A Systematic Study of the Photolysis of Some Dialkyl Disulfides in a Rigid Glass at 77°K

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A number of primary, secondary and tertiary aliphatic disulfides have been photolyzed in a hydrocarbon matrix at 77°K using super high pressure mercury lamps together with appropriate filter. The spectral changes have been recorded and the reaction products, obtained after warm-up, have been identified using GLC.

All primary and secondary disulfides (except Me_2S_2) behave in an analogous stoichiometrically simple way (in contrast to *tert.* butyldisulfide). Strong evidence is presented for the view that the only detectable overall reaction occurring during photolysis is

$$R_1R_2CHSSCHR_1R_2 \rightarrow R_1R_2C=S + HSCHR_1R_2.$$

The presence of both reaction products has been established.

The spectral changes during the photolysis of dimethyl disulfide are only initially analogous to those of the other primary disulfides. Upon prolonged irradiation unknown reactions occur, leading to the formation of carbonmonosulfide, CS, among other products.

A n experimental study of the possibilities of determining bond-formation energies by direct measurement of the enthalpy change accompanying the radical recombination process

$$2R \cdot \rightarrow R_2$$
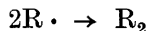
must of course start with the elucidation of the conditions under which one specified, known radical can be produced, quantitatively determined and stored for a sufficiently long period of time. Thus, it is obvious that one should first investigate the homolytic splitting of symmetrical compounds, R—R.

In this field the general lack of knowledge, particularly regarding the stoichiometry of radical formation processes, is such that no guidance can be obtained from the literature in selecting the class of compounds to be studied.

8

However, it has been stated repeatedly in the literature that disulfides upon irradiation can be split into intermediate thiyl radicals: $R_2S_2 \rightarrow 2RS \cdot$.

In recent reviews Bateman, Moore and Porter [1] and Parker and Kharasch [2] have summarized the experimental indications for the homolytic splitting of the S—S bond under different conditions and they conclude that convincing evidence exists for the homolysis of this bond in photochemical reactions, whereas purely thermal homolysis of the S—S bond in organic di- and poly-sulfide molecules at temperatures below 140°C has not yet been conclusively demonstrated. Lewis and Lipkin [3], when illuminating diphenyl disulfide in a rigid matrix at liquid-air temperature, produced a yellow color that disappeared when the sample was brought to room temperature. This color was believed to be due to the free radical $C_6H_5S \cdot$. Barltrop, Hayes and Calvin [4] photolyzed trimethylene disulfide at 77°K in an EPA matrix. Upon photolysis the cell content became pale salmon-colored and the original disulfide peak at 330 mμ disappeared almost completely. When the temperature of the sample was raised a few degrees above liquid nitrogen temperature, the glass lost its rigidity and the cell content rapidly became turbid owing to the formation of polymers. More than 50 % of the original disulfide was recovered. The result from the photolysis was believed to be a diradical $\cdot S(CH_2)_3S \cdot$ which partly polymerized upon warming up. The results of experiments with six simple symmetrical alkyl- and aryl disulfides, aiming at the trapping of free radicals produced under pyrolytic as well as photolytic conditions, have been published by Michaelsen [5]. Among the disulfides sublimed onto a cold finger *in vacuo* and photolyzed *in situ* only the aryl disulfides gave a red deposit, which was thought to be due to free radicals formed through homolysis of the S—S bond. When the disulfides were pyrolyzed in vapor phase by allowing them to pass through a furnace kept above 350°C, a colored deposit collected on the cold finger. This deposit was believed to contain radicals, partly of the type RSS$\cdot$ (yellow deposit) and partly of the type RS$\cdot$ (red deposit); the alkyl disulfides gave a deposit predominantly of the former type.

It seemed therefore reasonable to assume that the photolysis of simple disulfides under conditions favorable for the stabilization of intermediate products formed might lead to the isolation and characterization of thiyl radicals.

The technique chosen (Ref. [9]) was to photolyse the disulfide in a rigid organic matrix at 77°K and to study, primarily, the changes of the UV- and visible spectra. This technique, which has been well established mainly through the work of Norman and Porter [6] and Porter and Strachan [7,8], was early used by Lewis and Lipkin for studying the photolysis of diphenyl disulfide [3]. The present study, however, is only concerned with investigations of aliphatic disulfides. The spectra of these compounds are much less complicated and, moreover, the analysis of possible primary and secondary reaction products is easier to perform.

EXPERIMENTAL TECHNIQUE

Photolysis. The photolysis set-up, consisting of two super high-pressure mercury lamps (900 W each), 35 mm cells filled with nickel sulphate solution (285 g $NiSO_4,6H_2O$ per liter) and exchangeable glass filters, has been described elsewhere [9]. In the present investigation
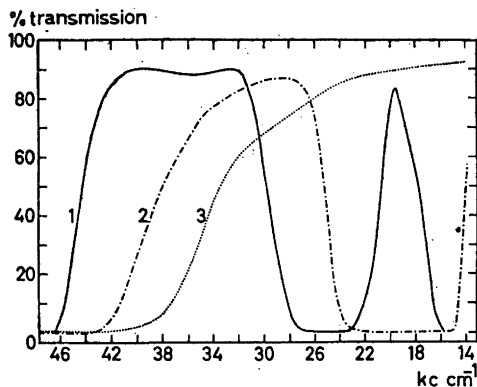
Fig. 1. Light transmission of filters used in the present work. (1) $NiSO_4$, $6H_2O$, 285 g/l, 3.5 cm. (2) Jena filter UG5, high wavenumber cut off 44.3 kc. cm^{-1}. (3) Jena filter WG7, high wavenumber cut off 43.6 kc. cm^{-1}.
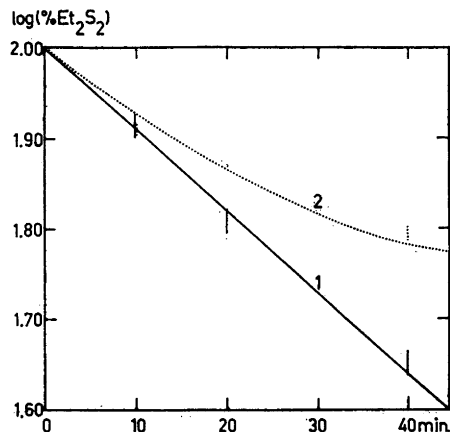
Fig. 2. Log(% remaining ethyl disulfide) from photolysis experiments in matrix B, plotted against time of irradiation (1) at 77°K, (2) at 298°K.

