

Some Observations on the Photolysis of Dimethyl Disulfide

Tamotsu UENO and Yoshimasa TAKEZAKI*

(Takezaki Laboratory)

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Reactions of ethylene and acetylene induced by the photolysis of dimethyl disulfide were observed together with some related phenomena.

No pressure change was detected in ethylene whereas in acetylene remarkable pressure decrease took place. From the observed facts, though rather qualitative, it has been supposed that the disulfide dissociates mainly into two CH_3S radicals on light absorption and CH_3S is somewhat inert as to the double bond addition and fairly easy to recombine into disulfide.

In their paper on the pyrolysis of dimethyl disulfide at about 300° , John A.R. Corpe and W.A. Bryce¹⁾ have suggested in connection with the complex nature of this reaction a possibility of the participation of CH_3S radicals produced by the scission of the S-S bond in substrate.

If CH_3S radicals were produced by the photolysis of this compound in the presence of unsaturates they would presumably add to the double bond even at lower temperatures and would initiate the chain polymerization in favorable cases, since the aliphatic sulfide radicals are well known as modifier of high polymerization of vinyl compounds and the addition of $\text{C}_2\text{H}_5\text{S}$ to acetylene has been reported to occur at 100° though under pressure²⁾.

In this case, because the S-H bond is fairly weaker than the C-H bonds ($D(\text{CH}_3\text{S}-\text{H})$ 88.8 kcal³⁾, $D(\text{CH}_2:\text{CH}-\text{H}) > 91$, about 100° ?⁴⁾, $D(\text{CH}:\text{C}-\text{H}) \leq 121$ ⁴⁾; $D(\text{CH}_3\text{S}-\text{SCH}_3) = 73.2$ ³⁾) the mode of the reaction of CH_3S must not be the abstraction of H atom to form CH_3SH . Furthermore, from the energetical stand point there can be another possibilities to produce CH_3 or H atom in the photolysis by 2537 Å light (see below), and with these processes, too, we may expect some pressure change in the disulfide-olefin systems.

With these expectations in mind we observed the photo-induced reactions of ethylene and of acetylene with dimethyl disulfide as a sensitizer and also some related phenomena. Although the results are rather qualitative and no decisive conclusion can yet be drawn at the present stage we are here to communicate about those features of interest.

EXPERIMENTALS

Dimethyl disulfide was prepared by the method cited by Stevenson et al.⁵⁾;

*上野 保, 竹崎 嘉真

by repeated extractions and fractionations the sample could stand uncolored for more than two months (n_D^{20} 1.5258; 1.5260⁶¹). Ethylene, acetylene and NO are of usual purity (>99%), but as the presence of oxygen and water vapor was found to cause remarkable disturbances they were in particular removed before use.

Light source was a D.C.-operated 15 w hot-cathode low-pressure mercury lamp with inert gas, most of light energy being confined to 2537 Å; in some cases where high intensity was needed an A. C.-operated high pressure mercury arc (250 w, 2537 Å reversed, band spectra with some continuous background) was used. Parallel beam collimated by a set of lenses and irises was thrown into a reactor, made of a glass cylinder (36 mm diameter and 50 mm length) with quartz windows mounted in an electric furnace whose temperature was kept constant within 0.01°.

Static method was applied, the pressure change being pursued manometrically by null method; the shift of the butyl phthalate manometer head was watched by a photocell and accurately drawn back to the original point time to time by the change of a balancing pressure produced by withdrawing a small plunger out of an air-tight box, the movement of the plunger was then transferred mechanically to a variable resistor consisting an arm of Wheatstone bridge, and the unbalance potential was recorded. Under the experimental condition the sensitivity was of the order of 10^{-3} mm Hg/min.

