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REPORT NUMBER 6

ION PHENOMENA

Final Report

by

Robert W. Kiser

May 1968



Physical Research Laboratory
RESEARCH LABORATORIES
Edgewood Arsenal, Maryland 21010

Contract DA-18-035-AMC-718(A)

KANSAS STATE UNIVERSITY
Department of Chemistry
Manhattan, Kansas 66502



56

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FOREWORD

The work described in this report was authorized under Project 1C622401A102, Chemical Agent Warning and Detection Techniques (U). This work was started 9 December 1965 and completed 31 July 1967. The experimental data are contained in notebooks KSU-182311-DLD-6 to KSU-182311-DLD-11 and KSU-182311-RES-3 to KSU-182311-RES-5.

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The information in this report has not been cleared for release to the general public.

Acknowledgments

Donald L. Dugger and Richard E. Sullivan have been instrumental in obtaining the experimental findings reported herein.

DIGEST

Mass spectrometric studies of trimethyl phosphorothionate, triphenyl phosphite, diallyl phosphite, diallyl allylphosphonate, triallyl phosphite, triallyl phosphate, and diphenyl phosphite were made to obtain more fundamental information for use in determining the ionization and dissociative ionization processes that occur upon electron impact with these organophosphorus compounds. Mass spectra, appearance potentials, clastograms and metastable transitions obtained in these studies are reported. These results are discussed in relation to a better understanding of the fragmentation pathways in this class of compounds. A summary table of all results determined under this contract is included, and a brief catalog, with literature references, of the mass spectra of organophosphorus compounds summarizes much of the available literature. Future correlative activities are suggested.

TABLE OF CONTENTS

STATEMENT OF PROBLEM	7
BACKGROUND	7
APPROACH TO THE PROBLEM	7
RESULTS	8
DISCUSSION	9
CONCLUSIONS	12
LITERATURE CITED	13
APPENDIX	15
DISTRIBUTION LIST	55
DOCUMENT CONTROL DATA - R&D, DD FORM 1473, WITH ABSTRACT AND KEYWORD LIST	57

ION PHENOMENA

1. STATEMENT OF PROBLEM

This work was initiated in order (1) to obtain mass spectra, (2) to make energetic studies by appearance potentials, and clastogram determinations, (3) to utilize metastable transition measurements in determining fragmentation pathways, and (4) to form negative parent molecule ions by bombardment of biologically active compounds containing P, N, and S by means of a polonium-210 alpha particle source.

2. BACKGROUND

Preliminary investigations of organophosphorus compounds such as GB and GD have indicated that these biologically active materials are ionized at low potentials (ca. 11.5 eV) and that at electron energies above approximately 15 eV there is significant fragmentation of the parent positive ion. However, the ionization and dissociative ionization processes are poorly understood, attributable largely to a lack of fundamental information concerning similar processes in simpler organophosphorus compounds. Because little or no information is available about the processes in the biologically active compounds, it is necessary to study both the simpler and the more complex organophosphorus molecules.

The study of both the positive and negative ions formed in the ionization and dissociation processes is important to understanding the fragmentation processes that occur. It has been reported that the G agents capture low energy electrons to form parent negative ions, but almost certainly other negatively charged fragment ions will be formed with higher energy electrons through dissociative electron attachment. No information is available about negative ion clastograms that would indicate possible routes of fragmentation of these species.

3. APPROACH TO THE PROBLEM

3.1 Materials

The materials to be studied included trimethyl phosphorothionate, triphenyl phosphite, diallyl phosphite, diallyl allylphosphonate, triallyl phosphite, triallyl phosphate, and diphenyl phosphite.

3.2. Equipment

The Bendix time-of-flight mass spectrometer, together with its various modifications, has been described in previous reports. (1-8)

3.3. Techniques of Study

The techniques of study have been outlined in detail in earlier reports. (4-8)

4. RESULTS

4.1. Trimethyl Phosphorothionate

Appearance potentials for twelve ions formed by electron impact from trimethyl phosphorothionate are given in Table 1. Processes for the formation of five ions are suggested, based on the energetics and clastogram data.

4.2. Triphenyl Phosphite

The 70 eV mass spectrum of triphenyl phosphite was determined and is shown in Figure 1. The clastogram for this molecule is shown in Figures 2 and 3. The appearance potentials listed in Table 2 indicate that the major ions in the mass spectrum of this compound are due to phenol, probably formed by thermal decomposition of the sample. Thus, the base peak at $m/q = 94$ has an appearance potential of 8.8 ± 0.2 eV as determined by electron impact, and the photoionization value for the ionization potential of phenol is known to be 8.5 eV. (9) This comparison and the other data of Table 2 strongly suggest that the majority of the ions below $m/q = 94$ are due to phenol. The small quantities of ions at $m/q = 149$, 156 and 167 precluded appearance potential measurements.

4.3. Diallyl Phosphite

The 70 eV mass spectrum of diallyl phosphite was given in Quarterly Progress Report No. 5. (8) The clastogram and several preliminary appearance potential measurements for ions formed from this compound by electron impact were given also in that report. (8) Table 3 given in the Appendix presents a more complete treatment of the previous data.

4.4. Diallyl Allylphosphonate

In Table 4 are listed appearance potentials for thirteen ions formed from diallyl allylphosphonate. However, only for four ions have probable processes of formation been indicated. The ions of $m/q = 79$, 80 and 81 may be due to PO_3^+ , HPO_3^+ and $H_2PO_3^+$, but the appearance potentials do not support this. It will be necessary in

future studies to utilize high resolution mass spectrometry in order to positively identify these ions and thereby permit the process assignments to be made from the energetics and observed metastable transitions.

4.5. Triallyl Phosphite

Even as with diallyl allylphosphonate, the $m/q = 79, 80$ and 81 ions are not established with sufficient certainty to permit the assignment of probable processes for these ions. Four ions that involve simpler fragmentation have been assigned probable processes in Table 5. Appearance potentials for twelve ions have been determined.

4.6. Triallyl Phosphate

Table 6 lists the principal ions in the 70 eV positive ion mass spectrum together with appearance potentials determined for six different ions using the energy compensation method. The energetic data have been employed in assigning probable processes wherever possible. However, a lack of certain knowledge of composition of many ions does not permit a more detailed analysis of the fragmentation processes at this time. The logarithmic elastogram for this compound is given in Figures 4 and 5.

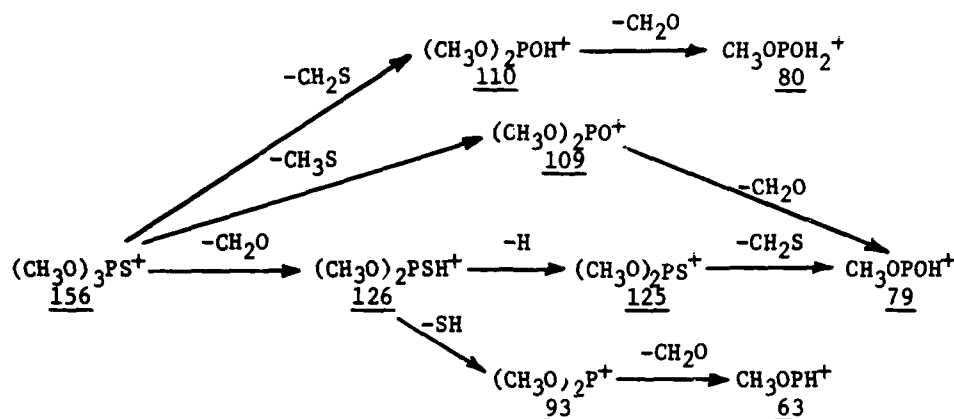
4.7. Diphenyl Phosphite

The 70 eV mass spectrum, the elastogram, and some preliminary appearance potentials for diphenyl phosphite were given previously in Quarterly Progress Report No. 5 (6). Table 7 presents evidence that the majority of the mass spectrum derives from phenyl, even as was noted for triphenyl phosphite. Apparently this is due to thermal decomposition of these materials; this should be studied further in future efforts.

