an important factor in the determination of product formation. Krypton and xenon deviate from the linearity since both are too rigid to allow product diffusion. This is clearly demonstrated by the equal efficiency of photolysis in xenon at 33°K and at 20°K; xenon at 33°K is still more rigid than krypton or methane at 20°K.

On the basis of infra-red observations, it appears unlikely that solute-solvent interactions contribute significantly to the observed differences in photolysis efficiency. The SCl stretching frequency of the isolated S_2Cl_2 is essentially the same in all matrices; namely 448 cm^{-1} in Xe; 449 cm^{-1} in Kr; 444 cm^{-1} in Ar, 450 cm^{-1} in CH_4; and 447 cm^{-1} in N_2. The differences are small and insufficient to indicate significant weakening of the S-Cl bond due to chlorine-rare gas interaction. Not ruled out is interaction between the chlorine and the matrix after photolysis, although as mentioned earlier, we did not observe any evidence for rare gas compound formation.

The photolysis results from the absorption of light of wavelengths λ 3100-4000Å corresponding in energy to 92-69 Kcal. It therefore appears that the strong S_2Cl_2 absorption at 2600Å is not responsible alone for the observed photolytic process. Rather, the weak absorption in the

region λ 3100-3300Å seems most important.

The fact that photolysis occurs equally well in xenon at M/R from 200 to 3000 eliminates solute-solute processes as being responsible for S_2 formation. The S_2 observed therefore results from isolated S_2Cl_2 molecules. Also, the photolytic process in the gas phase must be closely analogous to the process in the matrix, because of the similarity in results obtained when photolyzing during deposition.

Two primary processes are possible with the absorption of a photon in the energy range of 69 to 92 kcal.

$$S_2Cl_2 + h\nu \rightarrow S_2Cl + Cl \qquad (1)$$

$$S_2Cl_2 + h\nu \rightarrow SCl + SCl \qquad (2)$$

Processes involving the breakage of more than one bond with the absorption of a single photon are not feasible in this energy range.

The intramolecular process,

$$S_2Cl_2 + h\nu \rightarrow S_2Cl_2^* \rightarrow S_2 + Cl_2 \qquad (3)$$

is energetically possible when the excitation energy is greater than about 40 kcal. Possibly contributing to this process is the molecular geometry and the relatively short chlorine-chlorine distance of 4.11Å. This process leads directly to S_2 formation.

Depending on the primary process (1) or (2), the formation of S_2 would occur by secondary photolysis, or reactions:

$$S_2Cl + h\nu \rightarrow S_2 + Cl \qquad (4)$$

$$S_2Cl + Cl \rightarrow S_2 + Cl_2 \qquad (5)$$

$$SCl + SCl \rightarrow S_2 + Cl_2. \qquad (6)$$

Reactions (4), (5), and (6) are all energetically favorable. Reaction (6) however should have a relatively high entropy of activation which surely would cause it to be slower than the others. Competing with reaction (5) would be the recombination reaction:

$$S_2Cl + Cl \rightarrow S_2Cl_2 \qquad (7)$$

The overall observed photolysis efficiency would be the net result of S_2 formation minus recombination losses. It seems likely that the rate of photolysis to S_2 should remain nearly independent of matrix and therefore, the observed decrease in S_2 formation in the lower melting solids might represent an increase in the recombination efficiency of the fragments. The recombination reaction should depend substantially on the nature of the matrix because of the necessity for the chlorine atoms to diffuse.

The SCl radicals could also recombine via the reaction:

$$SCl + SCl \rightarrow S_2Cl_2 \qquad (8)$$

This process is expected to be less favorable for the following reasons. First, similar to reaction (6), it should have a relatively high entropy of activation; second, if the radicals escape from the matrix "cage" during photolysis, recombination due to diffusion would not be expected to occur because of size; and third, if the radicals remain in the matrix cage, xenon, the most rigid matrix, should show the highest recombination efficiency. This is contrary to what is observed.

The energy of the absorbed photon is sufficient not only to break either the S-S or S-Cl bond, but also to impart excess energy to the

fragments. Atomic fragments such as a chlorine atom would likely migrate to a lattice site removed from the remainder of the molecule. Thus the recombination should depend on diffusion rates of the fragments. Milligan[5] has demonstrated that atoms of moderate size can diffuse under certain conditions; the rates depend on atom size, matrix rigidity, and absolute temperature.