Jena filters (WG7 and UG5) have been used. Fig. 1 shows the light transmission for the solution proper and the filters.

Spectrophotometry. The cell compartment accomodating two 17 × 19 mm quartz cells used both for photolysis and spectrophotometry (Unicam recording spectrophotometer SP 700) has been described elsewhere [10].

Experimental procedure. All solutions were prepared and transferred under rigorously anhydrous conditions as even traces of water interfered, particularly in the short wavelength region [11]. The filling and handling of the quartz cells as well as the general procedure for the photolysis and the spectrophotometer has been described elsewhere [9]. All concentrations given in this paper are referred to room temperature. The actual concentration at 77°K is greater by a factor of 1.32 for solutions in matrix A and 1.30 for solutions in matrix B (see below). The values of molar extinction given have all been corrected for this change in concentration.

Gas-liquid chromatography (GLC) was used to search for reaction products after photolysis. In these experiments disulfide solutions were irradiated in 0.5 mm sealed, clear quartz capillary tubes kept at 77°K in a quartz Dewar vessel equipped with an appropriate heating device to prevent condensation on the outer surface. After photolysis the quarts tubes were opened at 15°C (to avoid evaporation of solvents) and 1 μl samples were withdrawn using a fine glass capillary pipette and transferred to a Pye Argon Chromatograph equipped with an ionization detector. The chromatograph had been rebuilt to accomodate columns of 7 mm inner diam. and 120 cm length, either one or three in series.

Materials

Dimethyl disulfide (British Drug House, b.p. 108.5°/760 mm), *diethyl disulfide* (Eastman chemicals, b.p. 89°/120 mm), *dipropyl disulfide* (Eastman chemicals, b.p. 89°/22 mm), *di-isopropyl disulfide* (Eastman chemicals, b.p. 72°/20 mm), *dibutyl disulfide* (Eastman chemicals, b.p. 101°/10mm), *di-isobutyl disulfide* (Eastman chemicals, b.p. 85°/10—11mm), *di-t-butyl disulfide* (Phillips Petr. Co., b.p. 67.5°/9 mm) and *1-butanethiol* (British Drug

House, b.p. 98°/760 mm) were all purified by two successive fractional distillations through a glass column, 50 × 1.2 cm, packed with Fenske helices, 4 mm in diam., main fractions being collected at given b.p.'s and pressures. The samples of the compounds used in the experiments showed no impurities when analyzed with GLC except for dipropyl disulfide, which contained less than 0.1 % of an unknown substance.

Didecyl disulfide was prepared from fractionallydistilled, pure 1-decanethiol by oxidation with iodine. Owing to decomposition, the disulfide obtained could not be further purified by fractional distillation even at low pressures. It was therefore dissolved in absolute ethanol and slowly frozen out on a cold finger using dry ice as a refrigerant. The procedure was repeated twice.

Di-sec-butyl disulfide. A sample of pure 2-butanethiol, prepared from the corresponding bromide and thiourea, Ref. [12], p. [479], was oxidized with iodine. After two successive fractional distillations at 91°/10 mm a faintly yellow product was obtained, which showed less than 0.1 % impurities (GLC).

Di-cyclohexyl disulfide. Pure cyclohexanethiol, prepared from the corresponding bromide and thiourea, was oxidized with iodine. The disulfide was fractionally distilled twice at 98°/2 mm. The colorless main fraction showed less than 0.5 % impurities (GLC).

Di-neopentyl disulfide. *Neo*pentylmercaptan prepared from *neo*pentyl alcohol and *p*-toluene sulfonylchloride [13] was oxidized with iodine. The disulfide was purified by twofold fractional sublimation in vacuum and was recovered as a white solid, m.p. 40—41°C. GLC showed less than 0.1 % impurities.

Cyclohexanethione was prepared from cyclohexanone according to Sen [14]. The substance was fractionally distilled in vacuum into five receiver flasks which were cooled one by one with liquid nitrogen during the distillation and sealed off as soon as a sufficient quantity had been collected. The deep-red colored fraction, boiling at 66°/16 mm, was used for the experiments.

2, 4, 6-Trimethyl trithiane (a and β) were prepared from thioacetaldehyde, HCl and H_2S [15]. M.p. 101°C and 125—126°C, respectively.

Solvents. All hydrocarbons used, isopentane (techn. grade), pentane (pure grade), *neo*-hexane (pure grade) and 3-methyl pentane (techn. grade), were supplied by Phillips Petroleum Company. They were carefully purified by fractional distillation followed by adsorption on silica gel, the details have been described elsewhere [16].

The matrix forming hydrocarbon mixtures used in this work were:

Isopentane (6 parts)
3-Methyl pentane (1 part) } called matrix A

*Neo*hexane (8 parts)
Pentane (3 parts) } called matrix B

Some properties of these mixtures will be given elsewhere [16,17].

RESULTS

Preliminary experiments

In order to see if an extremely low quantum yield at 77°K could make the photolysis of the disulfide molecule impossible, a 20 mM solution of Et_2S_2 in matrix B was photolyzed in quartz capillary tubes both at room temperature and at 77°K. Besides the disulfide, the hydrocarbon mixture contained 0.1 % octane as a reference substance for the gas chromatographic analysis. After photolysis and warm-up, five identical samples were withdrawn from each tube and run through the gas chromatograph. The ratio

$$\frac{\text{area under } Et_2S_2 \text{ peak}}{\text{area under octane peak}}$$

was taken as a measure of the disulfide concentration. The results are given in Table 1 which shows that the quantum yield is of the same order of magnitude at the two different temperatures.

Table 1. Photolysis of 20 mM Et_2S_2 in matrix B, 0.1 % octane added. WG7 filters.

