Thermal Decomposition of Bis-(O, O-dimethylthionophosphoryl)-disulfide

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Thermal Decomposition of Bis-(O, O-dimethylthionophosphoryl)-disulfide. Kazuyuki Mar-
kawa, Yoshihiro Shuto, Eiji Taniguchi and Yasutaka Miyoshi (Faculty of Agriculture, Kyushu

6. Bis-(O, O-dimethylthionophosphoryl)-disulfide の熱分解  前川一之, 首藤義司, 谷口栄二,三好健之 (九州大学農学部) 48. 11. 8 受理

O,O-Dimethylldithiophosphoric acid, (MeO)x-P-SH, derived from methanol and P2S, is an
important intermediate of various organic phos-
phorus pesticides9). The pK' value of this acid
is 1.55 (in 79.6 ethanolic solution)9). Its redox
potential has not been reported, but it is supposed
to be considerably negative referred to hydrogen
electrode. In fact, it is easily oxidized to convert to
bis-(O, O-dimethylthionophosphoryl)-disulfide9).

When the disulfide is heated with p-dioxene in
the presence of hydroquinone, it converts to a
pesticide analogous to Delnav9). Some of bis-
(O, O-dialkylthionophosphoryl)-disulfides have
insecticidal activities9).

However, chemical properties of the disulfide
have not been sufficiently clarified9). In particular,
the thermal lability of this compound has not

* Abb. The disulfide: bis-(O, O-dimethylthiono-
phosphoryl)-disulfide,

been investigated in detail. The present paper
deals with an investigation of the thermal decom-
position of this disulfide under the anhydrous
condition.

Experimental

1) Redox potential

The redox potential of a system of the disulfide
and O,O-dimethylthiophosphoric acid was mea-
sured by the polarographical method using 0.1
M, pH 7 phosphate buffer solution containing 25% 
S methanol, 16% ethanol, and (MeO)x-P-SH and 
S [(MeO)x-P-S-]2 (in molar ratio of 1 : 1). Other
experimental conditions are shown in Fig. 1.

From the results shown in Fig.1, the redox
potential (Eo) was calculated as -0.304±0.005V,
vs. normal hydrogen electrode.
2) **Differential thermal analysis**

The analysis was carried out using a thermoflex-unit of Rigaku-Denki. The rate of the programming temperature was 5°C/min. Other conditions are shown in Fig. 2. Fig. 2 shows that as the temperature rose an endothermic reaction occurred at 61°C. An exothermic reaction started at about 140°C and reached the maximum at 174°C. At this point the weight loss was about 39%. Thus, the disulfide decomposed explosively at about 140°C and evolved a gaseous mixture.

3) **Gas produced by the pyrolysis of the disulfide**

The experiment was performed in order to clarify components of the gaseous mixture produced by the exothermic degradation reaction. Three grams of the disulfide was weighed into a bent, narrow-necked glass tube (about 10ml), then was gradually heated in an oil-bath. The evolved gas was trapped in a tube cooled by dry-ice and acetone. The trapped sample was examined by gas chromatography-mass spectrometry. The results are shown in Table 1 and Fig. 3. The relative amounts of the products varied remarkably, depending on the conditions of the decomposition, but the components contained in the mixture were not changed. The identification of compounds isolated by gas chromatography was performed by comparison of mass spectra with authentic samples.

Mass spectra were determined at 75 eV on an JEOL OISG instrument with source temperature 230°C. As shown in Fig. 3, \( \text{CH}_3\text{S-S-CH}_3 \) (peak 1), \( \text{S}_2 \), \( \text{CH}_3\text{O})_2\text{P-S-CH}_3 \) (peak 4) and \( \text{CH}_3\text{O})_2\text{P-S-CH}_3 \) (peak 6) were identified. From the mass spectrum of the peak 1, \( \text{CH}_3\text{S-CH}_3 \) (m/e 62) and \( \text{CH}_3\text{S}^+ \) (m/e 47) were recognized (the peak 1 may be due to \( \text{CH}_3\text{S-CH}_2 \) or \( \text{CH}_3\text{SH} \)). Chemical
composition of peaks other than those mentioned here still remain to be investigated.