5. DISCUSSION

5.1. Trimethyl Phosphorothionate

Utilizing the metastable transition data, the results from the appearance potential determinations, and the elastograms obtained, the following partial fragmentation scheme may be constructed.



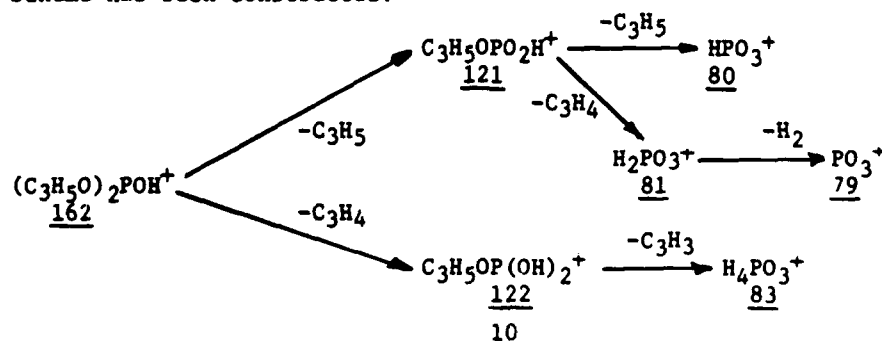
From the metastable transition data, the second process in Table 1 for the formation of the $m/q = 79$ ion is preferred; thus, the value of $\Delta H_f(79^+) = 126$ kcal/mole is also preferred. This indicates that the $m/q = 79$ ion is predominantly CH_3OPOH^+ . The unique fragmentations involving the retention and loss of the sulfur atom suggest either that the CH_3 group is very mobile or that rapid equilibria may be established between isomeric forms of these gaseous ionic species.

5.2. Triphenyl Phosphite

In that the mass spectrum and appearance potentials determined suggest that phenol may be formed from this compound through thermal decomposition, and that the present observations do not differentiate any phenol from the ions formed directly from the title compound by electron bombardment, no further discussion of the present results is merited.

5.3. Diallyl Phosphite

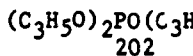
The absence of the parent ion, and the very low appearance potential for the lowest energetic requirement of the fragment ions suggests that the ionization potential of the parent molecule is approximately 10.0 eV. From the clastogram data and the appearance potentials determined in this work, the following partial fragmentation scheme has been constructed:



Report No. 5. (8)

5.4. Diallyl Allylphosphonate

of that proposed earlier: (8)



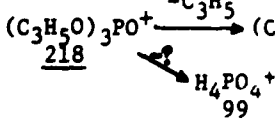
potential of diallyl allylphosphonate is approximately 10 0 eV.

5.5. Triallyl Phosphite

No. 5. (8) The ionization potential is estimated to be approximately 8.8 ev, as determined from the lowest appearance potential measured in these studies.

5.6. Triallyl Phosphate

the following fragmentation scheme is proposed:



From the appearance potential data, it is suggested that the ionization potential of triallyl phosphate is approximately 9.8 eV.

5.7. Diphenyl Phosphite

Even as with the triphenyl phosphite, the mass spectrum and appearance potentials suggest that phenol may be formed from this compound through thermal decomposition. Therefore, no further discussion of the present results is merited.

6. CONCLUSIONS

It is suggested that future work concentrate on (1) negative ions formed from the various organophosphorus compounds, (2) high resolution mass spectra and precise mass measurements to permit the identification of many of the positive ions formed from these compounds, and (3) detailed metastable transition studies to establish more fully the fragmentation pathways occurring in these compounds. All of these data, together with that obtained under the present contract effort, should yield a reasonably satisfactory body of information capable of providing further insights from correlative studies of the data.

Included in Table 8 in the Appendix is a complete summary of all the findings obtained in these studies. This information, taken together with that summarized in Table 9 and the various other literature-reported results, will provide future investigators with much of the needed material. It is easily concluded that even the data of Tables 8 and 9 are not complete and that additional work will be necessary even in the correlative efforts.

All remaining quantities of the G agents, EA materials, and related substances have been destroyed by hydrolysis in strongly alkaline Chlorox and 15% KOH in 50/50 v/v ethanol-water solutions. HD was similarly treated, except that only Chlorox was employed. All materials and equipment, including the storage refrigerator, have been decontaminated so that no safety hazard remains. Gas masks and atropine sulfate syringes have been stored subject to recall by Edgewood Arsenal.

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APPENDIX

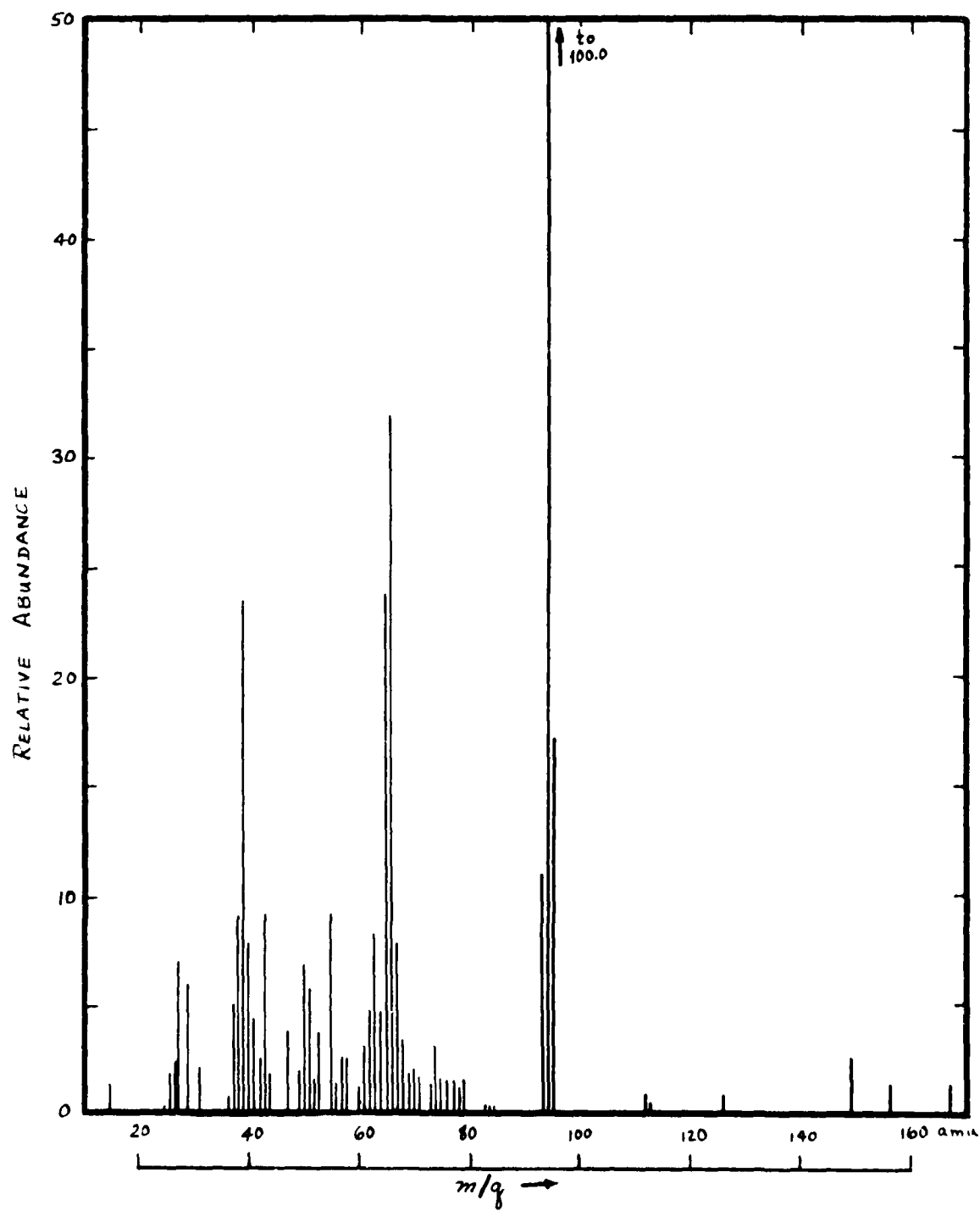


Figure 1. Mass spectrum of triphenyl phosphite. (7 eV).