In the S_2Cl_2 system, the order of diffusion rates should be:

$$S \sim Cl > S_2 \sim SCl \sim Cl_2 > S_2Cl > S_2Cl_2$$

The probability of the diatomics diffusing at 20°K should be quite small except perhaps in N_2. It is this fact which makes reaction (2) the least attractive of the primary processes. We conclude, therefore, that the S-S bond probably remains intact in the photolytic process. Further evidence for this conclusion is provided by the fact that S_2 is also produced by photolysis of S_2Br_2 in methane at 20°K.[7] In S_2Br_2, the S-S bond retains essentially the same strength as in S_2Cl_2, whereas the S-Br bond is weaker than the S-Cl bond.

The ultimate fate of the Cl in the system was not determined, since the Cl atomic absorption occurs outside the observed spectroscopic range. Also, the Cl_2 absorption is broad in matrices and would have been too weak to be observed.

Reactions of Products

The observation of the decrease of the S-Cl stretch intensity in N_2 at 20°K suggest that photolysis occurs in N_2, and that the S_2 is being lost by reaction processes. The presence of sulfur on the target after warm-up supports this interpretation. It is conceivable that S_2 diffuses

to a limited extent in N_2 at 20°K leading to intermolecular reactions to form longer sulfur chains. These species would give broad S-S absorption spectra in the 2500-3000 λ region, the same region as S_2Cl_2. It is improbable that they would be noted. ClCO was not observed as a product in CO and therefore Cl atoms are not directly proven to be the primary photolytic products. The IR absorptions at 1770 cm^{-1} and 804 cm^{-1} and conceivably a part of the absorption at 857 cm^{-1} are possibly due to Cl_2CO, $(ClCO)_2$, or some other CO and Cl containing species. The molecular geometry of S_2Cl_2 may favor the formation of a chlorine-carbonyl compound such as $(ClCO)_2$ rather than independent ClCO radicals. The fact that our observations were made at 20°K rather than at a lower temperature also complicates the system because of possible diffusion.

COS is only observed, when photolysis occurs at wavelengths shorter than 2800Å (101 Kcal). It results from the reaction of sulfur atoms with the CO matrix. The sulfur atoms are produced by secondary photolysis of S_2

$$S_2 + h\nu \rightarrow 2S \qquad (9)$$

Under the conditions employed, formation and subsequent photolysis leads to a substantial equilibrium concentration of COS.

CONCLUSIONS

Photolysis of matrix isolated S_2Cl_2 yields S_2 as the only identified product; no Cl is observed. The overall quantum yield of S_2 depends on the rigidity of the matrix. Photolysis is as efficient between 3100 and 4000Å, as at 2800Å where S_2Cl_2 absorbs strongest. Above 2800Å the S-S bond apparently remains essentially intact in the photolytic process.

Photolysis in N_2 and CO yields secondary products under certain conditions, and CO reacts with photolysis products with formation of Cl-C bonds.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation and by the United States Atomic Energy Commission. The authors wish to thank Professor L. Brewer for the use of equipment.

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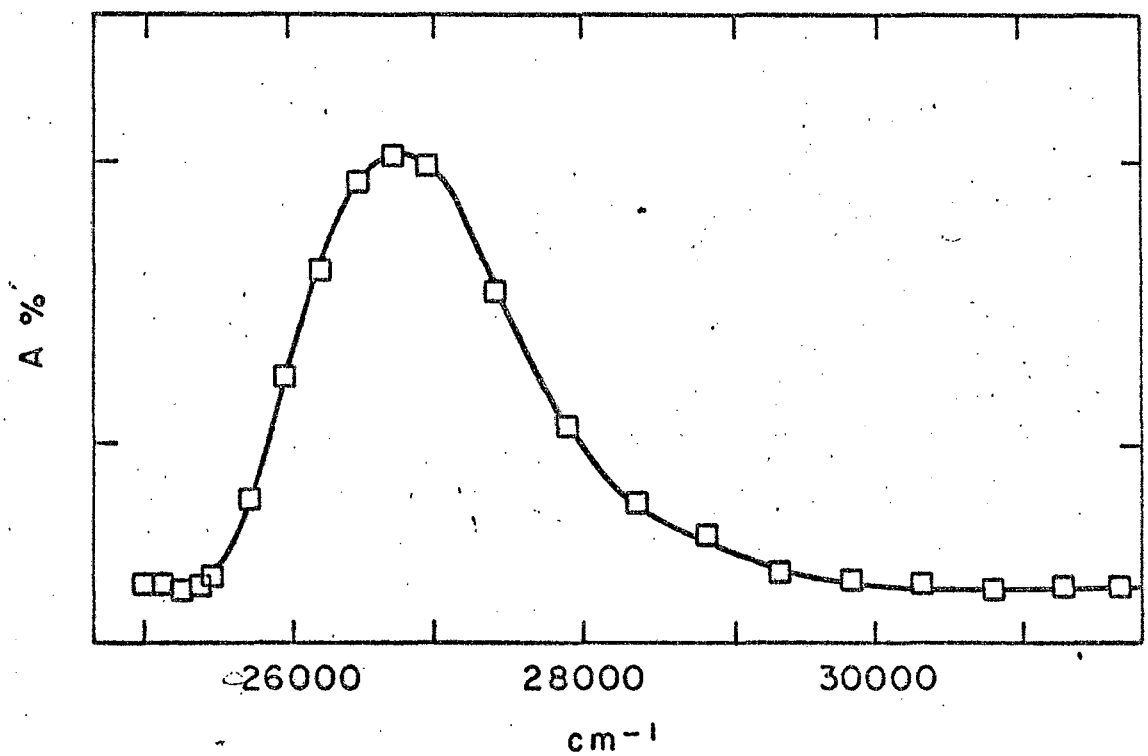
Table I

