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<th>Title</th>
<th>Thermal Decomposition of Bis-(O, O-dimethylthionbphosphoryl)-disulfide</th>
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<tbody>
<tr>
<td>Author(s)</td>
<td>MAEKAWA, Kazuyuki; SHUTO, Yoshihiro; TANIGUCHI, Eiji; MIYOSHI, Yasutaka</td>
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Kyoto University
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Reference


Thermal Decomposition of Bis-(O,O-dimethylthionophosphoryl)-disulfide. Kazuyuki Makawa, Yoshihiro Shuto, Eiji Taniguchi and Yasutaka Miyoshi (Faculty of Agriculture, Kyushu University) Received November 8, 1973. Botyu-Kagaku, 39, 21, 1974.

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

Bis-(O,O-dimethylthionophosphoryl)-disulfide は酸化還元電位 -0.302 volt で容易に酸化され、bis-(O,O-dimethylthionophosphoryl)-disulfide, (disulfide と略) を生成する。この disulfide は加熱によって比較的容易に分解される。Disulfide の示差熱分析では、140°C 位から発熱的に発熱反応が始まることがわかった。この時発生するガスは、GC-MS 分析により調べた結果、CH₃SH, CH₃SCH₃, CH₂-S-S-CH₃, (CH₃O)₂P-S-CH₃, (CH₃O)₂P-S-CH₃ などであった。この際の重量の減少は 39.1%であった。また disulfide は比較的低温でも変化することが観察された。即ち、融点附近の温度で数時間保った後の IR では 1300 cm⁻¹ に P-S の吸収があらわれ、NMR で δ 2.25 ppm に S-CH₃ の信号が見られること、およびその強度から、P-O-CH₃ から P-S-CH₃ への転移が推察された。

O₂, O-Dimethyldithiophosphoric acid, (MeO)₂P-SH, derived from methanol and P₂S₄ is an important intermediate of various organic phosphorus pesticides. The pK' value of this acid is 1.55 (in 7% ethanolic solution). 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)-disulfide. When the disulfide is heated with p-dioxene in the presence of hydroquinone, it converts to a pesticide analogous to Delnav. Some of bis-(O,O-dialkylthionophosphoryl)-disulfides have insecticidal activities.

However, chemical properties of the disulfide have not been sufficiently clarified. In particular, the thermal lability of this compound has not been investigated in detail. The present paper deals with an investigation of the thermal decomposition of this disulfide under the anhydrous condition.

**Experimental**

1) Redox potential
The redox potential of a system of the disulfide and O₂, O-dimethylthiophosphoric acid was measured by the polarographical method using 0.1 M, pH 7 phosphate buffer solution containing 25% methanol, 16% ethanol, and (MeO)₂P-SH and [(MeO)₂P-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 (E₀) was calculated as -0.304±0.005V. vs. normal hydrogen electrode.
Determination of the redox potential \((E_0)\) of a system of the disulfide and \(O, O\)-dimethylidithiophosphoric acid by the polarography.
Dumping 25\(\mu\)F, Hg : 0.5mg/sec.
Drop time=4.5 sec.

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.

Fig. 1. Determination of the redox potential \((E_0)\) of a system of the disulfide and \(O, O\)-dimethylidithiophosphoric acid by the polarography.

\[ E_0 = \text{volts vs. SCE} \]

Fig. 2. Differential thermal analysis of the disulfide.

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 a JEOL QSG instrument with source temperature 230°C. As shown in Fig. 3, \(\text{CH}_3\text{-S-S-CH}_3\) (peak 1) \(\text{S}\), \((\text{CH}_3\text{O})_2\text{P-S-CH}_3\) (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, \(\text{CH}_3\text{-S-S-CH}_3\) (m/e 62) and \(\text{CH}_3\text{-S}\) (m/e 47) were recognized (the peak 1 may be due to \(\text{CH}_3\text{-S-S-CH}_3\) 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

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>
</tr>
<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>
</tr>
<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. 4. Main processes were the $\alpha$-and $\beta$-cleavages for the phosphorus atom, corresponding to $m/e$ 125 (CH$_3$O)$_2$P$^+$, and $m/e$ 157 (CH$_3$O)$_2$PS$_2^+$ respectively. Then $m/e$ 157 eliminated sulfur atoms to form the base ion peak $m/e$ 93(CH$_3$O)$_2$ -P$^+$, which was followed by further elimination to form $m/e$ 63 CH$_3$O-PH. The peak $m/e$ 125 was decomposed into $m/e$ 79 HO-P-OCH$_3$, then $m/e$ 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 $n$-hexane: toluene=4 : 1 and spots were visualized by UV-lamp or spraying 0.5% 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.