4) Mass spectrometry of the disulfide

From the spectrum of the disulfide, the fragmentation sequence can be presented as shown in Fig. 4. Main processes were the \( \alpha \)-and \( \beta \)-cleavages for the phosphorus atom, corresponding to m/e 125 (\( \text{CH}_3\text{O}\))_2P^+\, and m/e 157 (\( \text{CH}_3\text{O}\))_2P\text{S}_2^+\, respectively. Then m/e 157 eliminated sulfur atoms to form the base ion peak m/e 93(\( \text{CH}_3\text{O}\))_2P^+, which was followed by further elimination to form m/e 63 \( \text{CH}_3\text{O-PH} \). The peak m/e 125 was decomposed into m/e 79 HO-P-OCH\(_3\), then m/e \( \text{47 PO} \). These fragmentation patterns (shown by the gothic type in Fig. 4) seem to be reliable by the observation of metastable ions, shown in Table 2, and by referring to the literature\(^6,7,8\).

5) The change of the disulfide at a relatively low temperature

After the disulfide sealed in a glass tube was maintained at 58°C for 5 to 10 hours, it was examined by means of TLC, IR, NMR and Mass spectrometry. The results obtained are as follows:

(a) TLC and column chromatography:—After being heated, the sample was applied to TLC (Silicagel HF 254). The suitable developing solvent was \( \pi \)-hexane : toluene = 4 : 1 and spots were visualized by UV-lamp or spraying 0.5% \( \text{PdCl}_2 \) in 1 N HCl. It was discernible from the TLC that the disulfide was decomposed by the mild heating into four main and a few minor compounds. Rf values of these four main products were 0.44 (\( \alpha \)), 0.35 (\( \beta \)), 0.30 (\( \gamma \)) and 0.00 (\( \delta \)), while that of the disulfide was 0.25.

Table 1. Gas chromatogram* of decomposed disulfide.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min.)</th>
<th>Relative amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4</td>
<td>5.7</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>13.0</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>1.0</td>
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<tr>
<td>4</td>
<td>5.1</td>
<td>16.0</td>
</tr>
<tr>
<td>5</td>
<td>10.6</td>
<td>1.8</td>
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<tr>
<td>6</td>
<td>12.9</td>
<td>26.9</td>
</tr>
<tr>
<td>7</td>
<td>16.7</td>
<td>6.4</td>
</tr>
<tr>
<td>8</td>
<td>20.1</td>
<td>0.8</td>
</tr>
<tr>
<td>9</td>
<td>24.3</td>
<td>5.2</td>
</tr>
<tr>
<td>10</td>
<td>25.9</td>
<td>6.0</td>
</tr>
<tr>
<td>11</td>
<td>33.3</td>
<td>1.0</td>
</tr>
<tr>
<td>12</td>
<td>38.2</td>
<td>0.6</td>
</tr>
<tr>
<td>13</td>
<td>41.8</td>
<td>0.1</td>
</tr>
<tr>
<td>14</td>
<td>53.3</td>
<td>15.5</td>
</tr>
</tbody>
</table>

* Gas chromatography was carried out under following conditions:
- Column 3m x 3mm, glass
- Packing 3% Silicon SE-30 on Chromosorb W-AW 60-80 mesh
- Oven temp. 70-120°C
- Carrier gas He, flow 15ml/min.
- Injection temp. 165°C
- Separator temp. 150°C
- Chart speed 10mm/min.

Fig. 3. Mass spectrometry of some peaks of the gas chromatogram. (Number refers to the peak of Table 1)
- Ionizing volt.: 75 eV, Accel. pot.: 3.5 KV, Trap curr.: 60\( \mu \)A,
- Sample temp.: 130°C, Chamber temp.: 230°C, Scan speed: 7min.