Matrix	Melting Point (°K)	Photolysis time to appearance of equal amount of S_2 absorption (min.)
Xe	161	5
Kr	116	40
CH_4	90	40
Ar	84	55
CO	74	90
N_2	63	120



XBL686-3039

Fig. 1 Absorption spectrum of a 1:1000 mixture of S_2Cl_2 in methane at 20°K.

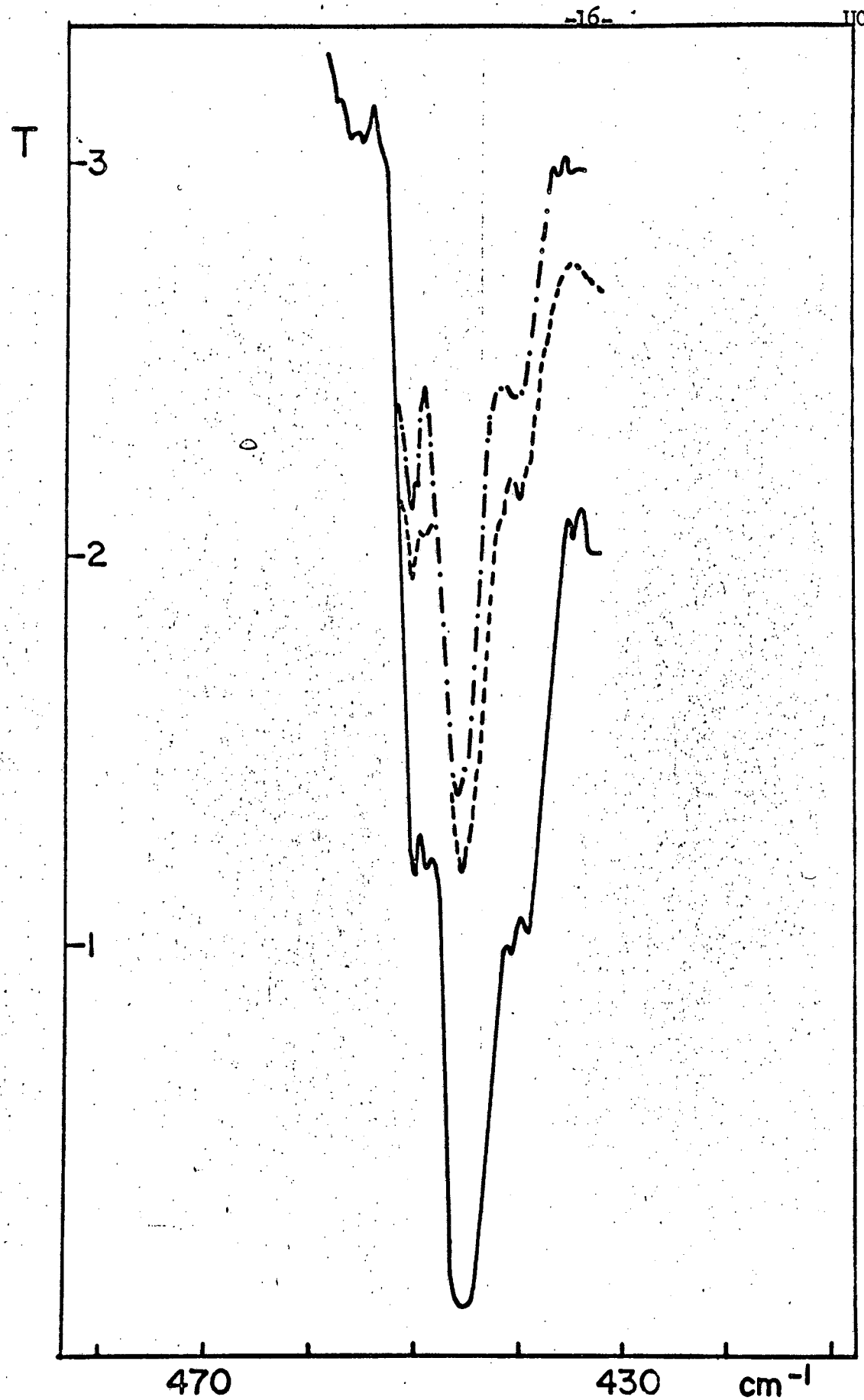


Fig. 2 Infrared absorption of a 1:300 mixture of S_2Cl_2 in Xe after 5 min.——, 12 min. - - - -, and 17 min. -.-.-., photolysis.

