Original Article

Thermal Decomposition of *O,O*-Dimethyl *O*-(3-Methyl-4-Nitrophenyl) Phosphorothioate—Autocatalytic Decomposition Mechanism*

Takayoshi MAEDA, Misako KAWASHIMA, Yoriko OGASAWARA
and Kozo TSUJI**

*Research Department, Pesticides Division, Sumitomo Chemical Co., Ltd.,
Konohana-ku, Osaka 554, Japan*

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It was observed that the apparent degradation rate of fenitrothion (Sumithion®) in a closed system is significantly greater than that in an open system. For this observation, there is proposed the autocatalytic degradation mechanism by dimethylsulfide, which is evolved through the decomposition of *S*-methyl-Sumithion and catalyzes the rearrangement of Sumithion into *S*-methyl-Sumithion. It is supposed that decomposition not only at high temperature but also at lower temperature such as room temperature, would be subject to this mechanism. As far as the catalytic potential of dimethylsulfide is concerned, it was found that additions of 0.4 to 1.6 w/w % of the thioether to Sumithion accelerated decomposition by more than 20 to 50 times. Some kinds of metal salt also facilitated the isomerization of Sumithion, but calcium dodecylbenzene sulfonate (surfactant) showed almost no effect. Kinetic studies were also carried out. Decomposition rate of Sumithion, *S*-methyl-Sumithion and Sumioxon were measured.

INTRODUCTION

Thermal decomposition of alkyl phosphorothioates have been known to involve thiono-thiolo rearrangement occurring at rather high temperatures above 130°C, followed by further decomposition. For instance, the isomerizations of *O,O*-dimethyl *O*-(4-nitrophenyl) phosphorothioate (methylparathion) and *O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate: (Sumithion®) into *S*-methyl isomers have been reported to take place when heated at 150°C.^{1,2)} It has also been reported¹⁻⁴⁾ that prolonged heating of *O,O*-diethyl *O*-(4-nitrophenyl) phosphorothioate (parathion), methylparathion and *O,O*-dimethyl *S*-(1,2-dicarboethoxy)ethyl phosphorodithioate (malathion)

gave further decomposition products which were insoluble in acetone. McPherson *et al.*⁵⁾ proposed the two-step mechanism of thermal decomposition of methylparathion.

We have elucidated⁶⁾ the thermal decomposition mechanism of Sumithion to consist of three steps which correspond to the three exothermic peaks in the differential thermal analysis diagram of the pesticide in air. The first step (150–190°C) is attributed to Sumioxon formation with sulfur dioxide gas evolution, the second step (210–235°C) to dimethyl sulfide gas evolution through *S*-methyl-Sumithion and polyphosphate formation, and the third step (270–285°C) to carbonization of phenolic rings and evolution of dimethyl sulfide, dimethyl disulfide and ethane gases. In the nitrogen atmosphere, on the other hand, the first step does not take place, and two step decomposition occurs according to an essentially similar mechanism to McPherson's.

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** To whom correspondence should be addressed.

We further studied the thermal stability of Sumithion by storing it at various temperatures which were rather lower than that expected for *S*-methyl isomerization, and we found that the decomposition rate was appreciably different between in a glass ampoule and in an open system. Contrary to our expectation, storage of Sumithion in the closed system caused more degradation than storage in the open system. In connection with this phenomenon, we tried to elucidate the nature of the catalytic decomposition of Sumithion in detail.

EXPERIMENTAL

1. Materials

Sumithion and related organophosphorous compounds used in this study were synthesized in the Pesticide Synthetic Laboratory, Pesticides Division, Sumitomo Chemical Co., Ltd.

Compound (Abbrevia- tion)	Chemical name	Purity
Sumithion (SMT)	<i>O,O</i> -dimethyl <i>O</i> -(3-methyl-4-nitrophenyl) phosphorothioate	100% or 96.8%
<i>S</i> -methyl- Sumithion (<i>S</i> -Me-SMT)	<i>O,S</i> -dimethyl <i>O</i> -(3-methyl-4-nitrophenyl) phosphorothiolate	98.1%
Sumioxon	<i>O,O</i> -dimethyl <i>O</i> -(3-methyl-4-nitrophenyl) phosphate	96.2%
Bis-Sumithion (Bis-SMT)	<i>O</i> -methyl <i>O,O</i> -bis(3-methyl-4-nitrophenyl) phosphorothioate	95% up
4-NMC	3-methyl-4-nitrophenol	95% up

Potassium *O*-methyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate [potassium salt of Desmethyl-Sumithion: Kdms] was prepared by the reaction of Sumithion with potassium *N,N*-dimethyldithiocarbamate in refluxing methanol for 30 minutes, and confirmed by PMR spectrum. Calcium dodecylbenzenesulfonate was supplied from Matsumoto Yushi Co. Other chemicals, which were free from water and reagent grade, were supplied from Wako Pure Chemical Industries, Ltd.