RESULTS AND DISCUSSION

Dimethyl disulfide vapor was found to exhibit strong light absorption below 3000 Å and at least one maximum at 2480 Å; at 2537 Å absorption attains 87.5%

Table 1

disulfide mm	C ₂ H ₄ mm	O ₂ mm	H ₂ O mm	Temp. °C	Hg lamp pressure	$d\Delta p/dt$ mm/min	I_{abs}^{**} mm/min	$\frac{d\Delta p}{dt}/I_{abs}$
4.0				58	} high and low	<0.004*	} ca. 0.1*** for high pr. lamp	<0.04
14.0			63	<0.004		<0.04		
15.0			63	<0.004		<0.04		
14.1		38.0		68	low	<0.004	0.022	<0.1
13.1	75			58	} low	<0.002*	0.020	<0.1
9.2	180			165		<0.002	0.022	<0.1
7.5	150	1.6		61	} low	0.041	0.016	2.5
13.0	150	2.0		60		0.072	0.021	3.4
7.7	180	11.0		58		0.045	0.016	2.8
7.8	140	1.5	0.9	58	low	<0.002	0.016	<0.1

* Respectively maximum sensitivity.

** Expressed by (absorbed light quanta)/(Avogadro No.)(reactor vol.)(react. temp. °K)

*** For high pressure lamp I_{abs} is only approximate, see the text.

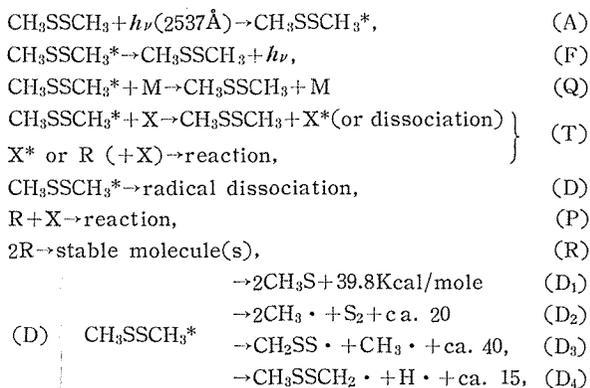
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in a 10 cm column of 6.25 mm Hg vapor at 20°, i.e., the absorption coefficient (natural log.) is 6.08×10^5 cc/mol cm.

In Table 1 results are given on the reactoin with ethylene together with some related runs. The pessure change was always below the sensitivity of the apparatus in disulfide only, disulfide-oxygen, or disulfide-ethylene binary mixture even for the highest light intensity or highest temperature, and although the intensity measurement was only approximate (by calibrated photocell PZV-50 for the low pressure lamp; for the high pressure lamp effective absorbed light was roughly estimated from the pressure change in NO admixture comparing with that by the low pressure lamp) the pressure decrease per quantum absorbed seems quite small if any. However, if oxygen is added to the disulfide-ethylene mixture evident pressure drop appears on irradiation, but in this case addition of water vapor as the third substance seems to suppress the reaction.

On the other hand, when the mixtures of disulfide and NO or of disulfide and acetylene were irradiated pronounced pressurè decrease could be observed as shown in Table 2.

Here we would write down the following possible schemata as to the fate of disulfide on light absorption :



M : inert substance, X : reactants, R : free radical or atom.

The excitation process (A) is self-evident, and aside from the extent of (F) and (Q) the results in Table 2 make us to conceive the occurrence of (T) and/or (D) followed by (P).

Now, we are able to say that NO will, also in this case, combine with free radicals to produce stable compounds since the energy required to lift NO to the lowest excited level or to dissociate, i. e., (T), is higher than 113 kcal of 2537 Å light. Then the fact that $d\Delta p/dt/I_{abs}$ is about unity in disulfide-NO system suggests that every absorbed quantum will produce two radicals (inclusive of atoms) and, if any, non-volatile substance per one disulfide, excluding (F) and (Q), provided that the addition products RNO remain all in gas phase, and this seems very plausible because of the minuteness of the reaction and of the invariance of $d\Delta p/dt/I_{abs}$ between 48° and 82°, though both are not so convincing. The diminution of pressure decrease by the addition of NO in the disulfide-acetylene system (Table 2) can be well explained when we assume the above-deduced radical dissociation

Table 2.