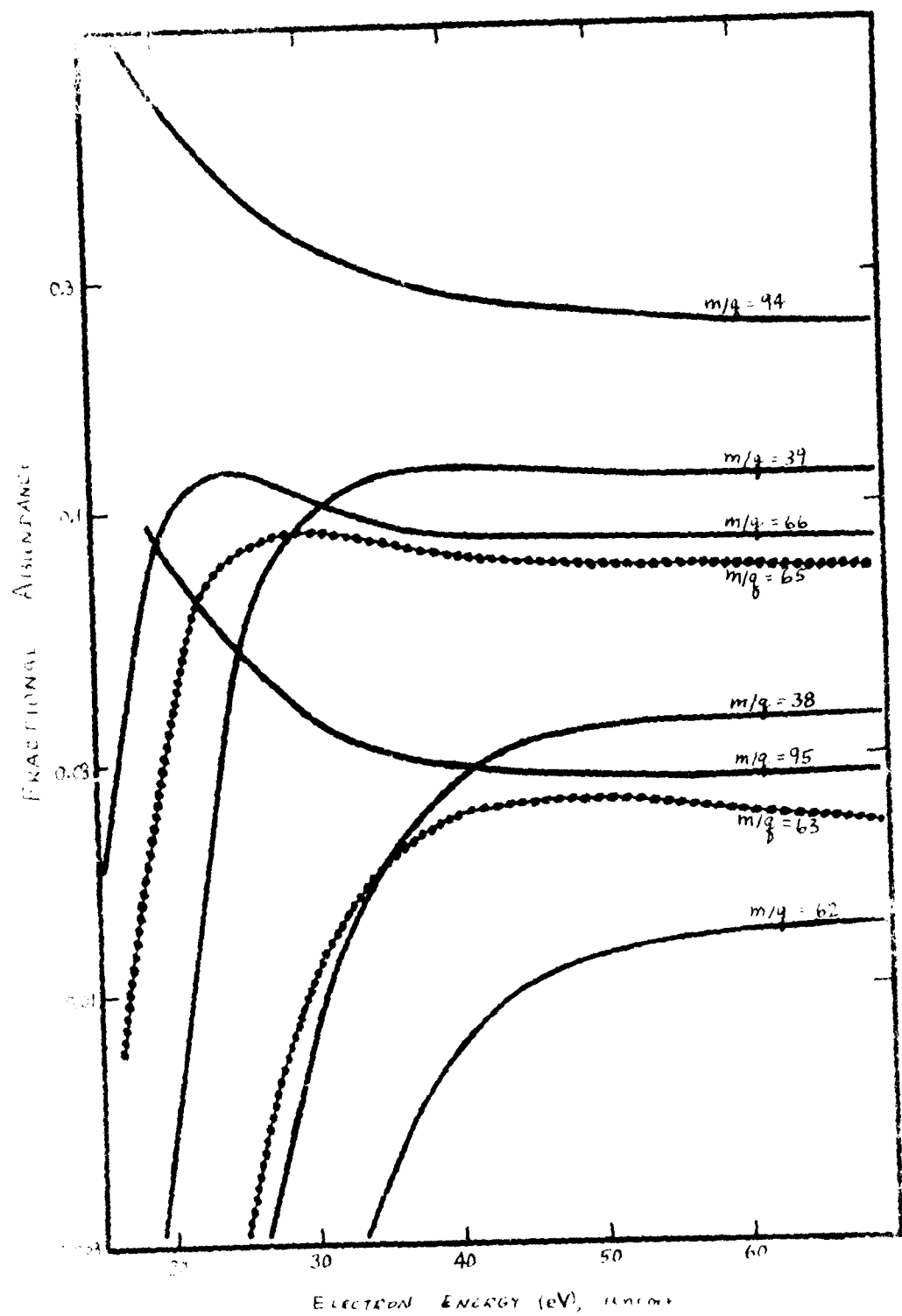


FIGURE 1. IONOSPHERIC DATA FOR THE IONOSPHERE

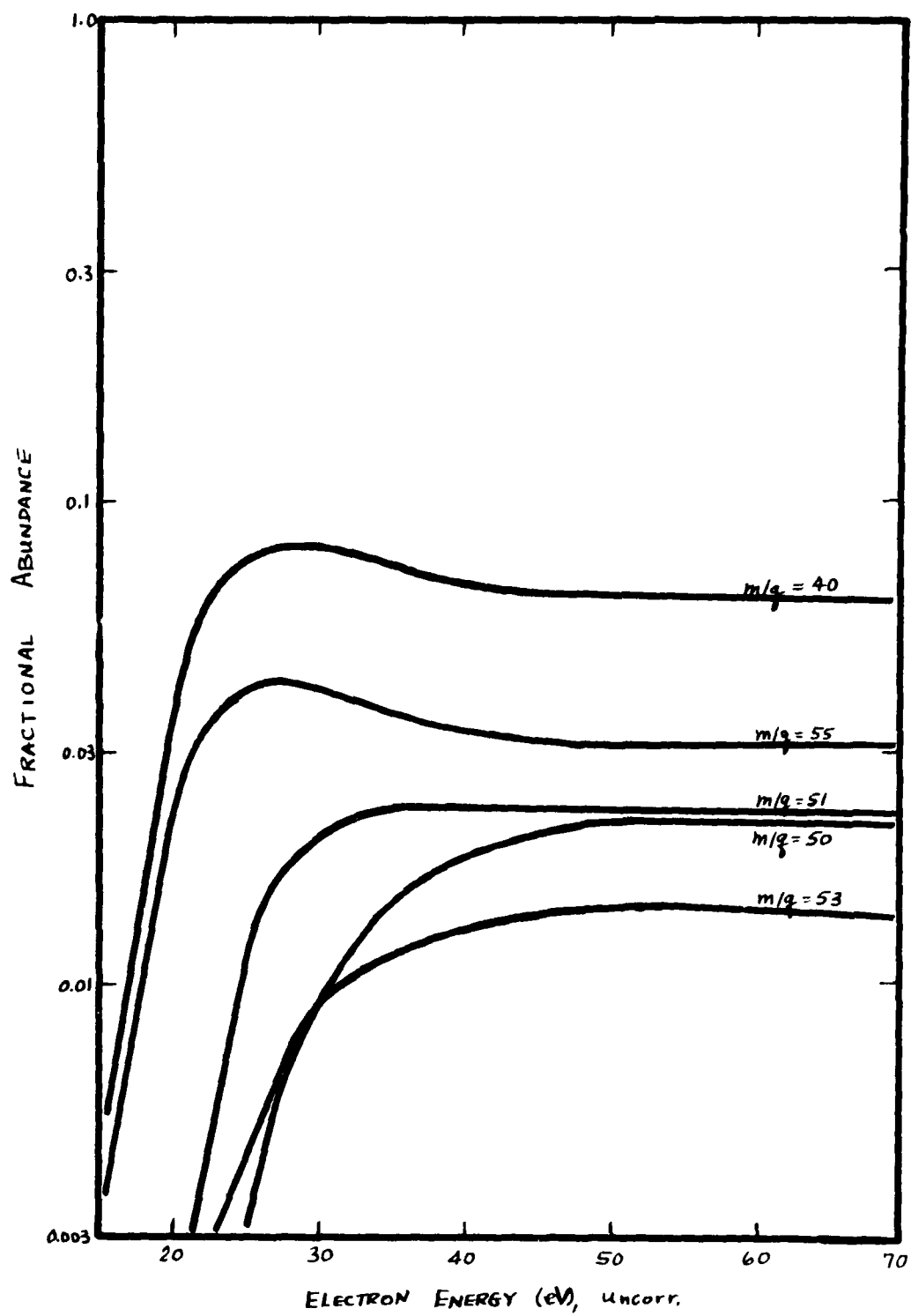


Figure 3. Logarithmic Glancegram for Triphenylborohide ion.

