

Experimental

Preparation of bis-(*O,O*-dimethyl-thiono-phosphoryl) disulfide: The disulfide was prepared as described by M. I. Kabachnik *et al.*⁽⁴⁾ from sodium *O,O*-dimethyl-dithiophosphate with iodine. The product was recrystallized from ethanol. m. p. 50-51°C (reference value⁽⁴⁾ 51-52°C)

Differential thermal analysis: The experiments were carried out using Rigaku-Denki Thermoflex (TG-DTA) instrument, using aluminum as a reference in the atmosphere of air and platineels for thermocouples. Thermal and gravimetric changes during the reaction were recorded automatically in the forms of thermal gravimetric and differential thermal curves. Twenty to thirty mg of the disulfide was heated at appropriate temperatures isothermally or at rising temperature at the rate of 5°C per minute.

Analyses of gaseous mixture evolved by the decomposition without water: Ten milligrams of the disulfide was heated at 120° and 200° in pyrolysis furnace. The gaseous products which were captured with a liquid nitrogen trap, were again gasified, and a combined gas-chromatography and mass-spectrometry (GS-MS) was employed for structure determination of the components, using a Shimadzu-LKB model 9000 instrument, fitted with 3m × 3mm I. D. spiral glass column packed with 25% TLEP on Shimalite AW/DMCS (60-80 mesh) with the column oven temperature at 70°C using helium gas as the carrier gas. The composition of the mixture was estimated using a Shimadzu model GC-5A PTF instrument equipped with a thermal conductivity detector. The operating conditions were essentially the same as for combined GC-MS described above.

Analyses of gaseous mixture evolved under wet conditions: In an oil bath, was placed a three necked flask fitted with a magnetically stirred scrubber, a thermocouple, and a short glass outlet tube, the terminal of which was connected to a graduated cylinder to measure the volume of the decomposition gas. The graduated cylinder was filled with 0.1N hydrochloric acid saturated with hydrogen sulfide. Approximately 30g of the disulfide and 10g of water were heated at 60°C,

80°C and 100°C. The gaseous products were analyzed using gas chromatography.

Thermal decomposition reaction under adiabatic conditions: A 50ml four-necked flask, fitted with a thermocouple, a mechanical stirrer, and two glass outlet tubes, was packed in a one-liter mantle heater with glass wool. In the flask were placed 50g of the disulfide and 17.5g of water and were first rapidly heated up to 70°C and then gradually at the rate of 0.15°C per minute to 85°C.

Results

The thermal stability of the disulfide in the absence of water was studied by differential thermal analyses. Under isothermal conditions, gravimetric and differential thermal curves indicated that the disulfide was stable at 83°C, but decomposed gradually at 102°C. At 121°C the decomposition was completed after 2.7 hours heating with a loss of 49.3% of total weight in the form of gas. When the reaction temperature was raised at the rate of 5°C per minute, the exothermal decomposition of the disulfide started at 133°C and reached the maximum at 170°C.

Under the presence of water, the disulfide decomposed at lower temperature than without water. Table 1 gave percentage of the undecomposed disulfide when heated under the isothermal

Table 1. The undecomposed disulfide in the presence of water under the isothermal conditions.

Hour	The intact disulfide (%)	
	60°C	80°C
0	99.6	99.6
1	99.6	95.3
2	99.4	91.4
3	99.0	67.2
6.5	—	0.0

conditions at 60°C and 80°C. The decomposition did not occur at 60°C, but did by 32.8 percent at 80°C after 3 hours heating and completed after 6.5 hours. When the heating temperature was raised up to 100°C, an abrupt exothermal decomposition occurred. Judging from the temperature inside the reaction vessel, it rose abru-

ptly well over the bath temperature. When the reaction was allowed to proceed under adiabatic conditions where the heat of reaction was accumulated, the exothermal decomposition occurred at 85°C.

The composition of the thermal decomposition gas was given in Table 2. When the decomposition was carried out without water, the evolution of gaseous products took place only slightly even at 120°C and 200°C. The main components of the decomposition gas were methylsulfide, methyldisulfide and methanol.

In the presence of water, the gas evolution was initiated after 2 hours at 80°C, reached the maximum rate after 3 hours, and subsided after 6 hours heating. The decomposition gaseous mixture consisted mainly of hydrogen sulfide, methanol and methyl mercaptan. At 100°C the gaseous mixture initiated to evolve after 18 minutes, reached the maximum rate after 28 minutes, diminished after 42 minutes, and ceased after 60 minutes. An abrupt rise of the temperature in the reaction vessel was observed with the maximal evolution of the decomposition gas.