2. Apparatus

Evolved gas analysis (EGA) was carried out by an apparatus made in the Central Research Laboratory, Sumitomo Chemical Co., Ltd.,

which was composed of a differential thermal analysis (DTA) and a quadrupole mass spectrometer. The decomposition products were identified and their amounts were measured by a gas-liquid chromatograph (*glc*) equipped with a flame ionization detector (Shimadzu-3BF), a high performance liquid chromatograph (HPLC) with a UV detector (254 nm) (Waters 3000), and a proton magnetic resonance (PMR) spectrometer (Hitachi R-24B).

3. Heat Treatment of Sumithion

About 0.1–8.4 g (0.4–30 mmole) of Sumithion was heated in a glass ampoule at various temperatures for specified periods. Each sample was analyzed after heating and its content of Sumithion was determined by means of *glc*, HPLC and PMR. Unless noted, heating of the sample was carried out under nitrogen atmosphere in a sealed glass ampoule, and the content of Sumithion and reaction products were determined by *glc*.

4. Decomposition of Sumithion, *S*-Methyl-Sumithion and Sumioxon

Remaining percentages of Sumithion (initial percentage; 98.8–99.7%), *S*-methyl-Sumithion (98.1%) and Sumioxon (96.2%) after storage at 80 and 100°C for specified periods were determined as described above.

RESULTS AND DISCUSSION

Figure 1 shows the stability of SMT at 120°C and 130°C in closed and open systems. *S*-Me-SMT was identified as the main decomposition product. It is obvious that SMT is more stable in the open system than in the closed system. The decomposition rate of SMT is remarkably increased with heating time. For example, after heating for 6 hours at 120°C, only 4.9% of SMT decomposed, while more than 14.7% decomposed during the next 6 hours at the same temperature. This behavior in the closed system strongly suggests the autocatalytic degradation mechanism, in which decomposed products would play an important role in the acceleration of decomposition of SMT.

In order to get more information about decomposition products, HPLC analysis (Table 1) and EGA analysis of heat treated SMT were carried out at 80, 130 and 200°C. In the low

Table 1 Determination of Sumithion content and its decomposition products after heating at 100°C for 8–56 hours, by HPLC.

Heating period (hr)	Compound (%)					
	I	II	III	IV	V	VI
0	98.80	0.06	0.19	—	—	—
8	92.36	2.02	0.40	—	tr.	tr.
24	88.14	6.59	0.13	0.45	0.02	0.70
32	85.99	9.01	0.13	0.51	0.06	0.77
48	78.86	13.37	0.08	0.73	0.06	0.92
56	76.99	14.97	0.06	0.79	0.12	1.03

I: Sumithion, II: *S*-methyl-Sumithion, III: Bis-Sumithion, IV: Sumioxon, V: *S*-methyl-bis-Sumithion, VI: 3-methyl-4-nitrophenol.

temperature decomposition, as shown in Table 1, *S*-Me-SMT was confirmed to be the main decomposition product and as minor products Bis-SMT (III), Sumioxon (IV), *S*-methyl *O,O*-bis(3-methyl-4-nitrophenyl) phosphorothiolate (*S*-Me-Bis-SMT) (V) and 4-NMC (VI) were found. This result was almost the same as that of our previous DTA study carried out in the nitrogen atmosphere (open system) at higher temperatures (up to 193°C and/or more).⁶⁾

Fig. 1 Thermal decomposition of Sumithion and production of *S*-methyl-Sumithion at 120 and 130°C in the sealed glass ampoule (closed system) and unsealed glass ampoule (open system).

The EGA analysis showed an appreciable amount of dimethyl sulfide and dimethyldisulfide evolved by keeping SMT at 130°C for 30 minutes (open system). The temperature of 130°C is lower than the temperature of sulfide evolution, 210–235°C (peak II region in the DTA diagram), which was found by DTA study in our previous paper.⁶⁾ These findings suggest that the decomposition takes place also at lower temperature according to an essentially similar mechanism to that of higher temperature or to McPherson's.⁵⁾ It is obvious that even at low temperature, SMT, though very slowly, isomerizes into *S*-Me-SMT, followed by further decomposition to dimethyl sulfide and poly aryl metaphosphates. The fact that *S*-Me-SMT, once formed from SMT, is ready to decompose further is well understood from the results of the study of thermal decomposition of SMT, *S*-Me-SMT and Sumioxon (Figs. 2 and 3) at 80 and 100°C, which are summarized in Table 2. It is clear that compared with the decomposition percentage of SMT, the decomposition of *S*-Me-SMT is larger while that

Fig. 2 Thermal stability of Sumithion (A), *S*-methyl-Sumithion (B) and Sumioxon (C) at 80°C.