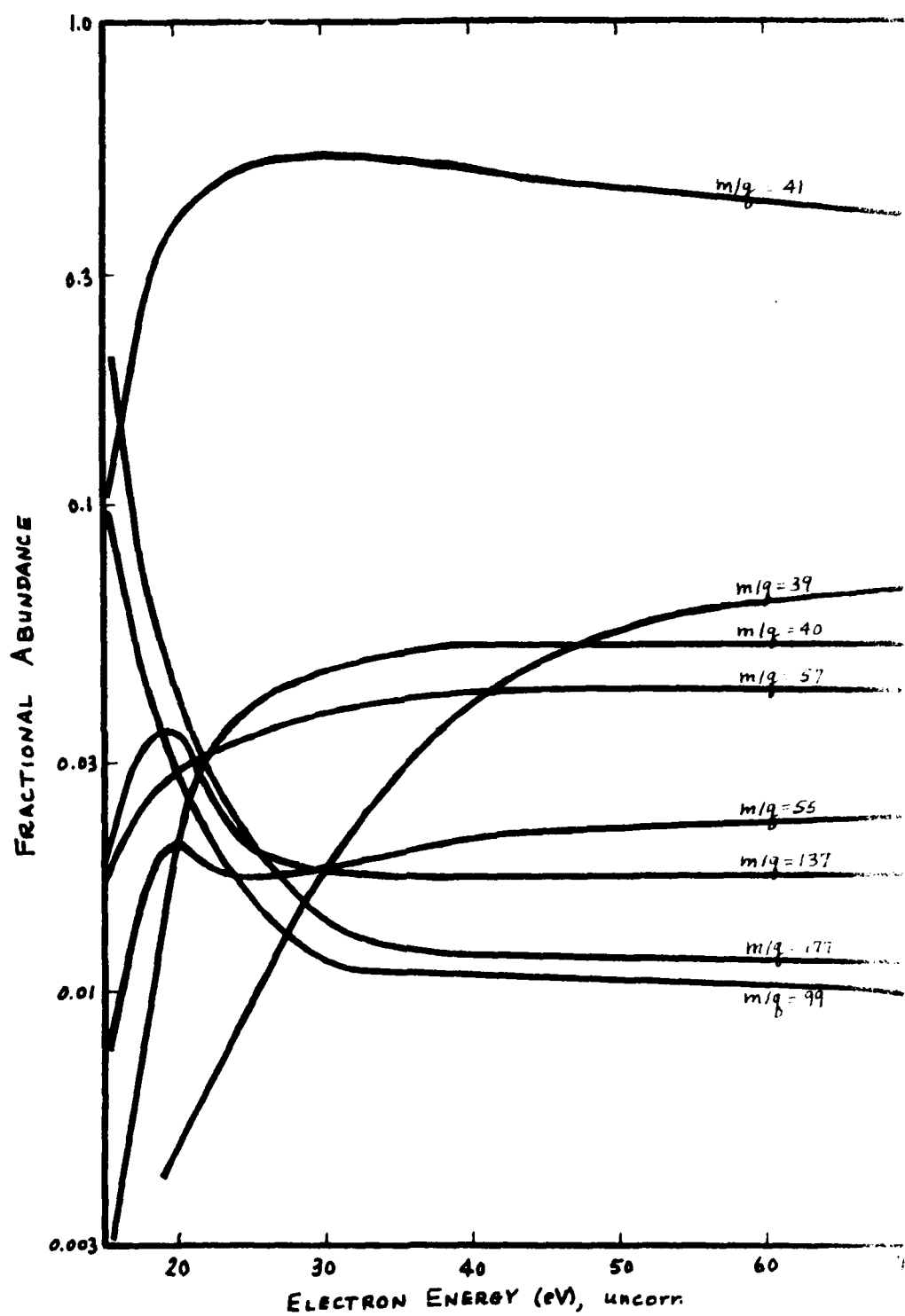


Figure 4. Logarithmic Clistogram for Triallyl Borate.

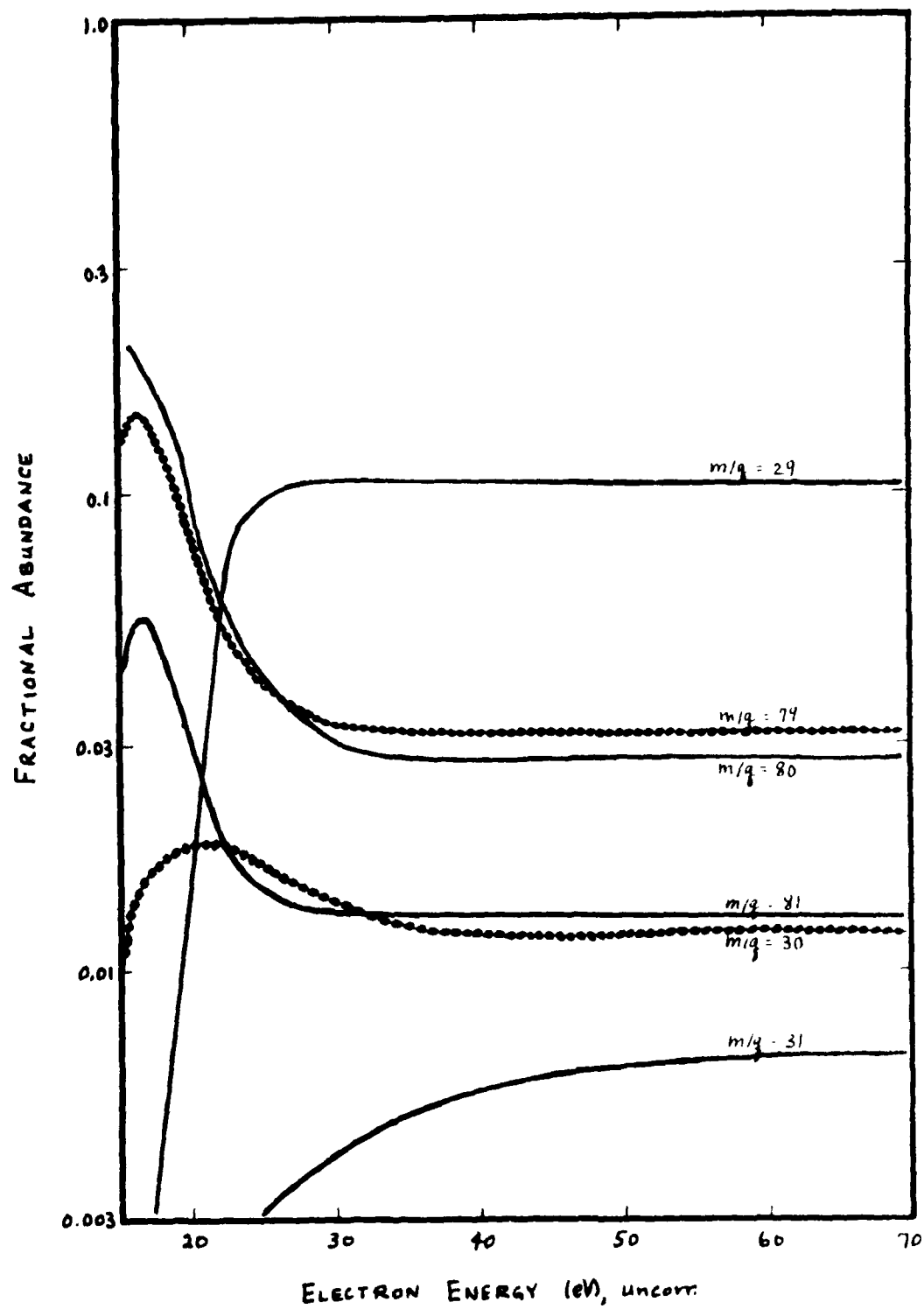


Figure 5. Logarithmic plot of fractional abundance vs. electron energy.