Time of photolysis	Remaining Et_2S_2 %			
	at 298°K	Mean value	at 77°K	Mean value
10 min	80.5		84.4	
	82.5	81.5	80.5	82.5
20 min	76.0		64.3	
	74.6	75.3	64.7	64.5
40 min	62.0		42.4	
	62.7	62.4	47.0	44.7

A plot of log(% remaining Et_2S_2) against the time of photolysis (Fig. 2) indicates the expected first order decay at 77°K, whereas at room temperature the rate constant of the reaction seems to decrease for prolonged photolysis, probably as a result of the formation of light absorbing secondary reaction products which reduce the amount of active light.

When photolyzed under the same conditions methyl disulfide decomposed at about the same ratio as Et_2S_2. However, for 77°K the decay did not fit a first order plot.

When a mixture of methyl- and ethyl-disulfides was exposed to UV-light, the mixed disulfide was formed. The equilibrium for this mixture has recently been studied [18]. To check if this also occurs in a rigid environment, a solution containing 20 mM Et_2S_2, 20 mM Me_2S_2 and 0.1 % octane in matrix B was photolyzed in quartz capillary tubes both at 77°K and at room temperature. The results from the gaschromatographic analyses are shown in Table 2, which

Table 2. Photolysis of 20 mM Me_2S_2 and 20 mM Et_2S_2 in matrix B, 0.1% octane added. WG7 filters.

Time of photolysis	Me_2S_2/octane	MeSSEt/octane	Et_2S_2/octane	K
20 min at room temp.	2.26	4.60	1.97	4.7
	1.81	3.94	1.74	4.9
	1.47	3.88	1.79	5.6
			Mean value	5.1
40 min at room temp.	1.67	3.39	1.42	4.8
	1.95	3.93	1.53	5.1
	1.34	3.49	1.60	5.6
			Mean value	5.2
2 min at 77°K	2.62	0.14	3.45	
5 min at 77°K	2.59	0.17	3.42	
10 min at 77°K	2.13	0.19	3.16	
20 min at 77°K	1.90	0.25	2.94	
30 min at 77°K	1.67	0.22	2.45	
40 min at 77°K	1.31	0.22	1.98	
Blank, unphotolyzed	2.86	0.10	3.63	
	2.80	0.16	3.58	

gives the ratio of "area under disulfide peak"/"area under octane peak". In addition the equilibrium constant $K = \dfrac{[\text{MeSSEt}]^2}{[\text{Me}_2\text{S}_2][\text{Et}_2\text{S}_2]}$ is given for the photolysis at room temperature, this constant being corrected for the different response of the detector for various disulfides. This correction is taken from Ref. [18] as the same detector was used in both experiments.

As is seen from Table 2 the mixed disulfide is formed very rapidly at room temperature and the value of K is already after 20 min of photolysis very close to the equilibrium constant previously reported (average 5.6). At 77°K, however, no significant correlation can be found between the amount of mixed disulfide formed and the time of photolysis. The small amount of mixed disulfide found at 77°K is probably formed during the manipulation of the quartz capillary tubes. The reaction may, for instance, be caused by the ultraviolet light produced when the tubes are melted off in a hydrogen flame. It is of interest to notice that most spectrophotometric experiments have been performed in *ca.* 400 times more dilute solutions, in which the average distance between neighbouring disulfide molecules is increased by a factor of 7 (*cf.* below).

From the preliminary experiments it was apparent that, to a considerable extent, disulfide disappears irreversibly during photolysis followed by warm-up. At 77°K the decomposition reaction was found to be, within the limits of error, unimolecular, indicating a direct dependance on the excitational process. Further, the experiments with mixtures of disulfides show that, whatever the reaction mechanism is, an excited disulfide molecule cannot diffuse in the solid matrix to be able to react with a second disulfide molecule.

Although the preliminary results, concerning the possibility of utilizing the chosen method for thermochemical studies of radical recombination energies, were discouraging, it was felt necessary to gain further knowledge of the causes for the apparent failure. Only in this way can one devise experimental conditions, whereby the original idea could be successfully realized.

Spectrophotometric results

Primary alkyl disulfides. A cell containing 0.4 mM butyl disulfide in matrix A together with an appropriate reference cell were cooled down to 77°K inside the cell compartment previously described. An ultraviolet spectrum was recorded after which the solution was photolyzed for a few minutes using WG7 filters. When a new spectrum was recorded shortly after the end of the photolysis period the disulfide peak at 40 kc. cm^{-1} had decreased (Fig. 3). Repeated recordings of the spectrum at various times showed no change in transmission after the end of the photolysis as long as the liquid nitrogen level was kept above the optical path. Repeated photolysis resulted in a further decrease of the disulfide peak and if the spectra after various times of photolysis were recorded on the same paper an isosbestic point at 40.85 kc. cm^{-1} showed up.

The various curves were analyzed and log(% remaining disulfide) at different wavenumbers was plotted against the time of photolysis. A strict first
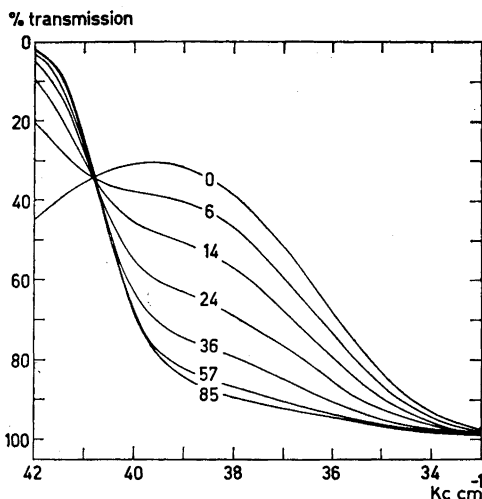
Fig. 3. Photolysis of 0.4 mM butyl disulfide in matrix A at 77°K. The figures give the time of photolysis in minutes.
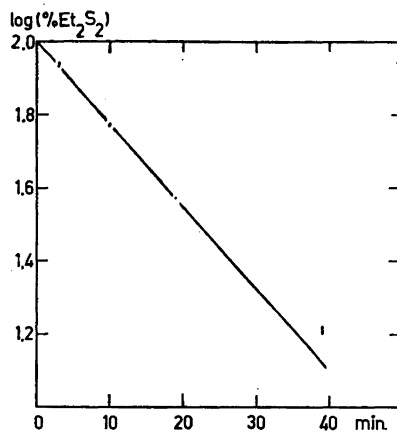
Fig. 4. Log(% remaining butyl disulfide) from photolysis in matrix A at 77°K, plotted against time of irradiation.

order decay was found in a small wavenumber region for photolysis times less than *ca.* 30 min. Fig. 4 shows the results from a typical run; the vertical extent of the four marks represents the maximum deviation when the disulfide concentration is measured at four equally spaced wavenumbers from 37.6 to 38.8 kc. cm^{-1}. Outside this wavenumber region the calculated values did not fit the straight line indicating the formation of light-absorbing reaction products.