Fig. 3 Thermal stability of Sumithion (A), S-methyl-Sumithion (B) and Sumioxon (C) at 100°C.

Table 2 Relative decomposition rate of Sumithion and related compounds (neat) at 80 and 100°C.

Temperature	Sumithion	S-methyl-Sumithion	Sumioxon
80°C	0.0647	0.143	0.0276
100°C	0.387	0.497	0.0742
Decomposition rate (Decomposition %/hr)			

of Sumioxon is smaller.

Of the decomposition products of SMT, dimethylsulfide whose boiling point is 37°C, is

the most probable one concerned with its autocatalytic decomposition of SMT in the closed system. As shown in Table 3, by the addition of 4 mmole of dimethylsulfide to 24 mmole of SMT, as much as 26% of SMT (6.2 mmole) was converted into S-Me-SMT after standing at 60°C for 30 minutes, although SMT alone is stable even at more severe conditions, indicating that isomerization of SMT into S-Me-SMT is catalyzed by dimethylsulfide. It is also clear that potassium salt of des-methyl-fenitrothion, the anion of which is supposed to be an intermediate moiety in the thiono-thiolo rearrangement,⁷⁻¹¹⁾ also catalyzed the isomerization, but not as effectively as dimethyl sulfide.

Accordingly, it would be reasonable to suppose the autocatalytic decomposition mechanism shown in Fig. 4 for the thermal decomposition of SMT especially in the closed system. Dimethyl sulfide produced by the decomposition of S-Me-SMT catalyzes the rearrangement of SMT to S-Me-SMT (circle I), acting as a methyl group acceptor of methoxy methyl of SMT to form a reaction intermediate compound, that is, the trimethyl sulfonium salt of des-methyl-SMT. Such type of compound has

Table 3 Reactivity of Sumithion with molecules containing sulfur atom.

Reaction conditions				Reaction products		
(mmole)	(mmole)	Temp. (°C)	Period (min)	Unreacted ^{a)} SMT (%)	S-methyl ^{a)} SMT (%)	Others (%)
SMT (24)	+ CH ₃ SCH ₃ (4)	60,	30	73	26	—
SMT (24)	+ $\begin{array}{c} \text{CH}_2\text{---CH}_2 \\ \\ \text{CH}_2\text{---CH}_2 \end{array} \text{S}$ (4)	60,	30	100	(No reaction)	
		100,	30	18	61	21
SMT (24)	+ Kdms ^{b)} (4)	60,	30	100	(No reaction)	
		100,	30	77	20	3
		100,	90	70	22	8
		100,	210	49	34	21
SMT (24)		100,	180	100	(No reaction)	
		100,	360	100	(No reaction)	

^{a)} S-methyl-Sumithion percentage was calculated from the ratio of integration value of S-methyl protons to that of the methyl protons attached to aromatic ring, which can be estimated to be Sumithion used.

^{b)} Potassium salt of Des-methyl-Sumithion;

Fig. 4 Proposed mechanism of autocatalytic decomposition of Sumithion.

already been known to be transformed into an *S*-methyl isomer, releasing dimethyl sulfide.⁸⁻¹¹⁾ *S*-Me-SMT would produce an additional amount of dimethyl sulfide by further decomposition (circle II). The more the amount of dimethyl sulfide accumulates, the more the decomposition of SMT accelerates and ultimately very rapid decomposition occurs. Besides this report on SMT, the autocatalytic decomposition of organophosphorous compounds has been reported only in the case of malathion EC formulation, where dithiophosphoric acid, formed by the decomposition of malathion, causes acceleration of the decomposition.¹²⁾

In order to further clarify the catalytic decomposition of SMT in the presence of a thioether, a model reaction of SMT with tetrahydrothiophen (THT) was investigated. This was used instead of the combination of SMT and dimethylsulfide because THT has

Fig. 5 Catalytic decomposition of Sumithion by tetrahydrothiophene (THT) in 50% xylene solution at 100°C. THT concentrations are 0 (A), 0.4 (B), 0.8 (C) and 1.6% (w/w) (D).

a suitable boiling point (121°C) for carrying out the experiment easily and is less reactive than dimethyl sulfide as shown in Table 3. Figure 5 represents the time course of SMT decomposition at 100°C in 50% xylene solution in the presence of THT. From Fig. 5, the initial decomposition rate was obtained as shown in Table 4. It should be noticed that the addition of as small an amount of thioether as 0.4 to 1.6 w/w% caused the catalytic decomposition of SMT, accelerating the decomposition by 20 to 50 times. So it would be reasonable to conclude that in the actual case, when dimethyl sulfide instead of THT is included and when Sumithion technical grade is not diluted with solvent, a much larger acceleration in decomposition would take place.