Table 1. Mass Spectrum and Appearance Potentials of the Principal Positive Ions formed from Trimethyl Phosphorothionate.²

m/e	70 eV Relative Abundance	Appearance Potential (eV)	Probable Process		ΔH _{ion} (KJ/mole)
156	27.5	9.0 ± 0.2	SP(OCH ₃) ₃	→ SP(OCH ₃) ₃ ⁺	8
126	19.5	11.5 ± 0.2		→ HSP(OCH ₃) ₂ ⁺ + CH ₂ O	87
125	10.0	13.3 ± 0.4		→ SP(OCH ₃) ₂ ⁺ + CH ₂ O + H	78
93	100.0	12.8 ± 0.3		→ P(OCH ₃) ₂ ⁺ + CH ₂ O + SH	88
79	11.0	15.5 ± 0.3	{		70
			→ PO ₃ ⁺ + 2CH ₃ + CH ₃ S		
			→ CH ₃ OPOH ⁺ + CH ₂ S + CH ₃ O		155
63	17.0	16.2 ± 0.3		→ PS ⁺ + ?	
47	19.6	17.3 ± 0.3		→ PO ⁺ + ?	
45	5.4	15.9 ± 0.3		→ CHS ⁺ + ?	
31	14.7	16.0 ± 0.3		→ OCH ₃ ⁺ + ?	
30	2.2	13.1 ± 0.2		→ CH ₂ O ⁺ + ?	
29	11.0	17.0 ± 0.3		→ CHO ⁺ + ?	
15	4.2	18.9 ± 0.5		→ CH ₃ ⁺ + ?	

Source: Applied Chemistry, 1964, 10, 100.

Table 2. Mass Spectrum and Appearance Potentials for the Principal Positive Ions Observed from Triphenyl Phosphite.^a

m/q	70 eV Relative Abundance	Appearance Potential (eV)	Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
167	1.4			
156	1.4			
149	2.6			
94	100.0	8.2 ± 0.2 ^b	$\text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}^+$	
66	32.0	13.1 ± 0.2	$\rightarrow \text{C}_5\text{H}_6^+ + \text{CO}$	
65	23.7	14.4 ± 0.2	$\rightarrow \text{C}_5\text{H}_5^+ + \text{CO} + \text{H}$	
40	7.8	15.2 ± 0.2	$\rightarrow \text{C}_3\text{H}_4^+ + ?$	
39	23.3	17.4 ± 0.2	$\rightarrow \text{C}_3\text{H}_3^+ + ?$	

a) Estimated $\Delta H_f[\text{P}(\text{OC}_6\text{H}_5)_3] = -78$ kcal/mole.

b) Known ionization potential of phenol (by photoionization) is 8.50 eV. (9)

Table 3. Mass Spectrum and Appearance Potentials of the Principal Positive Ions formed from Diallyl Phosphite.

m/q	70 eV Relative Abundance	Appearance Potential (eV)	Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
121	36.5	10.6 ± 0.2	$(C_3H_5O)_2POH \rightarrow C_3H_5OPO_2H^+ + C_3H_5$	59
83	8.7	11.0 ± 0.3	$\rightarrow H_4PO_3^+ + C_3H_3 + C_3H_4$	-28
80	22.8	10.4 ± 0.2	$\rightarrow HOPO_2^+ + 2C_3H_5$	23
79	9.5	11.2 ± 0.2	$\rightarrow PO_3^+ + C_3H_5 + C_3H_4 + H_2$	28
58	25.0	11.0 ± 0.5	$\rightarrow C_3H_5OH^+ + ?$	
57	69.8	11.5 ± 0.3	$\rightarrow C_3H_5O^+ + ?$	
55	10.9	11.7 ± 0.2	$\rightarrow C_3H_3O^+ + ?$	
41	100.0	13.9 ± 0.2	$\rightarrow C_3H_5^+ + ?$	
39	54.5	16.2 ± 0.3	$\rightarrow C_3H_3^+ + ?$	

a) Estimated $\Delta H_f[(C_3H_5O)_2POH] = -153$ kcal/mole.

Table 4. Mass Spectrum and Appearance Potentials of the Principal Positive Ions formed from Diallyl Allylphosphonate.^a

m/z	7 eV Relative Abundance	Appearance Potential (eV)	Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
161	100	10.4 ± 0.2	$(\text{C}_3\text{H}_5\text{O})_2\text{PO}(\text{C}_3\text{H}_5) \rightarrow \text{C}_3\text{H}_5\text{OPO}_2(\text{C}_3\text{H}_5)^+ + \text{C}_3\text{H}_5$	70
123	6.2	10.9 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{P}(\text{OH})_3^+ + \text{C}_3\text{H}_3 + \text{C}_3\text{H}_4$	-16
101	13.3	11.0 ± 0.2	$\rightarrow \text{PO}_2(\text{OH})(\text{C}_3\text{H}_5)^+ + \text{C}_3\text{H}_4 + \text{C}_3\text{H}_5$	39
115	12.8	12.2 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{PO}_2\text{H}^+ + \text{C}_3\text{H}_5 + \text{C}_3\text{H}_4\text{O}$	134
91	17.5	11.6 ± 0.2	$\rightarrow ?$	
93	26.5	11.1 ± 0.2	$\rightarrow ?$	
95	37.2	11.9 ± 0.2	$\rightarrow ?$	
103	11.3	12.5 ± 0.2	$\rightarrow \text{H}_4\text{PO}_2^+ + ?$	
105	16.5	11.0 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{OH}^+ + ?$	
127	60.1	12.5 ± 0.3	$\rightarrow \text{C}_3\text{H}_5\text{O}^+ + ?$	
129	10.5	13.8 ± 0.2	$\rightarrow \text{C}_3\text{H}_4\text{O}^+ + ?$	
141	100.0	14.6 ± 0.5	$\rightarrow \text{C}_3\text{H}_5^+ + ?$	
143	1.00	17.9 ± 0.3	$\rightarrow \text{C}_3\text{H}_3^+ + ?$	

^a Estimated $\Delta H_f[(\text{C}_3\text{H}_5\text{O})_2\text{PO}(\text{C}_3\text{H}_5)] = -138 \text{ kcal/mole.}$

Table 5. Mass Spectrum and Appearance Potentials of the Principal Positive Ions Formed from Triallyl Phosphite.^a

m/q	Relative Abundance	70 eV Appearance Potential (eV)	Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
161	4.3	9.15 ± 0.15	$(\text{C}_3\text{H}_5\text{O})_3\text{P} \rightarrow (\text{C}_3\text{H}_5\text{O})_2\text{PO}^+ + \text{C}_3\text{H}_5$	65
173	1.8	10.1 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{OPO}_2\text{H}_3^+ + \text{C}_3\text{H}_3 + \text{C}_3\text{H}_4$	-10
181	4.0	10.5 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{PO}_3\text{H}^+ + \text{C}_3\text{H}_5 + \text{C}_3\text{H}_4$	51
195	3.2	11.0 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{OPOH}^+ + \text{C}_3\text{H}_4\text{O} + \text{C}_3\text{H}_5$	131
21	14.8	10.8 ± 0.2	$\rightarrow ?$	
80	9.5	10.2 ± 0.2	$\rightarrow ?$	
79	13.1	10.4 ± 0.2	$\rightarrow ?$	
67	5.9	11.2 ± 0.2	$\rightarrow \text{H}_4\text{PO}_2^+ + ?$	
57	9.0	11.9 ± 0.2	$\rightarrow \text{C}_3\text{H}_5\text{O}^+ + ?$	
55	5.1	12.2 ± 0.2	$\rightarrow \text{C}_3\text{H}_3\text{O}^+ + ?$	
42	6.3	11.9 ± 0.2	$\rightarrow \text{C}_2\text{H}_2\text{O}^+ + ?$	
41	100.0	13.3 ± 0.2	$\rightarrow \text{C}_3\text{H}_5^+ + ?$	
39	21.3		$\rightarrow \text{C}_3\text{H}_3^+ + ?$	

^a) Estimated $\Delta H_f[(\text{C}_3\text{H}_5\text{O})_3\text{P}] = -114$ kcal/mole.