Fig. 4. Main processes were the \( \alpha \)-and \( \beta \)-cleavages for the phosphorus atom, corresponding to m/e 125 (\( \text{CH}_3\text{O}\))_2P^+\, and m/e 157 (\( \text{CH}_3\text{O}\))_2P\text{S}_2^+\, respectively. Then m/e 157 eliminated sulfur atoms to form the base ion peak m/e 93(\( \text{CH}_3\text{O}\))_2P^+, which was followed by further elimination to form m/e 63 \( \text{CH}_3\text{O-PH} \). The peak m/e 125 was decomposed into m/e 79 HO-P-OCH\(_3\), then m/e \( \text{47 PO} \). These fragmentation patterns (shown by the gothic type in Fig. 4) seem to be reliable by the observation of metastable ions, shown in Table 2, and by referring to the literature\(^6,7,8\).

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<tr>
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<td>38.2</td>
<td>0.6</td>
</tr>
<tr>
<td>13</td>
<td>41.8</td>
<td>0.1</td>
</tr>
<tr>
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- Oven temp. 70-120°C
- Carrier gas He, flow 15ml/min.
- Injection temp. 165°C
- Separator temp. 150°C
- Chart speed 10mm/min.
In order to isolate the reaction products which were detected by TLC, the column chromatography in equivalent conditions to TLC was carried out (column: Silica gel, solvent: n-hexane-toluene = 4:1). Among the separated fractions only γ-fraction was present in sufficient quantity to be scrutinized.

(b) Analysis of γ-fraction:

<table>
<thead>
<tr>
<th>Metastable ion (m/e)</th>
<th>Degradation passway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>Calcd.</td>
</tr>
<tr>
<td>199.0</td>
<td>(250)</td>
</tr>
<tr>
<td>314</td>
<td>199.04</td>
</tr>
<tr>
<td>154.4</td>
<td>(220)</td>
</tr>
<tr>
<td>220</td>
<td>154.14</td>
</tr>
<tr>
<td>112.6</td>
<td>(188)</td>
</tr>
<tr>
<td>188</td>
<td>112.56</td>
</tr>
<tr>
<td>98.8</td>
<td>(142)</td>
</tr>
<tr>
<td>204</td>
<td>98.84</td>
</tr>
<tr>
<td>55.1</td>
<td>(93)</td>
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<td>93</td>
<td>55.09</td>
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<tr>
<td>50.0</td>
<td>(79)</td>
</tr>
<tr>
<td>125</td>
<td>49.93</td>
</tr>
<tr>
<td>42.6</td>
<td>(63)</td>
</tr>
<tr>
<td>93</td>
<td>42.57</td>
</tr>
</tbody>
</table>

These results suggest that the γ-fraction is a compound where one methyl group of the disulfide migrated intramolecularly from 0 to S (Fig. 6, 1).
Fig. 5. IR-spectra of the disulfide (1) and the fraction isolated from the heated disulfide (2) (KBr)

The fragmentation of the mass spectra showed differences between the disulfide and the fraction as shown in Table 3. On the spectrum of the fraction, for example, the appearance of the peak of m/e 236 and the intensity of the peak of m/e 172 are characteristic.

Cooks and Gerrard\(^{13}\) reported that the mass spectra of O-methyl-O,O-diphenyl-phosphorothioate and S-methyl-O,O-diphenyl-phosphorothiolate were characteristic in a relative intensity between the ion peaks corresponding to M-CH\(_3\), M-PhS and PhS: by electron impact the thiolate gave a predominant M-CH\(_3\) ion along with less intensive ions of M-PhS and PhS, while the latters were more intensive and the former less intensive in the thioate. Furthermore, the occurrence of PhSMe\(^{−}\) rather than PhSPh\(^{−}\) in the thiolate served to distinguish it from the thioate although rearrangements between substituents in the phosphorothioate and phosphorothiolate gave rise to both ions.

In the mass spectra of bis-(O,O-dimethylthio- phosphoreryl)-disulfide and the heated sample, the splitting of the disulfide bond and/or the alpha-cleavage of the -P(S)-S- are much predominant as even in the spectrum of the heat-isomerized disulfide the M-CH\(_3\) ion is hardly observed; many ions were common in both spectra.

