殺虫剤サリチオンと関連環状リン酸エステル類の質量スペクトル分析

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Mass Spectrometry of the Insecticide Salithion and Related Cyclic Phosphorus Esters*

Nobuhiro FUKUHARA** and Morifusa ETO

Department of Agricultural Chemistry, Kyushu University, Fukuoka 812, Japan

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Mass spectrometry of fifteen benzodioxaphosphorins and dioxaphosphoranes including the insecticide salithion was studied. The mass fragmentation of saligenin cyclic phosphorus esters is characteristic as follows: 1) β–Cleavage of an exocyclic ester bond occurs with charge retention on the phosphorus moiety in the phosphate and phosphorothionate esters, whereas α–cleavage is dominant in the thiolate esters. 2) The thiono type esters lose SH. 3) Thiono–thiolo rearrangement occurs particularly in the aryl phosphorothionates. 4) No proton rearrangement occurs in the process of ester cleavage. 5) Fragmentation of non-phosphorus containing moiety is similar with that of saligenin.

INTRODUCTION

The insecticide salithion (2–methoxy–4*H*–1, 3,2–benzodioxaphosphorin 2–sulfide) is unique in the structure, that is, a six-membered cyclic phosphorothionate derived from *o*–hydroxybenzyl alcohol (saligenin).[1,2] The phenyl phosphate and phenylphosphonate analogs are neurotoxic and synergistic with the insecticide malathion.[3] The *S*–methyl isomer of salithion is a useful phosphorylating agent named MTBO.[4] Many papers relating on the mass spectrometry of organophosphorus compounds including pesticides have appeared.[5–9] However, only a little of papers deals with cyclic phosphorus esters. This paper describes the mass spectrometry of salithion and some related cyclic phosphorus esters. They showed interesting patterns of fragmentation.

MATERIALS AND METHODS

Salithion was purified by recrystallization of the technical product from methanol, m.p. 55–56°C. 2–Methylthio–4*H*–1,3,2–benzodioxaphosphorin 2–oxide (MTBO) was obtained by isomerization of salithion.[10] Other cyclic phosphorus esters were prepared in this laboratory as previously reported.[11–13]

Mass spectra were measured with a Hitachi RM4 spectrometer or a Nihon Denshi JMS-01SG mass spectrometer by direct introduction at 70 or 75 electron volts.

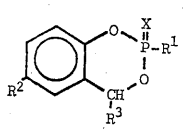
RESULTS AND DISCUSSION

Fifteen cyclic phosphorus esters, including salithion (**1**), salioxon (**8**) and MTBO (**6**), derived from saligenin (**1–10**), 1–(5–chloro–2–hydroxyphenyl)ethanol (**11–12**), and 1,3–propanediols (**13–15**) were selected for the mass spectrometric study. Their spectra are summarized in Table 1 and 2. All the cyclic phosphorus esters show distinct molecular radical ions with considerable intensity; the ions were observed as base peaks in the phosphonate and phosphonothionate esters of saligenin (**4**, **5**, **10**), as moderate peaks in the phosphate, phosphorothionate, and phosphorothiolate esters (**1–3**, **6–9**) (15–94%), and as relatively weak peaks (10–48%) in the propanediol derivatives (**13–15**).

The initial fragmentation of salithion (**1**) occurs by the β–cleavage of the exocyclic

* Studies on Saligenin Cyclic Phosphorus Esters with Insecticidal Activity (Part 14)

** Present address: Central Institute, Mitsui-Toatsu Chemical Co., Yokohama.



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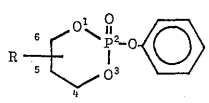


II

ester bond PO–CH_3, giving a relatively intense peak (*m/e* 201; 11%) with the charge on the phosphorus moiety (**1a**) (Scheme 1). The oxygen analog of salithion (**8**) gives a more intense peak at *m/e* 185 similarly by the *β*–cleavage (70%). Even the phenyl phosphate (**9**) gives a similar fragment ion M^+–C_6H_5 (*m/e* 185; 10%), though the corresponding thiono ester (**2**) does not. This *β*–cleavage is characteristic with salithion and the related saligenin cyclic phosphorus esters. In usual open-chain phosphorus esters, *β*–cleavage occurs in phosphorothiolates but seldom in phosphorothionates and phosphates, producing ions with the charge retention on the non-phosphorus moieties, except some *S*–methyl phosphorothiolates which give small peaks of M^+–CH_3.[7,8]