Discussion

The above results indicated that the disulfide decomposes in different mechanisms according to the absence or presence of water. Without water, it decomposed at 102°C and the exothermal decomposition occurred at 170°C. The evolution of decomposition gas took place only gradually and the main components of the gas were methylsulfide, methyldisulfide and methanol.

In the presence of water, the disulfide started to decomposed around 80°C, and the exothermal reaction occurred at 100°C. During the induced exothermal decomposition the temperature inside the reaction vessel rose to above 200°C. Under adiabatic conditions, the exothermal decomposition occurred even at 85°C. Under these conditions the evolution of the gas took place vigorously, and its main components were hydrogen sulfide, methanol and methylmercaptan.

The difference in the mode of decomposition according to reaction conditions, suggests that the mechanisms are different to each other. The presence of water may probably drive the decomposition reaction hydrolytically.

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Table 2. The components and compositions of the decomposition gas of the disulfide.

Conditions	Variation in the volume of gaseous products (ml/min. mol.)	Components and compositions (weight percent)						
		H ₂ S	CS ₂	CH ₃ SH	CH ₃ SCH ₃	CH ₃ SSCH ₃	CH ₃ OH	the others (H ₂ O)
Heating at 200°C in the absence of water	—	0.4	0.1	5.7	25.9	25.7	34.2	7.8
Heating at 120°C in the absence of water	—	0	0	0	17.7	78.6	4.0	0
Under isothermal conditions at 80°C in the presence of water	2 hours heating	12	83.0	0	0.2	0.4	0	3.8
	3 hours heating	388	69.5	0	1.8	0	20.8	7.9
	6 hours heating	4	9.1	0	74.7	1.1	1.0	5.4
Exothermal decomposition at 100°C in the presence of water	18 mins heating	12	3.4	0	15.2	0.9	2.9	66.2
	28 mins heating	1,564	87.7	0	1.2	0	9.2	1.8
	42 mins heating	352	54.1	0	13.1	0.4	2.6	27.4
	60 mins heating	2	6.1	0	74.0	2.2	0	78

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Reference

- 1) Schrader, G.: German Patent; 1,011,416

(1955).

- 2) Malatesta, L. and F. Laverone: *Gaz. Chim. Italiana*, 8, 596 (1951).
- 3) Ping-Fang, Hu, Li Shou-Cheng and Cheng Wan-Yi: *Acta Chim. Sinica*, 22, 49 (1956).
- 4) Kabachnik, M. I. and T. A. Mastrykova: *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 121-5 (1953).

Thermal Decomposition of Bis-(*O,O*-dimethylthionophosphoryl)-disulfide. Kazuyuki MAEKAWA, 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, 首藤義博, 谷口栄二, 三好康之 (九州大学農学部) 48. 11. 8 受理

種々の有機燐農薬の重要な中間体である *O,O*-dimethylthiophosphoric acid 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 位から爆発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, CH_3SH , CH_3SCH_3 , $\text{CH}_3\text{-S-S-CH}_3$, $(\text{CH}_3\text{O})_2\text{-P(=O)-S-CH}_3$, $(\text{CH}_3\text{O})_2\text{-P(=S)-S-CH}_3$ 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, 融点附近の温度に数時間保った後の IR では 1300 cm^{-1} に P=O の吸収があらわれ, NMR で δ 2.25 ppm に S-CH_3 の signal が見られること, およびその強度から, P-O-CH_3 から P-S-CH_3 への転移が推察された。

O,O-Dimethyldithiophosphoric acid, $(\text{MeO})_2\text{-P(=S)-SH}$, derived from methanol and P_2S_{10} , is an important intermediate of various organic phosphorus pesticides¹⁾. The pK' value of this acid is 1.55 (in 7% ethanolic solution)²⁾. 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 Delnav³⁾. Some of bis-(*O,O*-dialkylthionophosphoryl)-disulfides have insecticidal activities⁴⁾.

However, chemical properties of the disulfide have not been sufficiently clarified⁵⁾. 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.

Experimentals

1) Redox potential

The redox potential of a system of the disulfide and *O,O*-dimethyldithiophosphoric acid was measured by the polarographical method using 0.1 M, pH 7 phosphate buffer solution containing 25%

methanol, 16% ethanol, and $(\text{MeO})_2\text{-P(=S)-SH}$ and $[(\text{MeO})_2\text{-P(=S)-S-}]_2$ (in molar ratio of 1:1). Other experimental conditions are shown in Fig. 1.

From the results shown in Fig. 1, the redox potential (E_0) was calculated as $-0.304 \pm 0.005\text{V}$. vs. normal hydrogen electrode.

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