disulfide mm	NO mm	N ₂ mm	C ₂ H ₂ mm	temp °C	Hg lamp pres	iris	$d\Delta p/dt$ mm/min	I_{abs} mm/min	$d\Delta p/dt/I_{abs}$
7.0	40			62	} low	full open	0.016	0.016	1.0
14.0	78			48		//	0.019	0.020	0.95
13.0	37	136		78		//	0.020	0.020	1.0
//	//	//		//		No. 2	0.004	0.0037	1.1
13.5	35	133		82		full open	0.021	0.021	1.0
//	//	//		//		No. 1	0.010	0.010	1.0
//	//	//		//		No. 2	0.005	0.004	1.2
13.0	73	0		47		high	full open	0.12	} *
//	//	//		//	high KBP filler	// //	0.04		
2.3			210	68	} low	full open	0.027	0.007	3.9
9.2			232	//		//	0.085	0.018	4.7
9.0			131	49		//	0.080	0.017	4.3
10.0			160	164		//	0.14	0.021	6.7
10.0	25		204	52		//	0.016	0.018	0.9

* Runs for the rough estimation of effective quanta for high pressure lamp.

KBP=K-bipthalate 0.063 % aq. solution, 1 cm, which stops the light less than 3000Å sharply.

tion process (D) as the primary step.

In the photolysis of disulfide alone, small amount of methane and a slight whitish deposit, supposedly sulfur, were found in a long run, but no CH₃SH

Table 3.

disulfide mm	C ₂ H ₄ mm	temp °C	I_{abs} cc (NTP)	result	method
18.0		75	} ca.1	CH ₄ 0.03cc	Gas chromatography (own make)
14.0		25		CH ₃ SH not observed	Infrared (Perkin Elmer Model 21)
15		90		CH ₃ SH > 0.01cc	Gas chromatography
15	104	70		C ₂ , C ₃ , C ₄ olefin < 0.01cc	// //

* Expressed by (absorbed quanta) (gas const. in cc atom) (273K)/(Avogadro no.)

could be detected; in the run with acetylene no higher olefins could be found (Table 3). The formation of methane suggests (D₂) and/or (D₃) taking place to some extent, but these could not be the main part of the dissociation, because, recalculation of the estimation of Mandelcorn et al.⁷⁾ shows that at 165°, mixmum temperature here experimented, the rate constant of the addition of methyl to ethylene differs from that for acetylene only by a factor of 0.43, therefore, since we saw an evident reaction in the case of acetylene we can expect as well the reaction beginning with the addition of methyl to ethylene, and even if, though improbable as pointed out by Steacie⁸⁾ (see also ref. 10), the chain polymerization hardly took place at this temperature the pressure change due to

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the dimerization of resulting C_3H_7 radicals still should have been observed judging from the sensitivity of the instrument.

As for (D_4), it can be ruled out by the same argument since H atom adds by far easily to the double bond at low temperature.⁹⁾

Thus only (D_1) is left behind as the most probable primary step and by assuming this we can explain the absence of reaction in the photolysis of disulfide alone, in which the H abstraction by CH_3S must be negligible from the consideration on bond strength given before, in harmony with the result on CH_3SH photolysis¹¹⁾.

Furthermore, in cases where no reaction takes place such as in disulfide alone or the mixture with ethylene we have to accept the recombination reaction (R) occurring preferentially in order to account for the disappearance of radicals once formed, hence the next series follows on the reactivity of CH_3S under the conditions experimented :



Of course, recombination of CH_3S differs from others in the order of reaction and the relative rate depends on the concentration of that radical, but when compared with the ethylene polymerization photo-sensitized by methyl iodide at 130° ¹⁰⁾ where the quick recombination of CH_3 and I is well known, the recombination of CH_3S seems unusually easy relative to addition (cf. ref. 11).

There is one fact which appears contradictory at the present stage, that is, that no pressure change was observed in the disulfide-oxygen system whereas in the ternary mixture of disulfide, ethylene and oxygen pressure decrease could be well recognized (Table I, ethylene and oxygen mixture did not exhibit reaction on irradiation).

Although the absence of pressure change is by no means exclusive evidence of non-existence of reaction, this seems quite improbable in the system of free radical and oxygen. Then, if the free electron on the sulfur of CH_3S was inherently inactive against oxygen, why can oxygen induce the reaction of ethylene where the possibility of $CH_3SCH_2CH_2 \cdot$ formation has been rejected? More detailed investigation is in progress, as well as with other reactants such as propylene and butadiene.

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