The *α*–cleavage of the exocyclic group is dominant in the *S*–methyl isomer of salithion (MTBO; **6**) to give the base peak of M^+–SCH_3 (*m/e* 169). MTBO gives small peaks of *m/e* 201 (M^+–CH_3) (4%) and *m/e* 183 (M^+–SH) (2.5%) probably owing to the reverse thiono-thiolo rearrangement which occurred prior to fragmentation. The methylphosphonothionate (**4**) and the phenylphosphonate (**10**) give the *α*–cleavage ions at *m/e* 185 (M^+–CH_3) and 169 (M^+–C_6H_5), respectively, whereas the phenylphosphonothionate (**5**) does not. In the phenyl

Table 1 Mass spectra of cyclic phosphorus esters (I) derived from *o*–hydroxybenzyl alcohol and 1–(5–chloro–2–hydroxyphenyl)ethanol.

Comp. No.	X	R^1	R^2	R^3	*m/e* (%)
1	S	OCH_3 (salithion)	H	H	216(15), 201(11), 183(20), 153(20), 138(12), 137(12), 122(9), 121(16), 106(7), 105(9), 78(100), 77(29), 52(29), 51(38), 47(23)
2	S	OC_6H_5	H	H	278(20), 245(9), 185(13), 169(14), 150(8), 122(4), 121(6), 109(8), 106(1), 94(100), 78(8), 77(18), 56(30), 55(30)
3	S	OC_6H_4–*p*–OCH_3	H	H	308(79), 294(3), 275(31), 243(24), 242(19), 169(22), 154(23), 153(77), 139(100), 137(40), 122(33), 121(15), 108(12), 106(4), 105(10), 95(22), 78(23), 77(21), 62(50)
4	S	CH_3	H	H	200(100), 185(17), 167(37), 153(8), 137(10), 122(43), 121(23), 106(13), 105(14), 85(14), 78(59), 77(24), 63(14), 52(12), 51(18)
5	S	C_6H_5	H	H	262(100), 229(41), 165(13), 122(40), 121(18), 106(9), 105(16), 104(18), 96(60), 78(43), 77(28), 76(25)
6	O	SCH_3 (MTBO)	H	H	216(68), 201(4), 183(2.5), 170(13), 169(100), 168(25), 135(15), 121(7), 122(4), 106(16), 104(14), 78(86), 77(42), 63(3), 52(11), 51(18), 47(9)
7	O	OH	H	H	186(16), 185(4), 169(6), 122(23), 121(14), 106(87), 78(100), 77(18), 52(20), 51(20)
8	O	OCH_3 (salioxon)	H	H	200(71), 185(70), 169(5), 140(10), 122(80), 121(41), 106(23), 105(20), 95(20), 94(11), 78(100), 77(22), 65(20), 63(12), 52(23), 51(31)
9	O	OC_6H_5	H	H	262(94), 185(10), 181(54), 169(100), 164(37), 122(12), 121(23), 119(50), 118(50), 106(21), 94(85), 78(88)
10	O	C_6H_5	H	H	246(100), 217(22), 181(18), 169(16), 165(13), 125(9), 121(7), 106(46), 94(20), 78(97), 77(40), 52(24), 51(36)
11	O	OCH_3	Cl	CH_3	248(44), 233(100), 223(10), 205(11), 170(26), 155(25), 154(74), 150(20), 121(24), 105(20), 91(64)
12	O	C_6H_5	Cl	CH_3	294(47), 279(46), 216(5), 170(trace), 156(33), 154(100), 125(10), 91(65), 77(30), 51(30)

Table 2 Mass spectra of cyclic phosphorus esters (II) derived from 1,3-propanediols.

Comp. No.	R	*m/e*(%)
13	4-CH_3	228(48), 213(3), 200(6), 175(61), 174(94), 156(43), 130(36), 129(16), 115(7), 107(8), 94(100), 77(40)
14	4,4,6-tri-CH_3	256(18), 241(1), 215(4), 201(15), 175(100), 174(13), 156(11), 94(18), 83(16), 82(65), 77(14), 67(30)
15	4,5,6-tri-CH_3	256(11), 201(18), 175(100), 174(17), 156(13), 94(36), 83(36), 82(77), 77(20), 67(33), 55(39), 43(37), 41(36)