The frozen cells were brought to room temperature and the spectrum recorded as soon as possible. This could usually be started within 3—5 min after the disulfide containing cell was lifted up from the liquid nitrogen. Comparison
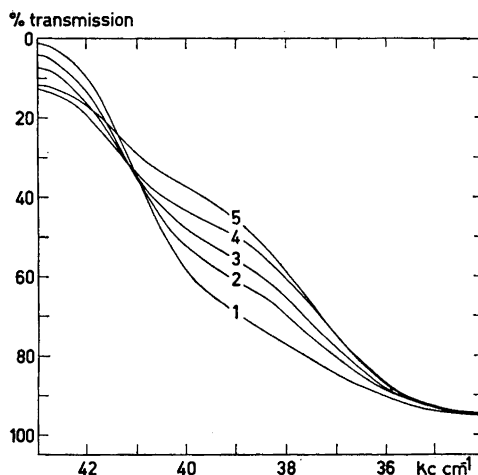
Fig. 5. Spectral changes of a 0.4 mM butyl disulfide, photolyzed at 77°K and brought to room temperature. After (1) 6 min., (2) 15 min., (3) 30 min., (4) 3 h, and (5) 24 h at 298°K.
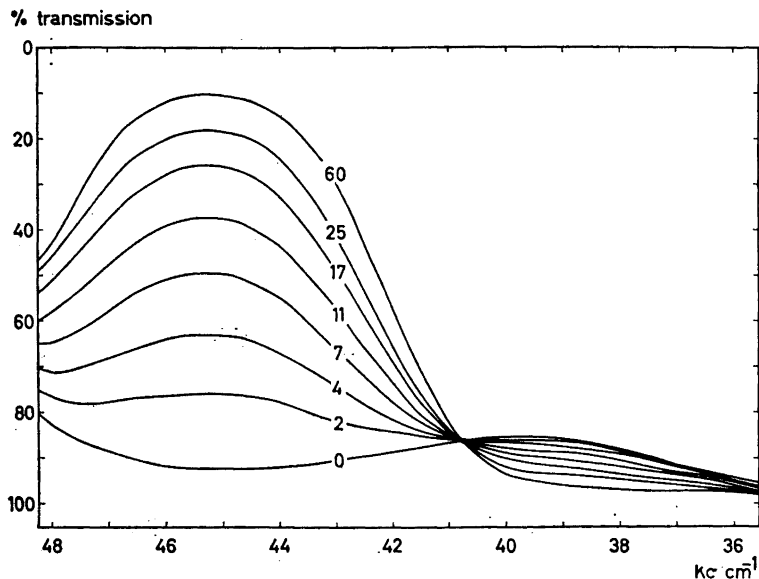
% transmission

Fig. 6. Photolysis of 0.05 mM butyl disulfide in matrix A at 77°K. The figures give the time of photolysis in minutes.

with the spectrum recorded before the cells were frozen down showed that the amount of remaining disulfide after warm-up was the same as the amount of remaining disulfide measured at 77°K after the last photolysis. The spectrum after warm-up changed slightly with time as shown in Fig. 5.

In order to study more carefully the high absorption peak which was developed during photolysis the experiment was repeated using 0.05 mM disulfide. Fig. 6 shows the spectra recorded after increasing times of photolysis. As is seen from the figure a broad band with a maximum at 45.2 kc. cm^{-1} was created. If the reaction product, responsible for this peak, was formed in the first-order decay reaction, its optical density ought to increase at any wave-number with time of photolysis according to the following equation *:

$$D = \varepsilon\, C_0 l(1-e^{-kt})$$

D = optical density
ε = molar extinction coefficient of the reaction product
C_0 = initial concentration of the disulfide
l = cell length
k = rate constant of the reaction
t = time of photolysis

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* It is obvious that this equation is valid also if two identical species are formed per disulfide molecule, the calculated molar extinction coefficient in this case being twice the true one.
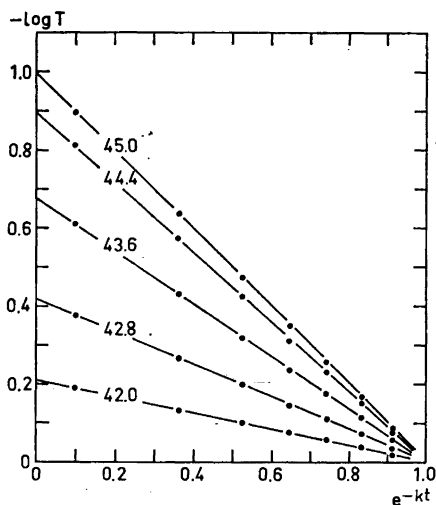
Fig. 7. Optical density plotted against e^{-kt} for various wavenumbers, indicated by figures; k equal to 0.046 min^{-1}.
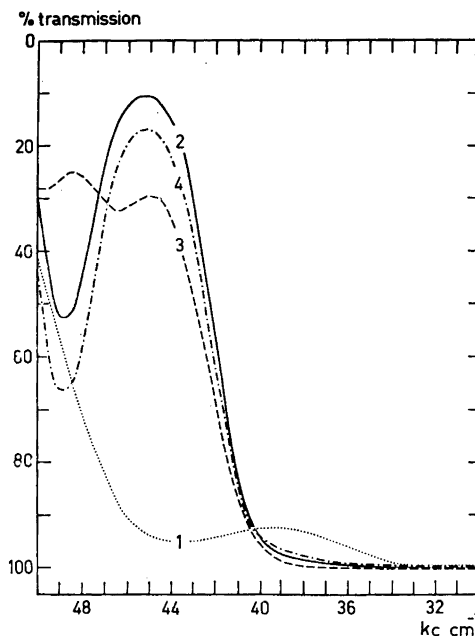
Fig. 8. Spectra of 0.05 mM butyl disulfide in matrix A. (1) Unphotolyzed at 77°K; (2) after 60 min. of photolysis at 77°K and (3) at 298°K; (4) after recooling to 77°K.