It is obvious from the decomposition mechanism shown in Fig. 4 that there may be mainly two or three ways for protection of SMT from undesirable degradations. The first way is to minimize the concentration of dimethyl sulfide

Table 4 Decomposition of 50% xylene solution of Sumithion in the presence of tetrahydrothiophene (THT) at 100°C.

THT/SMT % (w/w)	THT/SMT mole ratio	Decomposition percentage per hour	Relative decomposition rate
1.6	0.10	0.0214	50
0.8	0.05	0.0126	30
0.4	0.025	0.0074	20
0.0	0.0	0.0004	1

Table 5 Stability of Sumithion in the presence of metal salts (Remaining percentage of SMT^{a)}).

NaCl	KCl	CuCl	MgCl ₂	CaCl ₂	ZnCl ₂	AlCl ₃	FeCl ₃	SiCl ₄	SnCl ₄
96.5	95.4	92.0	92.3	95.0	46.3	11.9	2.2	89.2	0.1
(0)	(0.3)	(2.7)	(1.7)	(1.4)	(10.2)	(6.7)	(47.2)	(1.1)	(52.4)

^{a)} Remaining percentage of Sumithion was calculated after 10 mmole was heated at 40°C for 43 hours in the presence of 5 mmole of metal salt (anhydrous). Values in parenthesis are relative amount (%) of S-methyl-Sumithion to that of Sumithion used.

as in the case of storage in the open system. The second way is to suppress the production of S-Me-SMT which is the source of the sulfide. Beside heating or exposure to sunlight, a contamination of some kinds of metal salt could facilitate the rearrangement of SMT into S-Me-SMT. It is preferable that these factors causing S-Me-SMT formation should be eliminated from the system as much as possible. Therefore, the effect of various metal chlorides on the stability of SMT was examined. Among the metal chlorides examined (Table 5), zinc, aluminum, ferric, silicon and stannic chlorides are most active in causing the isomerization and potassium, cuprous, magnesium and calcium chlorides are moderate, and sodium chloride is inert. As in the case of formulation such as emulsifiable concentrate or wettable powder, calcium ion is frequently added to SMT as an anionic surfactant, the compatibility of SMT with calcium salt of dodecylbenzenesulfonic acid was examined (Table 6).

Table 6 Compatibility of Sumithion with calcium dodecylbenzenesulfonate (DBS-Ca).

Heating period at 110°C (hr)	Sumithion content (%)	Remaining percentage of Sumithion (%)
Initial ^{a)}	30.6	100
13.0	29.5	(96.4)
21.5	29.0	(94.8)
29.5	28.3	(92.5)
52.5	27.3	(89.2)
62.5	26.8	(87.6)
72.5	26.3	(85.9)
89.5	26.1	(85.3)

^{a)} Clear solution, composed of Sumithion (30%), DBS-Ca (7%) and xylene (63%).

It was found that the presence of calcium ion caused no significant degradation of SMT. And the third way would be to deactivate S-Me-SMT by changing it to some kind of inert compounds. We are continuing the investigation in order to get stabilizers for this purpose.

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要 約

フェニトロチオンの熱分解——自動触媒的分解機構*

前田尚良, 川島操子, 小笠原順子, 辻 孝三
密閉系でのフェニトロチオン (スミチオン®) の分解速度は, 開放系よりもかなり速いことを認め, 次のような自動触媒的熱分解機構を提唱した. 分解は S-メチル異性体を経由し, さらに S-メチル体の分解生成物であるジメチルチオエーテルによって異性化が加速される.

また室温のような低い温度でもこの分解機構が適用されると推察された. チオエーテルをスミチオンに 0.4~1.6 w/w % 添加すると, 20~50 倍以上スミチオンの異性化が加速されることがわかった. ある種の金属塩もスミチオンの異性化を速めるが界面活性剤のドデシルベンゼンスルホネートは無影響であった. また, スミチオン, S-メチルスミチオン, スミオキシソンの熱安定性を比較した.

* 有機リン農薬の分解 (第2報)