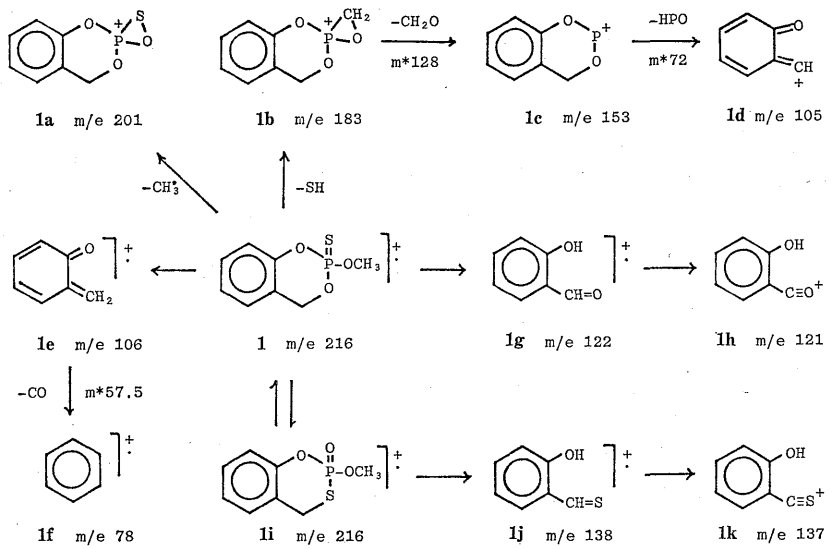
phosphate (**9**), α-cleavage is much more preferable than β-cleavage to give the base peak of $M^+-OC_6H_5$ ion (*m/e* 169) and a small peak of $M^+-C_6H_5$ ion (*m/e* 185; 10%), in contrast to the methyl phosphate (**8**), which gives a dominant β-cleavage product (*m/e* 185; 70%) and a minor α-cleavage one (*m/e* 169; 5%). The phenyl phosphorothionate (**2**) gives both the $M^+-OC_6H_5$ ion (*m/e* 185; 13%) and the $M^+-SC_6H_5$ ion (*m/e* 169; 14%). The latter must be produced by α-cleavage after the thiono-thiolo rearrangement. The corresponding non-phosphorus containing ions such as phenol radical ion (*m/e* 94; 100%) and $C_6H_5S^+$ (*m/e* 109; 8%) are observed. In the *p*-methoxyphenyl phosphorothionate (**3**), the rearrangement occurs much readily to give intense peaks of the *m/e* 169 ion (22%) and $CH_3OC_6H_4S^+$ (*m/e* 139; 100%) but negligible peaks of the *m/e* 185 ion and methoxyphenol radical ion *m/e* 124. Thus, the electron-induced thiono-thiolo rearrangement is very different from the thermal thiono-thiolo isomerization, in which no aryl group but an alkyl group migrates preferably from an ester group to thiophosphoryl.[5]

Another important initial fragmentation occurring in salithion and the related thiono esters (**1–5**) is the direct loss of SH from the molecular ions to give the M^+-SH ions. Although the loss of SH is favored wherever suitable substituents are present in the molecule,[14] no peaks of M^+-SH ions have been observed in the spectra of usual organophosphorus pesticides, *i.e.* dimethyl or diethyl phosphorothionates.[7,8] The latter and the oxygen analogs commonly show a McLafferty type rearrangement in which hydrogen migration to sulfur or oxygen is accompanied by ethylene elimination.[8,9,14] Similar rearrangements appear to occur in the propylene cyclic phenyl phosphates (**13–15**) giving intense ions at *m/e* 175 $[(HO)_3POC_6H_5]^+$ and *m/e* 174 $[(HO)_2P(O)C_6H_5]^+$, but not in the benzodioxaphosphorins including the 4-methyl derivatives (**11–12**).

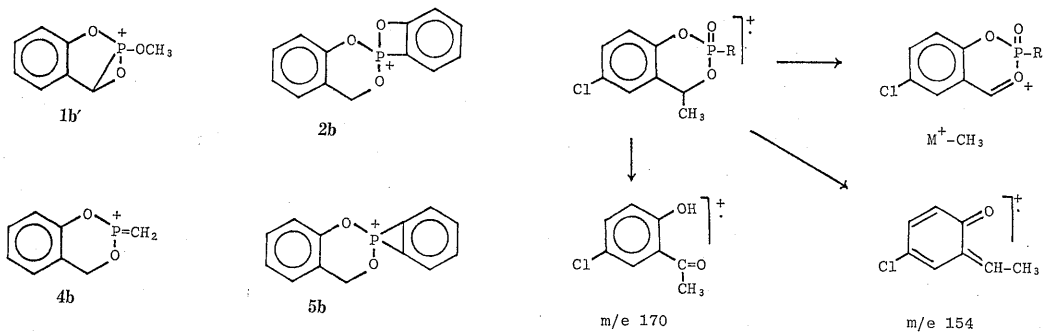
The chemical composition of the fragment ion *m/e* 183 from salithion (**1**) was decided by the accurate measurement in high resolution mass spectrometry as $C_8H_8O_3P$ (Found 183.020; Calcd. 183.021). Two structures **1b** and **1b'** are possible for the M^+-SH ion depending upon the hydrogen atom derived preferably from either the endocyclic methylene or the exocyclic methyl group.