Fig. 7 gives the optical density at various wavenumbers plotted against e^{-kt}. The optical density values have all been corrected for remaining unphotolyzed disulfide. A set of different values for k had to be tried until a particular value gave straight lines. In the given experiment k was found to be 0.046 min^{-1}, which corresponded to $t_{1/2} = 15$ min. The straight lines could be extrapolated to infinite time of photolysis ($e^{-kt} = 0$) and thus the molar extinction coefficient for the reaction product at 77°K could be obtained; log $\varepsilon_{max} = 3.96$.

A spectrum recorded a few minutes after the photolyzed solution was brought to room temperature is shown in Fig. 8 (curve 3). The high absorption peak was still present, although somewhat lowered and shifted about 0.2 kc. cm^{-1} towards higher wavenumbers. In addition, a more intensive absorption peak became visible at 48.4 kc. cm^{-1}. The appearence of this peak was fully reversibly dependent on the temperature *. Curve 4 (Fig. 8) shows the spectrum when the optical cells were cooled to 77°K for the second time. The small discrepancy between curves 4 and 2 could be ascribed to dilution of the photolysis product with some unphotolyzed disulfide solution remaining in

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* This temperature-dependent absorption is at present without explanation — it has been found in all cases studied with two exceptions — dimethyl and dicyclohexyl disulfide. By independent control experiments it has been established that the spectrophotometer is reliable down to 51 kc. cm^{-1}. *Added in proof:* Reference is made to a later publication [29].

the stem of the optical cell during photolysis. Repeated cycling of the probe between 77°K and room temperature always gave the same result as far as the appearence of the peak at 48.4 kc. cm^{-1} was concerned.

If the photolyzed solution was allowed to stand at room temperature, a slow decrease in absorption, as shown in Fig. 9, could be noticed. It was found that the ratio between the two maxima did not change. Similar experiments repeated with matrix B gave identical results, which was also the case when two sets of filters, other than WG7, were used in the light path, viz. WG6 and KG2, high wavenumber cut off at 41.2 and 40.6 kc. cm^{-1}, respectively.

All observations described have been reproduced in a number of runs and, further, experiments with ethyl-, propyl-, isobutyl- and neo-pentyl-disulfides have been performed, all showing the same detailed behaviour with exception of minor differences regarding the spectrophotometric characters of the photolysis product. The results have been summarized in Table 3. Decyl disulfide also gave the same results with the exception that the isosbestic point was observed at 39.7 kc. cm^{-1}. The solutions of this disulfide became turbid when frozen down to 77°K, and no accurate kinetic determinations could therefore be made. However, the rate of photolysis seemed to be considerably lower than that of the other primary disulfides. The spectrum of neo-pentyldisulfide did not differ from other primary or secondary alkyldisulfides. At room temperature in matrix A the maximum appeared at 39.0 kc. cm^{-1}; log $\varepsilon_{max} = 2.48$.

Secondary alkyl disulfides. The investigated secondary alkyl disulfides (isopropyl-, *sec*-butyl- and cyclohexyl) also gave analogous results (Table 3),
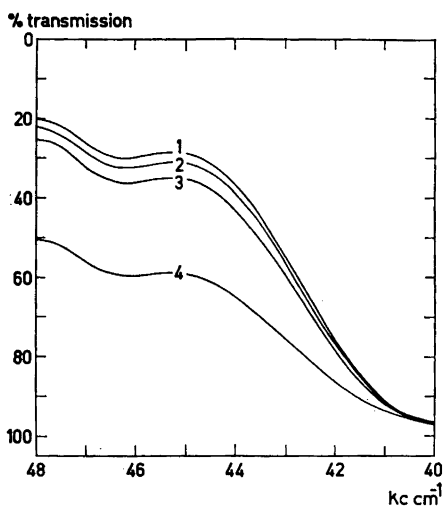

Fig. 9. Spectral changes of a 0.05 mM butyl disulfide, photolyzed at 77°K and brought to room temperature. After (1) 5 min., (2) 60 min., (3) 2.5 h, and (4) 18 h at 298°K.
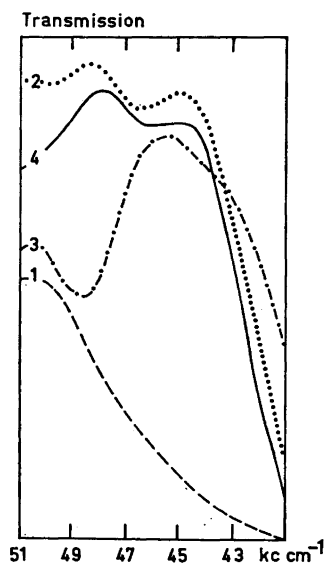
Fig. 10. Spectra of photolyzed disulfides, after warm-up. (1) Me$_2$S$_2$; (2) Bu$_2$S$_2$; (3) *sec*-Bu$_2$S$_2$ and (4) *neo*pentyl disulfide. The 100% line different for the various disulfides.

although the high absorption peak and the isosbestic point were shifted towards lower wavenumbers, 44.0 and 39.3 kc. cm^{-1}, respectively. The extrapolated log ε_{max} for the photolysis product at 77°K was also in this case about 4. The

Table 3. Spectrophotometric characters at 77°K of the photolysis product for various dialkyl disulfides. Figures in brackets indicate the number of experiments. The uncertainties are expressed as mean deviations.