The ion peaks corresponding to (IV), (II)

Table 3. Differences in fragmentation between the disulfide and the fraction isolated from the heated disulfide.**

<table>
<thead>
<tr>
<th>m/e</th>
<th>47</th>
<th>63</th>
<th>79</th>
<th>93</th>
<th>125</th>
<th>157</th>
<th>172</th>
<th>188</th>
<th>220</th>
<th>236</th>
<th>250</th>
<th>314(M(^{+}))</th>
<th>316</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disulfide</td>
<td>11.8</td>
<td>15.6</td>
<td>12.5</td>
<td>100</td>
<td>52.0</td>
<td>15.3</td>
<td>6.3</td>
<td>2.1</td>
<td>4.2</td>
<td>8.3</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated Disulfide</td>
<td>12.5</td>
<td>9.3</td>
<td>8.3</td>
<td>100</td>
<td>21.3</td>
<td>3.3</td>
<td>3.4</td>
<td>2.5</td>
<td>1.3</td>
<td>0.4</td>
<td>1.8</td>
<td>8.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The values of this table are shown in percentage to base ion peak m/e 93.

** Mass spectra were taken under following conditions:
- Ionizing volt 75 eV
- Sample temp. 42°C
- Scan speed 3 min.
- Ionizing curr. 200 A
- Chamber temp. 157°C
- Chart speed 0.8 cm/sec.
- Accel. Voltage 6.1 KV
especially (III) in Fig. 6, however, are considerably more intense in the heat-isomerized disulfide, suggesting a molecular rearrangement of the phosphorothioate to a thiolate such as (I).

The ions (II), (IV) and (III) may result from methyl migration in such ionized phosphorothiolate.

Acknowledgements: The authors are indebted to Dr. Y. Osazima of Faculty of Agriculture, Kyushu University for the measurements of the redox potential of the disulfide. They acknowledge Miss. S. Ishida, Mr. E. Kuwano and Mr. T. Okabe for their technical assistance.

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幼若ホルモンの代謝阻害剤としての類縁体の作用
Juvenile Hormone Analogs: A Possible Case of Mistaken Identity?

JH 活性をもつものとして、piperonyl butoxide (1), piperonyl 6,7-epoxy-3-ethyl-7-methyl-2-nonenyl ether (2), 10,11-epoxy-N-ethyl-3,7,11-trimethyl-2,6-dodecadienamide (3), isopropyl 11-methoxy-3,7,11-trimethylidodeca-2,4-dienoate (4), ethyl 3,7,11-trimethylidodeca-2,4-dienoate (5), 2-propynylphenylphosphonate (6) などが知られている。

一方、スズメガ(Manduca sexta), サギ(Prodenia eridania), バック (Schistocerca vaga), ニクバエ (Sarcophaga bullata), セクロビア炎 (Hyalophora cecropia) において、JH は 2 つの経路を経て dihydroxy acid に代謝される。一つは、まず esterase が作用して、epoxy acid が生成し、次いで epoxide hydrase が作用する系。他は、まず、epoxide hydrase が作用し、dihydroxy ester が生成し、次いで esterase が作用する系である。

in vitro での結果の結果、上記(1)〜(6)の化合物は、本来のホルモン活性を示すというより、昆虫に含まれる、JH の代謝経路を阻害することにより作用すると考えられる。

6 令期前の P. eridania の中腸薬物から酵素を調整し、その中へ、2 の位置を 14C でラベルした JH と上記化合物を加え一定時間培養後、TLC で分析した。その結果、(1) (2) (3) を加えた場合は、epoxy acid に、(4) (5) (6) を加えた場合は dihydroxy ester に radio activity が見られた。しかも (1) (2) (3) については、epoxy acid の生成の度合が多いこと。そこで、(1) (2) (3) は epoxide hydrase の阻害剤として、強く作用していることがわかった。

抄 録