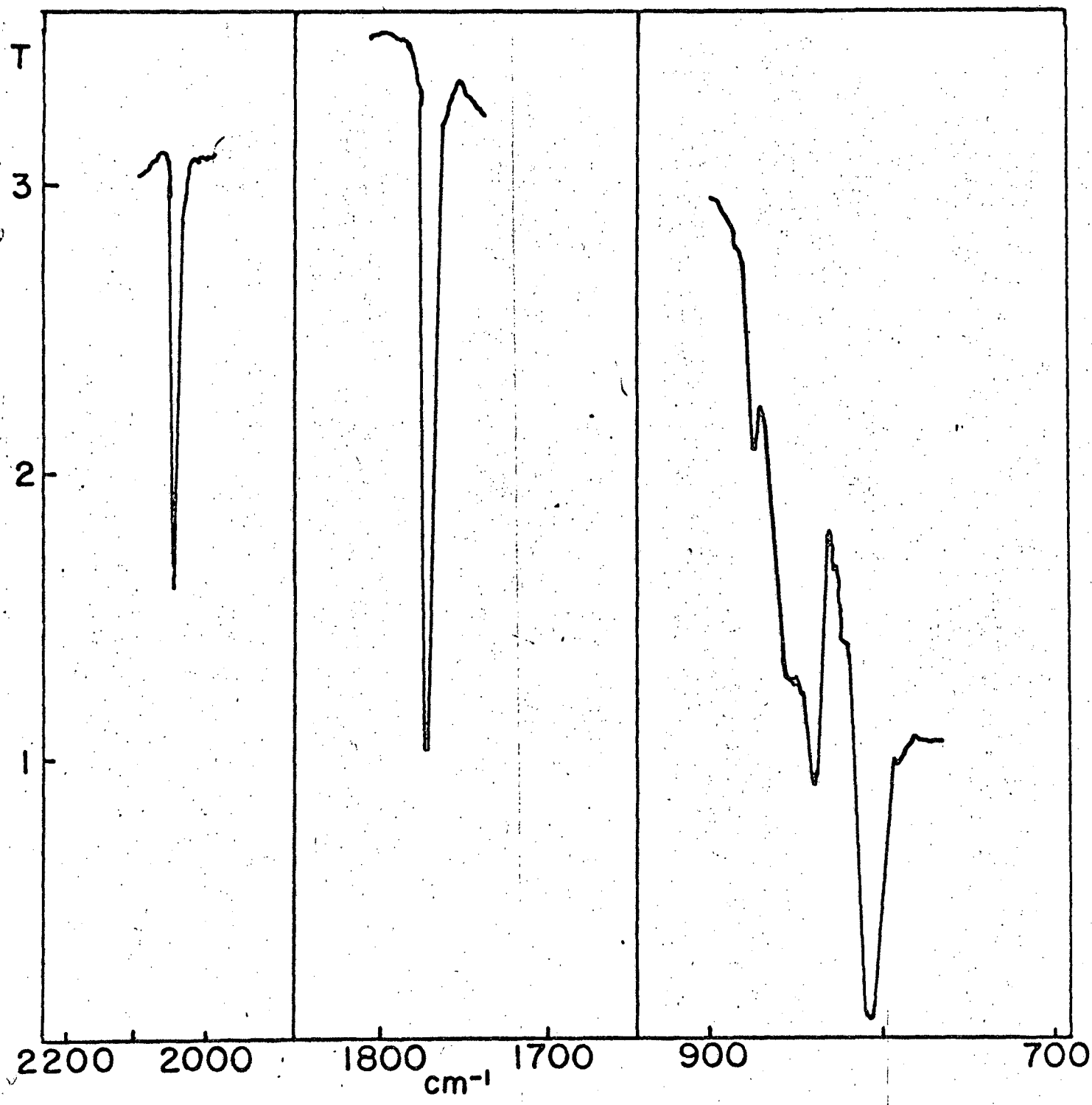


Fig. 3 Infrared absorptions produced by photolysis of a 1:300 mixture of S_2Cl_2 in CO at 20°K.

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