	Wavenumber of peak	Wavenumber of isosbestic point	log ε_{max}
Me$_2$S$_2$	48.07 (1)	43.31 ± 0.04 (4)	(3.8) (1)
Et$_2$S$_2$	45.50 ± 0.05 (5)	41.08 ± 0.03 (6)	3.91 ± 0.03 (3)
n-Pr$_2$S$_2$	45.27 ± 0.05 (2)	40.96 ± 0.06 (3)	4.0 ± 0.1 (1)
n-Bu$_2$S$_2$	45.21 ± 0.03 (7)	40.85 ± 0.04 (10)	3.94 ± 0.03 (6)
i-Bu$_2$S$_2$	45.06 ± 0.02 (2)	40.86 ± 0.02 (3)	3.91 ± 0.07 (2)
neo-Pentyl$_2$S$_2$	44.97 ± 0.02 (2)	40.55 ± 0.04 (2)	4 (2)
i-Pr$_2$S$_2$	44.00 ± 0.03 (2)	39.11 ± 0.03 (3)	3.96 ± 0.02 (2)
sec-Bu$_2$S$_2$	44.03 ± 0.04 (3)	39.26 ± 0.03 (5)	3.94 ± 0.02 (2)
Cyclohexyl$_2$S$_2$	44.60 ± 0.03 (2)	40.27 ± 0.03 (3)	3.91 ± 0.04 (2)

secondary disulfides gave somewhat different results after warm-up. For isopropyl- and sec-butyl-disulfides the two peaks visible at room temperature were moved closer to each other and the reversible one dominated so strongly in intensity that the original peak at 44 kc. cm^{-1} was visible only as a shoulder (Fig. 10, curve 3). Cyclohexyl disulfide gave no second peak upon warm-up; the maximum appeared at 44.6 kc. cm^{-1} both at 77°K and at room temperature.

Tertiary alkyl disulfides. The spectrum of tert-butyl disulfide does not show the disulfide maximum at 40 kc. cm^{-1} [19]; only a weak shoulder is seen at room temperature with inflections at ca. 40 and 44 kc. cm^{-1}*. When a solution in matrix A was cooled to 77°K a maximum became visible at 44.6 kc. cm^{-1} (log ε_{max} = 2.97); a minimum appeared at 46.7 kc. cm^{-1} (log ε_{max} = 2.87) and the absorption again increased at higher wavenumbers.

A 0.25 mM solution in matrix A was photolyzed at 77°K using UG5 filters. The disulfide maximum decreased during photolysis in the whole range 48—35 kc. cm^{-1}, neither the isosbestic point nor the high absorption peak was found. When the disulfide concentration had decreased to about 50 % of its initial value, the absorption again rose slowly and a new maximum appeared at 45.5 kc. cm^{-1}. After one and a half hours of photolysis the initial optical density was restored. The complicated kinetic pattern prevented a straightforward analysis. The 45.5 kc. cm^{-1} peak disappeared during warm-up, and the spectrum at room temperature showed only a continuously increasing absorption towards higher wavenumbers. After a second cooling to 77°K the peak became visible again.

Methyl disulfide gave, when photolyzed at 77°K in a 0.05 mM solution in matrix A with WG7 filters, a high absorption peak at 48.1 kc. cm^{-1}, an isosbestic point at 43.3 kc. cm^{-1} and an extrapolated value of log ε_{max} = 3.8; the last value is somewhat uncertain as the high wavenumber region made a precise measurement difficult. The spectrum at room temperature of the

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* If log ε is plotted against wave-length, the shoulder almost vanishes; cf. Ref.[14]
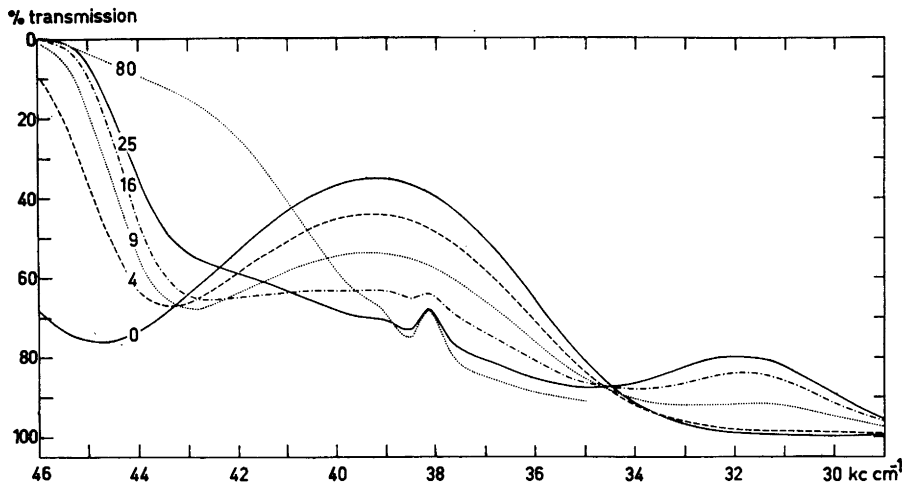
Fig. 11. Photolysis of 0.5 mM methyl disulfide in matrix A at 77°K. The figures give the time of photolysis in minutes.

photolysis product is shown in Fig. 10 (curve 1). The absorption decreased when the sample was allowed to stand at room temperature.

Fig. 11 shows results obtained with a 0.5 mM solution under otherwise identical conditions. The total time of photolysis in minutes is given with each curve. The three first curves all passed through the isosbestic point at 43.3 kc. cm^{-1}, but the curve recorded after 16 min showed a beginning additional absorbance at this wavenumber and a peak at 31.9 kc. cm^{-1} became clearly visible. The last two spectra show these characteristics even more pronounced, a further distinctive feature seen here is a double peak with maxima at 38.18 and 39.20 kc. cm^{-1}. At the end of the photolysis the cell content was turbid, and when the sample was brought to room temperature traces of a colorless precipitate were seen at the bottom of the cell. The spectrum now mainly consisted of one sloping line ranging from 46 to 28 kc. cm^{-1}. An inflection clearly indicated that the broad peak at 31.9 kc. cm^{-1} was still there but that the double peak at 38—39 kc. cm^{-1} had disappeared. It did not become visible again after recooling to 77°K.

Disulfides at high concentrations. Ethyl-, butyl- and cyclohexyl-disulfides have also been photolyzed in 5 mM solutions in matrix A at 77°K using WG7 filters. When irradiated for about an hour these solutions all gave a faint absorption in the visible part of the spectrum ranging from 30 to 17 kc. cm^{-1}. A weak maximum was found around 20 kc. cm^{-1}. The sample cell when lifted up and viewed perpendicularly to the light path showed two thin dark yellow layers close to the two parallel windows. The rest of the cell had a pale rose color which persisted when the sample was brought to room temperature whereas the yellow color disappeared when the cell content lost its rigidity. A spectrum recorded at room temperature showed an absorption between

23 and 17 kc. cm^{-1} with a maximum at 19.5 kc. cm^{-1}. However, the reduction in transmission never exceeded 10 % even at peak maximum.