It was demonstrated by the finding of a metastable ion *m/e* 128 in the mass spectrum of salithion that the M^+-SH ion (*m/e* 183) was transformed into a fragment ion *m/e* 153 by ejection of CH_2O in one step process. The chemical composition of the ion *m/e* 153 was decided as $C_7H_6O_2P$ by accurate mass determination (Found 153.014; Calcd. 153.011), indicating the structure as **1c**. Therefore, the structure **1b** is more preferable than **1b'** to give **1c** by CH_2O ejection (Scheme 1). Loss of SH from molecular ions is commonly found in the other cyclic P=S compounds (**2–5**). In these compounds hydrogen atom on the exocyclic substituents may be lost similarly in this process. The M^+-SH ions may be written as **2b**, **4b** and **5b**. Cooks and Gerrard have proposed that diphenyl phosphorochloridothioate loses an aromatic hydrogen to produce an M^+-SH ion.[14]

The fragment ion **1c** decomposes further to produce the *m/e* 105 ion, whose structure may be as **1d**, ejecting HPO as demonstrated by the presence of a metastable ion at *m/e* 72 (Scheme 1). The fragment ion *m/e* 153 is always accompanied by the *m/e* 105 ion in the spectra of such other compounds as the methylphosphonothionate (**4**) and *p*-methoxyphenyl phosphorothionate (**3**). However, the



Scheme 1 Fragmentation pathways of salithion.



Scheme 2

phenyl phosphorothionate (**2**) gives neither these fragment ions.

Other non-phosphorus containing fragment ions of salithion and some other saligenin cyclic phosphorus esters at *m/e* 122, 121, 106, and 78 are reminiscent of saligenin fragmentation.[15] The *m/e* 78 ion gives a base peak in the mass spectrum of salithion and appears commonly as a main peak in all the saligenin derivatives, except the phenyl phosphorothionate (**2**) which gives that only 8%. It may probably be $C_6H_6^{+\cdot}$. In the spectra of the methyl phosphate (**8**) and the phenylphosphonate (**10**) is found a metastable ion at *m/e* 57.5, which corresponds the conversion of a radical ion *m/e* 106 to the *m/e* 78 ion liberating CO as shown in Scheme 1. The *m/e* 122 ion has the chemical composition of salicylaldehyde. It may be not the precursor of the *m/e* 106 ion, because loss of atomic oxygen as the neutral species is required for the transformation and salicylaldehyde gives only a negligible peak at *m/e* 78.[16] Thus, there are two different pathways to give those fragment ions as shown in Scheme 1 by analogy of saligenin fragmentation.[15] Similar fragmentations are also observed in the spectra of the 6-chloro-4-methylbenzodioxaphosphorin derivatives (**11**, **12**), though the loss of a methyl group at the 4 position to give M^+-CH_3 ions is also prominent [*m/e* 233 (100%) for **11**; *m/e* 279 (46%) for **12**] as shown in Scheme 2. Moreover, the fragment ions at *m/e* 138 and 137 of salithion could be the thio-analogs of *m/e* 122 and 121 ions, respectively. Thiono-

thiolo rearrangement between the benzyl group and thiophosphoryl of salithion has been reported to be induced by light.[17] Thus, the fragmentation pathways of salithion are proposed as shown in Scheme 1.

Finally it is also a characteristic behavior of the cyclic phosphorus esters that no fragment ion at *m/e* 79 (CH_3OPOH^+) is formed from the methyl esters (**1**, **8**, **11**); the ion has been known to be formed almost without exception from usual methyl phosphorus esters such as methyl parathion.[6]

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要　　約

殺中剤サリチオンと関連環状リン酸エステル類の質量スペクトル分析

福原信裕，江藤守総

殺虫剤サリチオンを含む 15 種のベンゾジオキサホスホリンおよびジオキサホスホラン類の質量分析を行なった．サリゲニン環状リン酸エステル類は次のように特徴あるフラグメンテーションを示した．1) リン酸エステルとチオノリン酸エステルでは環外エステルの β-開裂が起こり，リン部分に電荷が残るが，チオールエステルでは α-開裂が主であった．2) チオノ型エステルは SH を失う．3) チオノ-チオール転位がとくにチオノリン酸アリールエステルで起こる．4) エステル開裂にさいしプロトン転位は起きない．5) 非含リン部分のフラグメンテーションはサリゲニンのそれに似ている．