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.: 60µA,
Sample temp.: 130°C, Chamber temp.: 230°C, Scan speed: 7min.
In order to isolate the reaction products which were detected by TLC, the column chromatography in equivalent conditions to TLC was carried out (column: Silicagel, solvent: \( \pi \)-hexane-toluene =4-1). Among the separated fractions only \( \gamma \)-fraction was present in sufficient quantity to be scrutinized. 

(b) Analysis of \( \gamma \)-fraction:

\[
\text{C}_{4} \text{H}_{12} \text{P}_{2} \text{S}_{4} (314)
\]

<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)^{2} \rightarrow 199.04</td>
</tr>
<tr>
<td>154.4</td>
<td>(220)^{2} \rightarrow 154.14</td>
</tr>
<tr>
<td>112.6</td>
<td>(188)^{2} \rightarrow 112.56</td>
</tr>
<tr>
<td>98.8</td>
<td>(142)^{2} \rightarrow 98.84</td>
</tr>
<tr>
<td>55.1</td>
<td>(93)^{2} \rightarrow 55.09</td>
</tr>
<tr>
<td>50.0</td>
<td>(79)^{1} \rightarrow 49.93</td>
</tr>
<tr>
<td>42.6</td>
<td>(63)^{1} \rightarrow 42.57</td>
</tr>
</tbody>
</table>

(c) IR, NMR and Mass spectra of the \( \gamma \)-fraction:

The absorption of P=O in the IR spectrum of \( \gamma \)-fraction appeared at 1300 cm\(^{-1}\). There were some differences from the disulfide in absorptions observed at 2980, 2940, 1440 and 1165 cm\(^{-1}\) (Fig. 5). NMR spectrum showed a signal due to S-CH\(_{3}\) at \( \delta = 2.25 \) ppm.

Signal (\( \delta \) ppm) Assignment N.B.

\( \gamma \)-fraction 3.68, 3.93 P-O-CH\(_{3}\) coupling with P \( J=0.25 \)

These results suggest that the \( \gamma \)-fraction is a compound where one methyl group of the disulfide migrated intramolecularly from 0 to S (Fig. 6, I).
The fragmentation of the mass spectra showed differences between the disulfide and the \( \gamma \)-fraction as shown in Table 3. On the spectrum of the \( \gamma \)-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-dimethylthionophosphoryl)-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) and

<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
Fig. 6. Main fragmentation of the disulfide and supposed fragmentation mechanism of the heat-isomerized disulfide.

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)\(^{10}\). The ions (II), (IV) and (III) may result from methyl migration in such ionized phosphorothiolate.

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抄 録

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?

ジェクロビア属の幼若ホルモンの一つは、methyltrans, trans, cis-10, 11-epoxy-7-ethyl-3,11-dimethyltrideca-2,6-dienoate (JH) である。その後、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-trimethyldeca-2,4-dienoate (4), ethyl 3, 7,11-trimethyldeca-2,4-dienoate (5), 2-propyl(piperyn)phenylphosphonate (6) などが知られている。

一方、スズメガ(Manduca sexta), ヤガ(Prodenia eridania), バッタ(Schistocerca vaga), ニクバエ(Sarcophaga bullata), セクロビア属(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 での実験の結果、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ように作用すると考えられる。

6令初期の P. eridania の胸足関節から醇酸を調製し、その中に、2の位置を ¹³C でラベルした JHと上記化合物を加えて一定時間培養後、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 の生成の度合いが多いこと、(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。

(北村実彬)