The yellow color was probably due to the photolysis of mercaptan formed from the disulfide [20]. Several filter combinations were tried, without positive result, in order to achieve a light induced splitting of the disulfide without simultanous photolysis of the mercaptan.

Mercaptans. Alkyl mercaptans when photolyzed at low concentrations (0.05 and 0.4 mM) in matrix A at 77°K using WG7 filters showed very small changes in the spectrum after as much as an hour of irradiation, the most characteristic sign being an *increased transmission* around 48 kc. cm^{-1}. Besides, the transmission was reduced by a few percent at the mercaptan peak for the most concentrated solution.

Cyclohexanethione. The spectrum of cyclohexanethione has been investigated by Sen [21] and by Janssen [22]. Janssen found in cyclohexane a broad band ranging from 25 to 17 kc. cm^{-1} with a maximum at 19.8 kc. cm^{-1}. He also found a rather high ultraviolet absorption owing to impurities but concluded that "cyclohexanethione has no strong absorption band (log $\varepsilon >$ 3.5) at wavelengths above 220 mμ". Owing to the high rate of equilibration between the thione- and its corresponding enethiol-form, 1-cyclohexenethiol, the recorded spectrum cannot, however, be very reliable in the UV-region [14].

A 0.1 mM solution in matrix A was prepared and the recording of a spectrum started within 30 min after the sealed-off flask containing cyclohexanethione was brought to room temperature (see under M a t e r i a l s). The spectrum at 25°C consisted of a rather broad band starting at 35 kc. cm^{-1} with one maximum at 43.8 kc. cm^{-1} and an inflection unveiling a second somewhat lower maximum at about 46.3 kc. cm^{-1}. At 77°K only one peak was seen at 44.3 kc. cm^{-1} (log ε_{max} = 3.74, assuming the substance to be pure thione-form); no trace of the second peak was visible. The 19.8 kc. cm^{-1} absorption maximum could be verified only at high concentrations (calculated total concentration 20 mM, 85 % transmission).

2, 4, 6-Trimethyl-trithiane. The spectrum of *sym*-trithiane was taken in ethanol and in matrix A at room temperature, and the results verified earlier measurements; with an absorption peak at 41.7 kc. cm^{-1} (log ε_{max} = 3.16) [23]. α- and β-2,4,6-trimethyl-trithiane were studied in 0.2 mM solutions in matrix A. Both spectra looked very similar to that of *sym*-trithiane (peak at 41.9 kc. cm^{-1}, log ε_{max} = 2.94).

Control experiments. Pure samples of the hydrocarbon solutions used were photolyzed at 77°K. When WG7 filters were used, half an hour of irradiation did not change the 100 %-line. If the glass filters were removed a further hour of photolysis caused a small change (about 10 %) around 48 kc. cm^{-1}, where the transmission *increased.*

Photolysis of butyl disulfide at room temperature was carried out in a 0.05 mM solution in matrix A. The absorption peak at 45.2 kc. cm^{-1}, found at low temperature, could be easily seen, although the spectrum was very obscure. However, the intensity was reduced by a factor of ten.

Gas chromatographic results

Butyl disulfide was photolyzed in quartz capillary tubes and analyzed for
1-butanethiol by means of the gas chromatograph. All experiments were carried
out at 77°K using WG7 filters. After irradiation the tubes were kept in liquid
nitrogen until they were opened for analysis. From each tube at least five
identical samples were withdrawn and put on the column. The mercaptan
could be quantitatively estimated by comparison with octane as reference
substance. Measurements were made using initial disulfide concentrations of
10 and 20 mM in matrix A. The time of photolysis varied from 10 to 60 min.
Mercaptan was found in all photolyzed samples, the amount varied with the
time of photolysis and in some of the tubes irradiated for one hour it corre-
sponded to a 60 % conversion of the initial disulfide assuming a 1:1 ratio.
Attempts were made to increase the yield. It seemed, however as if *ca.* 60 %
represented an upper limit. Unphotolyzed blanks showed no trace of mer-
captan.

DISCUSSION

Even the preliminary experiments have made clear three important points
for the elucidation of the chemical reactions occurring after irradiation of
disulfides: First, it was found that the disulfide irreversibly disappeared in the
reaction; secondly, the decomposition was found to be a first-order reaction.
Thirdly, it was shown that diffusion of disulfide molecules or alkyl thiyl
radicals must be completely or nearly completely hindered in the matrix
at 77°K.

The spectrophotometric investigations in all cases fully confirmed the
occurrence of irreversible chemical reactions upon photolysis. The very regular
change in spectral pattern obtained for primary and secondary disulfides
showing a precise isosbestic point at about 40 kc. cm^{-1} strongly indicated a
simple and well-defined chemical reaction to proceed during the irradiation.
Further, the kinetics corresponded strictly to that of a first-order reaction as
shown by the disappearance of disulfide as well as by the formation of a photo-
lysis product. Although every effort was made to detect spectrophotometric-
ally, after irradiation, the presence of some unstable species that might be
of a radical nature, no trace of such a species could be found by the method
used.

Taking the given facts into consideration it was concluded that the irradia-
tion initiates a chemical reaction which takes place in the nearest environment
of the excited disulfide molecule and leads to the formation of stable molecular
species.

Turning to the problem of the nature of this reaction, the following facts
must be considered. The difference in behaviour between the primary and the
secondary disulfides and the *tert.* butyl disulfide is striking. The spectral change
during photolysis of the last compound is complicated and does not allow a
simple analysis. The discrepancy can hardly be explained as a result of steric
factors, as *neo*-pentyl disulfide behaved normally. In the literature it has often
been postulated that hydrogen abstraction from an atom adjacent to a radical

site is very easily achieved. In particular, much evidence has been collected for a disproportionation of alkoxyl radicals according to the reaction [24]:

$$2 R_1R_2CHX \cdot \rightarrow R_1R_2C{=}X + HXCHR_1R_2$$

where X = O, R = H or Alk.

