Some Observations on the Photolysis of Dimethyl Disulfide

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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 CH₃S radicals on light absorption and CH₃S 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. Brycle have suggested in connection with the complex nature of this reaction a possibility of the participation of CH₃S radicals produced by the scission of the S-S bond in substrate. If CH₃S 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 C₂H₅S to acetylene has been reported to occur at 100° though under pressure.

In this case, because the S-H bond is fairly weaker than the C-H bonds (D(CH₃S-H) 88.8 kcal, D(CH₂ : CH-H)>91, about 100°, D(CH : C-H)≤121°; D(CH₃S-SCH₃)=73.2°) the mode of the reaction of CH₃S must not be the abstraction of H atom from CH₃SH. Furthermore, from the energetical stand point there can be another possibilities to produce CH₃ 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. ;

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by repeated extractions and fractionations the sample could stand uncolored for
more than two months ($n^2_1 = 1.5258$; 1.5260$^\circ$). 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$^\circ$.

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>
<thead>
<tr>
<th>disulfide</th>
<th>C₂H₄</th>
<th>O₂</th>
<th>H₂O</th>
<th>Temp. °C</th>
<th>Hg lamp pressure</th>
<th>$\frac{dA}{dt}$ mm/min</th>
<th>$I_{abs}**$ mm/min</th>
<th>$\frac{dA}{dt}/I_{abs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>58</td>
<td>high</td>
<td>&lt;0.004*</td>
<td>ca. 0.1***</td>
<td>&lt;0.04</td>
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<td></td>
<td></td>
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<tr>
<td>14.0</td>
<td>63</td>
<td>and</td>
<td>&lt;0.004</td>
<td></td>
<td>&lt;0.04</td>
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<tr>
<td>15.0</td>
<td>63</td>
<td>low</td>
<td>&lt;0.004</td>
<td></td>
<td>&lt;0.04</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>14.1</td>
<td>38.0</td>
<td>low</td>
<td>&lt;0.004</td>
<td>0.022</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
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<tr>
<td>13.1</td>
<td>75</td>
<td>58</td>
<td>low</td>
<td>&lt;0.002*</td>
<td>0.020</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
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<tr>
<td>9.2</td>
<td>180</td>
<td>106</td>
<td>low</td>
<td>&lt;0.002</td>
<td>0.023</td>
<td>&lt;0.1</td>
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<tr>
<td>7.5</td>
<td>150</td>
<td>1.5</td>
<td>61</td>
<td>0.041</td>
<td>0.016</td>
<td>2.5</td>
<td></td>
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</tr>
<tr>
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<td>150</td>
<td>2.0</td>
<td>60</td>
<td>0.072</td>
<td>0.021</td>
<td>3.4</td>
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<td>11.0</td>
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<tr>
<td>7.8</td>
<td>140</td>
<td>1.5</td>
<td>0.9</td>
<td>58</td>
<td>&lt;0.002</td>
<td>0.016 &lt;0.1</td>
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<td></td>
</tr>
</tbody>
</table>

* 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.
in a 10 cm column of 6.25 mm Hg vapor at 20°, i.e., the absorption coefficient (natural log.) is 6.08×10⁵ cc/mol cm.

In Table 1 results are given on the reaction with ethylene together with some related runs. The pressure 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 pressure 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:

\[
\begin{align*}
\text{CH}_3\text{SSCH}_3 + h\nu (2537\text{Å}) & \rightarrow \text{CH}_3\text{SSCH}_3^*, \\
\text{CH}_3\text{SSCH}_3^* & \rightarrow \text{CH}_3\text{SSCH}_3 + h\nu, \\
\text{CH}_3\text{SSCH}_3^* + \text{M} & \rightarrow \text{CH}_3\text{SSCH}_3 + \text{M} \quad \text{(Q)} \\
\text{CH}_3\text{SSCH}_3^* + \text{X} & \rightarrow \text{CH}_3\text{SSCH}_3 + \text{X} \quad \text{(or dissociation)} \\
\text{X}^* \text{ or R} (+ \text{X}) & \rightarrow \text{reaction}, \\
\text{CH}_3\text{SSCH}_3^* & \rightarrow \text{radical dissociation} \quad \text{(D)} \\
\text{R} + \text{X} & \rightarrow \text{reaction} \quad \text{(P)} \\
2\text{R} & \rightarrow \text{stable molecule(s)} \quad \text{(R)} \\
\text{CH}_3\text{SSCH}_3^* \quad \text{and (D)} & \rightarrow \text{2CH}_3\text{S} + 39.8\text{Kcal/mole} \quad \text{(D_1)} \\
& \rightarrow \text{2CH}_3 \cdot + \text{S}_2 + \text{ca. 20} \quad \text{(D_2)} \\
& \rightarrow \text{CH}_3\text{SS} \cdot + \text{CH}_3 \cdot + \text{ca. 40.} \quad \text{(D_3)} \\
& \rightarrow \text{CH}_3\text{SSCH}_2 \cdot + \text{H} \cdot + \text{ca. 15.} \quad \text{(D_4)} \\
\text{M: inert substance, X: reactants, R: free radical or atom.}
\end{align*}
\]

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 dissocia-
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Table 2.

<table>
<thead>
<tr>
<th>disulfide mm</th>
<th>NO mm</th>
<th>N₂ mm</th>
<th>C₂H₂ mm</th>
<th>temp °C</th>
<th>Hg lamp pres</th>
<th>iris</th>
<th>dΔp/dt mm/min</th>
<th>I₁₀₀₀ mm/min</th>
<th>dΔp/dt/I₁₀₀₀</th>
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</thead>
<tbody>
<tr>
<td>7.0</td>
<td>40</td>
<td></td>
<td>62</td>
<td></td>
<td>full open</td>
<td>0.016</td>
<td>0.016</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>78</td>
<td></td>
<td>48</td>
<td></td>
<td></td>
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<td>0.020</td>
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<tr>
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<td>0.0037</td>
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<td>0.021</td>
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<tr>
<td>13.0</td>
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<td>0</td>
<td>47</td>
<td></td>
<td>high full open</td>
<td>0.12</td>
<td>0.04</td>
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</table>

<table>
<thead>
<tr>
<th>disulfide mm</th>
<th>NO mm</th>
<th>N₂ mm</th>
<th>C₂H₂ mm</th>
<th>temp °C</th>
<th>Hg lamp pres</th>
<th>iris</th>
<th>dΔp/dt mm/min</th>
<th>I₁₀₀₀ mm/min</th>
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<tr>
<td>2.3</td>
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<tr>
<td>10.0</td>
<td>204</td>
<td>52</td>
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<td>0.14</td>
<td>0.021</td>
<td>6.7</td>
<td></td>
</tr>
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</table>

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

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

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 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. shows that at 165°, maximum 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 Steacie (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 \( \text{C}_2\text{H}_7 \) 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 \( \text{H} \) atom adds by far easily to the double bond at low temperature.\(^{2,3} \)

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 \( \text{H} \) abstraction by \( \text{CH}_3\text{S} \) must be negligible from the consideration on bond strength given before, in harmony with the result on \( \text{CH}_3\text{SH} \) photolysis\(^{11} \).

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 \( \text{CH}_3\text{S} \) under the conditions experimented:

\[
\text{NO} > \text{C}_2\text{H}_2 > \text{CH}_3\text{S} > (\text{O}_2 ?), \text{C}_2\text{H}_4.
\]

Of course, recombination of \( \text{CH}_3\text{S} \) 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 \( \text{CH}_3 \) and I is well known, the recombination of \( \text{CH}_3\text{S} \) 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 1, 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 \( \text{CH}_3\text{S} \) was inherently inactive against oxygen, why can oxygen induce the reaction of ethylene where the possibility of \( \text{CH}_3\text{SCH}_2\text{CH}_2 \cdot \) formation has been rejected? More detailed investigation is in progress, as well as with other reactants such as propylene and butadiene.

REFERENCES

(9) E. W. R. Steacie, *ibid.*, P. 423.