The same mechanism has been proposed by Coope and Bryce [25] for the thermal degradation of Me_2S_2. These authors found that 1 mole of MeSH was formed per mole of Me_2S_2, together with a product that was assumed to be polymeric thioformaldehyde. It is therefore suggestive that only those disulfides with at least one hydrogen atom in the α-position react in a simple manner as judged from the spectrophotometric evidence. The assumption was therefore made that the analogous reaction, X = S, occurs, following the homolytic splitting of the disulfide to identical thiyl radicals.

In accordance, the experiments showed butanethiol to be formed in increasing amounts during continued photolysis of butyl disulfide. The observation that the yield could not be increased above 60 % is in good agreement with the results obtained by Walling and Rabinowitz [26]. These authors studied the photolysis of 0.2—0.035 M isobutyl disulfide in cumene at 35°C and found that the yield of 2-methyl 1-propanethiol reached a constant level after a certain period of photolysis. They concluded that this level corresponded to a steady state in which the thiol was decomposed by the light at the same rate as it was formed.

Direct evidence for the formation of mercaptans even at 77°K is obtained from the photolysis experiments on disulfides at high concentrations. The yellow color formed upon prolonged photolysis, and irregularly distributed in the sample cell, was also found to be a general feature accompanying photolysis of mercaptans under otherwise similar conditions [20]. The subsequent photolysis of mercaptan formed in the primary chemical reaction also explains the fact that, at 0.4 mM concentrations, the kinetics of the reaction did strictly follow a first-order rate equation only until about 60—70 % of the disulfide was decomposed (Fig. 4).

Provided the above explanation holds, the second reaction product must be a thioaldehyde or a thioketone, depending on whether the disulfide used is primary or secondary. The ease with which the aliphatic thials and thiones trimerize or polymerize makes it extremely difficult to determine the physical properties of the monomers. The only known compound that could be used for the purpose of spectral comparison was cyclohexanethione which further suffers from the disadvantage that it rapidly isomerizes to cyclohexenethiol. Janssen [22] has pointed out that the visible absorption of the thione monomer gradually disappears at room temperature, whereas the ultraviolet absorption remains constant. As expected, both cyclohexenethiol and the trimerized cyclohexanethione exhibit absorption only in the UV-region.

The absorption spectra recorded for the photolysis products from cyclohexyl disulfide and from the sample of freshly distilled cyclohexanethione both show the same peak at 19.8 kc. cm^{-1}. Even if the aforementioned difficulties made a comparison at higher wavenumbers rather doubtful, it is striking that the high absorption maximum was found at 44.3 kc. cm^{-1} (log ε_{max} = 3.74) for the sample of cyclohexanethione and at 44.6 kc. cm^{-1} (log ε_{max} = 3.91)

for the photolysis products. In calculating ε_{max} for the sample of cyclohexa-
nethione it was assumed that the substance was pure. According to Sen [14],
a freshly distilled sample of cyclohexanethione holds only 62 % of thione-form,
the rest being the enethiol isomer. If this is accounted for, the recalculated
ε_{max}-value becomes 3.95. The excellent agreement may be fortuitous but
strengthens the almost obvious conclusion that the cyclohexanethione found
during photolysis cannot protomerize in the matrix. The spectrum extrapolated
from the kinetic measurements must therefore be due to pure thione-form
together with cyclohexanethiol. The molar extinction of thiol at $44-45$ kc. cm^{-1}
is in any case less than 3 % of that of the thione and thus the mercaptan does
not interfere significantly with the calculation.

After photolysis of a primary or secondary disulfide it has quite generally
been found that, after warm-up, the transmission increases at wavenumbers
above about 41 kc. cm^{-1} (Fig. 9) and decreases in the range $41-36$ kc. cm^{-1}
(Fig. 5). This change can best be explained by referring to the trimerization
of the thial or thione formed during photolysis *. The trimeric ethanethial has
a spectrum with a peak at 41.9 kc. cm^{-1}. The spectrum of the monomer, on the
other hand, has a broad maximum extending below 38 kc. cm^{-1} with the
doublepeaks at 45.4 and 48.5 kc. cm^{-1} (room temperature, absorption curve
corrected for the presence of ethanethiol and remaining disulfide). If the
absorption curves are plotted on the same diagram for a molar ratio of monomer
to trimer equal to 3:1, the curves intersect at 40.5 kc. cm^{-1} with an estimated
error of less than 0.5 kc. cm^{-1}. Thus, if a set of absorption curves were recorded
from time to time during the trimerization reaction, an isosbestic point should
be found at the intersection wavenumber. From the experiment a value of
40.5 kc. cm^{-1} was found.

As a whole the facts are strongly in favour of the suggested reaction. From
a mechanistic point of view the most simple explanation ** would be that the
primary step upon excitation is a symmetrical homolytic splitting of the
disulfide molecule into two identical thiyl radicals. The subsequent reaction
is governed by the close contact between the fragments. Owing to the cage
effect [28], the radicals cannot diffuse into the hydrocarbon matrix and have
to react either with each other or with matrix molecules. Apparently the
α-hydrogen abstraction is the most favoured reaction.

The photolysis of dimethyl disulfide (Fig. 11) initially showed the same
characteristics as the other primary disulfides studied, especially at low
concentrations. The increase in absorption above 43.3 kc. cm^{-1} with a peak
at 48.1 kc. cm^{-1} indicated the formation of monomeric thioformaldehyde.
Upon prolonged irradiation, however, presumably secondary photolysis reac-
tions occurred, leading to the formation of several products, one of which could
be identified as CS with a double peak at 38.18 and 39.20 kc. cm^{-1}. Carbon
monosulfide obtained by photolysis from CS_2 showed the CS double-peaks at
38.16 and 39.20 kc. cm^{-1} under otherwise identical conditions [9]. The reaction

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* At an early stage of the present investigation the increase in absorption between 41—36
kc.cm^{-1} was taken as an indication of a recombination reaction leading to an increase in the
amount of disulfide present in the solution; *cf.* Ref.[27]

** Owing to the presented experimental facts, an intramolecular rearrangement mechanism
with a four-membered ring structure in the transition state can not be excluded.

mechanism is unknown and further experimental studies must be made before an elucidation can be proposed.

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