Table 6. Mass Spectrum and Appearance Potentials for the Principal Positive Ions Formed from Triallyl Phosphate.^a

m/z	Relative Abundance	Appearance Potential (eV)	Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
177	3.8	10.2 $\pm$ 0.3	$(C_3H_5O)_3PO \rightarrow (C_3H_5O)_2PO^+ + C_3H_5$	15
157	4.4	10.2 $\pm$ 0.3	$\rightarrow C_3H_5OPO_3H^+ + C_3H_4 + C_3H_5$	16
69	2.1			
51	2.2			
20	6.2	10.9 $\pm$ 0.2	$\rightarrow H_2OPO_2^+ + C_3H_4O + 2C_3H_5$	22
70	7.0			
67	10.0	11.7 $\pm$ 0.2	$\rightarrow C_3H_5O^+ + ?$	
65	1.6			
41	100.0	11.3 $\pm$ 0.2	$\rightarrow C_3H_5^+ + ?$	
40	12.7		$\rightarrow C_3H_4^+ + ?$	
39	16.5	15.0 $\pm$ 0.3	$\rightarrow C_3H_3^+ + ?$	
31	1.7			
30	2.5			
29	26.5			

^a Data from [10, 11].

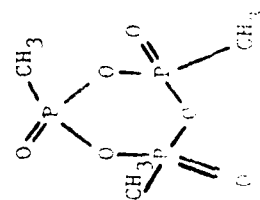
Table 7. Mass Spectrum and Appearance Potentials of the Principal Positive Ions Formed from Diphenyl Phosphite.^a

m/q	Relative Abundance	Appearance Potential (eV)	Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
167	0.3			
156	0.6			
149	1.4			
95	19.4			
94	100.0	8.5 $\pm$ 0.2	$\text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}^+$	
66	27.8	13.1 $\pm$ 0.2	$\rightarrow \text{C}_5\text{H}_6^+ + \text{CO}$	
65	19.3	14.5 $\pm$ 0.2	$\rightarrow \text{C}_5\text{H}_5^+ + \text{CO} + \text{H}$	
63	6.3	19.4 $\pm$ 0.3	$\rightarrow \text{C}_5\text{H}_3^+ + ?$	
55	6.3	13.9 $\pm$ 0.2	$\rightarrow \text{C}_3\text{H}_3\text{O}^+ + ?$	
50	5.3	18.9 $\pm$ 0.3	$\rightarrow ?$	
40	10.2	14.9 $\pm$ 0.2	$\rightarrow \text{C}_3\text{H}_4^+ + ?$	
39	18.0	17.6 $\pm$ 0.3	$\rightarrow \text{C}_3\text{H}_3^+ + ?$	
38	12.7	20.4 $\pm$ 0.9	$\rightarrow \text{C}_3\text{H}_2^+ + ?$	
29	7.0		$\rightarrow ?$	
27.5	7.7		$\rightarrow \text{C}_5\text{H}_5^{++} + \text{CO} + \text{H}$	

a) Estimated $\Delta H_f[(\text{C}_6\text{H}_5\text{O})_2\text{POH}] = -129$ kcal/mole.

Table 1. Summary of Mass Spectrometric Studies and Findings for Cyanophosphorus Compounds.

Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{CH}_3\text{-P-Cl} \\ \\ \text{Cl} \end{array}$	Parent ion is seen; other ions as well; nothing particularly unusual about mass spectrum.	I.P. = 9.49 eV; A.P.'s increase in a rather normal fashion.	$\begin{array}{c} 101^+ \rightarrow 66^+ \\ 116^+ \rightarrow 81^+ \rightarrow 45^+ \\ \quad \quad \quad \nearrow \quad \searrow \\ \quad \quad 46^+ \quad 44^+ \\ \quad \quad \quad \nearrow \quad \searrow \\ \quad \quad 15^+ \end{array}$	None observed. (TOF)	Cl^- is the only ion observed.
$\begin{array}{c} \text{O} \\ \\ \text{Cl-P-Cl} \\ \\ \text{Cl} \end{array}$	Parent ion is observed. Others about as anticipated.	I.P. = 11.4 eV (EC); A.P.'s increase in a rather normal manner.	$\begin{array}{c} 66^+ \\ \uparrow \\ 152^+ \rightarrow 117^+ \rightarrow 82^+ \\ \quad \quad \quad \nearrow \quad \searrow \\ \quad \quad 47^+ \end{array}$	None observed. (MS-9)	POCl_2^- , PO^- and Cl^- were found.
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-P-Cl} \\ \\ \text{Cl} \end{array}$	Trimer species was observed; apparently formed as a result of hydrolysis; in "hot source". MW corresponds to:	I.P. = ca. 11.5 eV (EC); A.P.'s increase in a rather normal manner.	Very difficult to interpret. However, $234^+ \rightarrow 219^+$	Have not been studied.	Have not been studied.



Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{S} \\ \parallel \\ \text{CH}_3\text{-P-Cl} \\ \\ \text{Cl} \end{array}$	Parent ion is observed; Others about as expected.	I.P. = 9.95 eV; A.P.'s increase in about the normal manner.		None observed. (TOF)	Cl ⁻ is most intense; also observed PSCl ₂ ⁻ and PC ⁻ ions.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{CH}_3 \end{array}$	Parent ion is observed.	I.P. = 10.48 eV; (10.43 on MS-9); low A.P. for 94 ⁺ (formed by loss of CH ₂ O). Otherwise, about normal.		$\begin{array}{l} 124^+ \xrightarrow{-\text{CH}_2\text{O}} 94^+ \text{ (RMU-6E) (MS-9)} \\ 94^+ \xrightarrow{-\text{CH}_3} 79^+ \text{ (RMU-6E) (MS-9)} \\ 109^+ \xrightarrow{-\text{CH}_2\text{O}} 79^+ \text{ (RMU-6E) (MS-9)} \\ 93^+ \xrightarrow{-\text{CH}_2\text{O}} 63^+ \text{ (RMU-6E) (MS-9)} \\ 79^+ \xrightarrow{-\text{CH}_3\text{OH}} 47^+ \text{ (TOF)} \end{array}$	Have not been studied.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	Parent ion is observed; remainder of spectrum is about as anticipated.	I.P. = 10.77 eV (10.73 with MS-9); A.P.'s increase in a rather normal manner.		$\begin{array}{l} 140^+ \xrightarrow{-\text{CH}_2\text{O}} 110^+ \text{ (MS-9)} \\ 110^+ \xrightarrow{-\text{CH}_2\text{O}} 80^+ \text{ (MS-9)} \\ 109^+ \xrightarrow{-\text{CH}_2\text{O}} 79^+ \text{ (MS-9)} \\ 109^+ \xrightarrow{-\text{CH}_3} 93^+ \text{ (TOF)} \end{array}$	Have not been studied.

Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{S} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	Parent ion is observed; 93 ⁺ is base peak; some indication of isomerization of ionic species to thiolate structures.	I.P. = 9.2 eV (EC) by TOF; A.P.'s are found to increase in a rather normal manner.	Rather difficult to interpret; however,	$\begin{array}{l} -\text{CH}_2\text{O} \rightarrow 126^+ \\ -\text{SH} \rightarrow 93^+ \\ -\text{CH}_2\text{S} \rightarrow 79^+ \\ -\text{CH}_2\text{O} \rightarrow 80^+ \\ -\text{CH}_2\text{O} \rightarrow 79^+ \\ -\text{CH}_2\text{O} \rightarrow 63^+ \end{array}$ (RMU-6E)	Have not been studied.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	Parent ion is observed.	I.P. = 10.06 eV (10.02 on MS-9); A.P.'s increase in a normal manner.		$\begin{array}{l} -\text{C}_2\text{H}_3 \rightarrow 155^+ \\ -\text{C}_2\text{H}_4 \rightarrow 153^+ \\ -\text{C}_2\text{H}_4 \rightarrow 139^+ \\ -\text{C}_2\text{H}_4\text{O} \rightarrow 138^+ \\ -\text{C}_2\text{H}_4 \rightarrow 127^+ \\ -\text{C}_2\text{H}_4 \rightarrow 125^+ \\ -\text{C}_2\text{H}_4 \rightarrow 111^+ \\ -\text{C}_2\text{H}_4 \rightarrow 99^+ \\ -\text{H}_2\text{O} \rightarrow 81^+ \\ -\text{C}_2\text{H}_4 \rightarrow 82^+ \\ -\text{C}_2\text{H}_3\text{O} \rightarrow 83^+ \end{array}$ (MS-9)	Have not been studied.

Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$ \begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{C}_2\text{H}_5 \end{array} $	Parent ion is observed.	I.P. = 10.39; A.P. of 94 ⁺ is low; C ₂ H ₄ and C ₂ H ₄ O are products here.		$ \begin{array}{l} 166^+ \xrightarrow{-\text{C}_2\text{H}_3} 139^+ \\ 166^+ \xrightarrow{-\text{C}_2\text{H}_4} 138^+ \\ 166^+ \xrightarrow{-\text{C}_2\text{H}_4\text{O}} 122^+ \\ 138^+ \xrightarrow{-\text{C}_2\text{H}_3} 111^+ \\ 139^+ \xrightarrow{-\text{C}_2\text{H}_4} 111^+ \\ 166^+ \xrightarrow{-\text{C}_2\text{H}_5\text{O}} 121^+ \\ 111^+ \xrightarrow{-\text{H}_2\text{O}} 93^+ \\ 109^+ \xrightarrow{-\text{H}_2\text{O}} 91^+ \\ 122^+ \xrightarrow{-\text{C}_2\text{H}_4} 94^+ \\ 121^+ \xrightarrow{-\text{C}_2\text{H}_4} 93^+ \\ 122^+ \xrightarrow{-\text{C}_2\text{H}_5} 93^+ \\ 110^+ \xrightarrow{-\text{C}_2\text{H}_4} 82^+ \\ 93^+ \xrightarrow{-\text{C}_2\text{H}_4} 65^+ \\ 29^+ \xrightarrow{-\text{H}_2} 27^+ \\ 65^+ \xrightarrow{-2(\text{OH})} 31^+ \end{array} $ (RMU-6E)	Have not been studied.

Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{S} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	Parent ion is observed.	I.P. = 8.41 eV; low appearance potential for 93 ⁺ ; have to postulate S ⁻ formation (?); Otherwise the spectrum is normal.		Studies not completed.	No negative ions are observed.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{CH}_2\text{COOCH}_3 \\ \\ \text{OCH}_3 \end{array}$	No parent ion is observed; 99 ⁺ also is not present; the P-CH ₂ COOCH ₃ bond is rather weak.	I.P. (estimated) = ca. 10.5-11.0 eV; at least four low energy A.P.'s are noted: 110 ⁺ , 109 ⁺ , 94 ⁺ , and 80 ⁺ .	Very difficult to interpret.	Studies not completed.	Have not been studied.
$\begin{array}{c} \text{EA 1232} \\ \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{CH}_3 \\ \\ \text{F} \end{array}$	Very small m/q = 99 peak; parent ion is present; CH ₃ -O bond is stronger than for alkoxy groups in other G agents.	I.P. = 11.7 eV; A.P. (82 ⁺) = 12.0 eV; A.P.'s of organic fragments not very high, indicating low fragmentation.		$\begin{array}{l} -\text{CH}_2\text{O} \rightarrow 82^+ \\ -\text{CH}_3 \rightarrow 67^+ \end{array}$ (TOF)	Low intensity F ⁻ observed.
$\begin{array}{c} \text{EA 1207} \\ \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{CH}_3 \\ \\ \text{F} \end{array}$	No parent ion; fair-sized (parent-H) ⁺ ; also there is a fair-sized (parent-CH ₃) ⁺ ion.	I.P. estimated = ca. 11.5-12.0 eV; A.P. (99 ⁺) is lower than the I.P. (125 ⁺); some processes are quite energetic.	Four ions show maxima: 99⁺, 82⁺, 111⁺ and 125⁺; The 99⁺ acts as a pseudo-parent.	$\begin{array}{l} -\text{C}_2\text{H}_5 \rightarrow 99^+ \\ -\text{CH}_2\text{O} \rightarrow 81^+ \\ -\text{OH} \rightarrow 82^+ \\ -\text{CH}_3 \rightarrow 67^+ \end{array}$ (TOF)	Low intensity F ⁻ observed.

Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
GA $ \begin{array}{c} \text{CH}_3 \\ \\ \text{O} \\ \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{N} \\ \quad \\ \text{CH}_3 \quad \text{CN} \end{array} $	Contains parent ion; many p-contg. ions do <u>not</u> contain CN group; most of the possible combinations of the ions are observed; base peak is m/q = 133; considerable impurities present; m/q = 70 remains unexplained; no m/q = 99.	I.P. = 9.44 eV; A.P. (70) = 11.65 eV; A.P.'s of m/q = 44 and 45 are low; they probably come from m/q = 70.	Clastogram including m/q = 70, 44 and 45 does <u>not</u> make much sense; In clastogram without these ions, the parent ion (162 ⁺) behaves as expected; m/q = 133, 108 and 123 show maxima; process suggested is: $ \begin{array}{c} 134^+ \quad 65^+ \\ \swarrow \quad \searrow \\ 162^+ \quad 133^+ \quad 108^+ \end{array} $	Have not been studied.	Low intensity CN ⁻ observed.
GB $ \begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ \text{HC}-\text{O}-\text{P}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{F} \end{array} $	No parent ion; fair sized (parent-CH ₃) ⁺ ion; very small 67 ⁺ and 82 ⁺ ; not as much hydrogen rearrangement as with other compounds.	I.P. (estimated) = ca. 12. eV; A.P. of 99 ⁺ is lower than that for 125 ⁺ .	$ \begin{array}{c} 125^+ \rightarrow 99^+ \\ \swarrow \quad \searrow \\ 140^+ \quad 81^+ \\ \swarrow \quad \searrow \\ 42^+ \rightarrow 41^+ \rightarrow 39^+ \end{array} $	Have not been studied.	In Melpar report many negative ions were listed; we have not been able to repeat these data; only observe a low intensity F ⁻ ion.
GD (EA 1210) $ \begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \quad \text{O} \\ \quad \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{O}-\text{P}-\text{CH}_3 \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{F} \\ \text{H}_3\text{C} \end{array} $	No parent ion; the base peak is 41 ⁺ ; a large 126 ⁺ ion is (parent-C ₄ H ₉) ⁺ ; also a large abundance of organic fragments.	I.P. (estimated) = ca. 12. eV; organic fragments involve highly energetic processes.	$ \begin{array}{c} 126^+ \rightarrow 99^+ \rightarrow 82^+ \\ \swarrow \quad \searrow \\ 182^+ \quad 69^+ \rightarrow 67^+ \\ \swarrow \quad \searrow \\ 84^+ \rightarrow 41^+ \rightarrow 39^+ \end{array} $	Have not been studied.	F ⁻ ion is of low intensity.

Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{GF} \\ \text{O} \\ \parallel \\ \text{C}_3\text{H}_5\text{O}-\text{P}-\text{CH}_3 \\ \\ \text{F} \end{array}$	No parent ion; very weak (R-O) bond; essentially no fragment ions above $m/q = 99$; no ion observed with cyclohexyl group attached to a P-containing fragment.	I.P. (estimated) = ca. 11. eV; A.P. for 67^+ is low; the A.P.'s of the organic fragments are not very great.	$\begin{array}{c} 99^+ \rightarrow 82^+ \rightarrow 67^+ \\ 180^+ \rightarrow 54^+ \\ 83^+ \rightarrow 41^+ \rightarrow 39^+ \end{array}$	$\begin{array}{c} -\text{OH} \\ 99^+ \rightarrow 82^+ \\ -\text{CH}_3 \\ 82^+ \rightarrow 67^+ \\ (\text{TOF}) \end{array}$	F^- ion of low intensity.
$\begin{array}{c} \text{C}_3\text{H}_5\text{O}-\text{P}-\text{OH} \\ \\ \text{OC}_3\text{H}_5 \end{array}$	Parent ion is not observed; base peak is 41^+ , 57^+ is also very abundant; gross fragmentation may be thermal in origin.	A.P. for 121^+ = 10.6 eV; suggests I.P. = 10.0 eV, approximately.	$\begin{array}{c} 121^+ \rightarrow 80^+ \\ 162^+ \rightarrow 81^+ \rightarrow 79^+ \\ 122^+ \rightarrow 83^+ \end{array}$	Have not been studied.	Have not been studied.
$\begin{array}{c} \text{C}_3\text{H}_5\text{O}-\text{P}-\text{OC}_3\text{H}_5 \\ \\ \text{OC}_3\text{H}_5 \end{array}$	Parent ion is not observed; base peak is 41^+ ; gross fragmentation may be thermal in origin; sample tends to polymerize in inlet system.	A.P. for 161^+ = 9.15 eV (EC); this suggests I.P. = approximately 8.8 eV; A.P.'s of 79^+ , 80^+ and 81^+ are surprisingly low.	$\begin{array}{c} 105^+ \\ 161^+ \rightarrow 121^+ \rightarrow 81^+ \\ 202^+ \rightarrow 120^+ \rightarrow 80^+ \\ 41^+ \rightarrow 39^+ \end{array}$	$\begin{array}{c} -\text{C}_3\text{H}_4 \\ 161^+ \rightarrow 121^+ \\ (\text{TOF}) \end{array}$ Probably many more may be observed with a magnetic instrument.	Have not been studied.

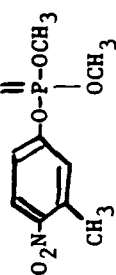
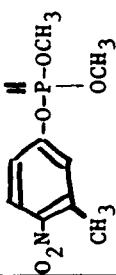
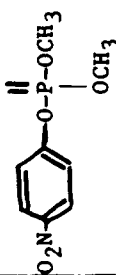
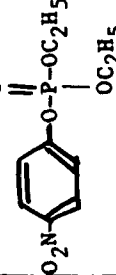
Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{O} \\ \\ \text{C}_3\text{H}_5\text{O-P-C}_3\text{H}_5 \\ \\ \text{OC}_3\text{H}_5 \end{array}$	Parent ion is not observed; base peak is 41 ⁺ ; 57 ⁺ is also very abundant; gross fragmentation may be thermal in origin.	A.P. for 161 ⁺ = 10.4 eV (EC) this suggests I.P. = approximately 10.0 eV; A.P.'s of 79 ⁺ , 80 ⁺ and 81 ⁺ are surprisingly low.	$\begin{array}{c} 105^+ \quad 81^+ \\ \uparrow \quad \uparrow \\ 202^+ \rightarrow 161^+ \rightarrow 121^+ \\ \downarrow \quad \downarrow \\ 120^+ \rightarrow 80^+ \\ \downarrow \quad \downarrow \\ 79^+ \end{array}$	Have not been studied.	Have not been studied.
$\begin{array}{c} \text{O} \\ \\ \text{C}_3\text{H}_5\text{O-P-OC}_3\text{H}_5 \\ \\ \text{OC}_3\text{H}_5 \end{array}$	Parent ion is not observed; 41 ⁺ is the base peak.	A.P. of 177 ⁺ 10.2 eV (EC); this suggests I.P. = approximately 9.8 eV.	$\begin{array}{c} 177^+ \rightarrow 137^+ \\ \swarrow \quad \searrow \\ 218^+ \quad 80^+ \\ \swarrow \quad \searrow \\ 99^+ \end{array}$	Have not been studied.	Have not been studied.
$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{-P-C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array}$	Parent ion is observed; base peak is (P-1) ⁺ ; fragmentation occurs through phenyl and H losses, with and without oxygen loss; p ⁺⁺ also seen.	Have not been studied.	$\begin{array}{c} 277^+ \rightarrow 199^+ \rightarrow 152^+ \\ \swarrow \quad \searrow \\ 278^+ \rightarrow 185^+ \rightarrow 183^+ \\ \swarrow \quad \searrow \\ 77^+ \rightarrow 51^+ \end{array}$	$\begin{array}{l} -\text{H} \rightarrow 277^+ \\ -\text{C}_6\text{H}_5 \rightarrow 199^+ \\ -\text{PO} \rightarrow 152^+ \\ -\text{H}_2 \rightarrow 183^+ \\ -\text{C}_2\text{H}_2 \rightarrow 51^+ \end{array}$ (RMU-6E)	Have not been studied.

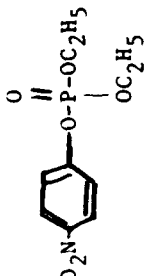
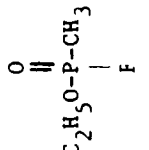
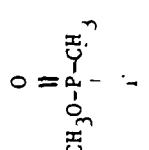
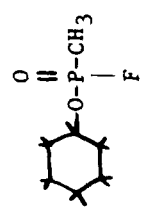
Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$\begin{array}{c} \text{C}_6\text{H}_5\text{O-P-OH} \\ \\ \text{OC}_6\text{H}_5 \end{array}$	Parent ion is not observed; base peak is 94^+ ion; mass spectrum is very suggestive of thermal decomposition to yield mostly phenol.	A.P. of 94^+ = 8.5 eV (EC); I.P. of phenol = 8.50 eV by P.I.; thus, 94^+ is $\text{C}_6\text{H}_5\text{OH}^+$, apparently formed by simple ionization of phenol.	Not too meaningful, since apparently largely due to phenol from thermal decomposition.	Have not been studied.	Have not been studied.
$\begin{array}{c} \text{C}_6\text{H}_5\text{O-P-OC}_6\text{H}_5 \\ \\ \text{OC}_6\text{H}_5 \end{array}$	Parent ion is not observed; base peak is 94^+ ion; mass spectrum is very suggestive of thermal decomposition to yield mostly phenol; small amounts of 149^+ , 156^+ , and 167^+ observed.	A.P. of 94^+ = 8.8 ± 0.2 eV (EC); I.P. of phenol = 8.50 eV by P.I.; thus, 94^+ is $\text{C}_6\text{H}_5\text{OH}^+$, apparently formed by simple ionization of phenol.	Not too meaningful, since apparently largely due to phenol from thermal decomposition.	Have not been studied.	 most intense at $m/q = 93$; also $(\text{C}_6\text{H}_5\text{O})\text{PO}^-$ at $m/q = 233$ observed; others at $m/q = 133$ and 217.

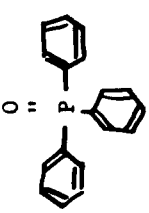
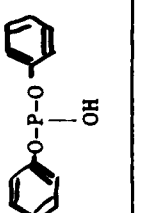
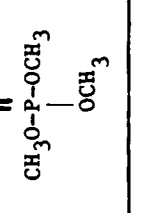
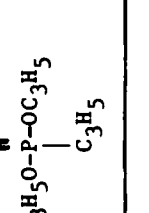
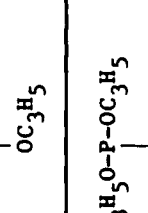
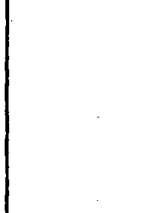
Formula	Mass Spectra	Energetics	Clastograms	Metastables	Negative Ions
$C_6H_5NO_2$	Both parent positive and negative ions observed; base peak in negative ion spectrum is NO_2^- ; base peak in positive ion spectrum is $C_6H_5^+$.	Have not been studied.	Have not been studied.	$123^+ \rightarrow 93^+$ (-NO) $123^+ \rightarrow 77^+$ (-NO ₂) $123^+ \rightarrow 76^+$ (-HNO ₂) $107^+ \rightarrow 93^+$ (-N) $107^+ \rightarrow 77^+$ (-NO) $93^+ \rightarrow 65^+$ (-CO) $65^+ \rightarrow 39^+$ (-C ₂ H ₂) $39^+ \rightarrow 37^+$ (-H ₂) $77^+ \rightarrow 51^+$ (-C ₂ H ₂) $75^+ \rightarrow 51^+$ (-C ₂) $123^+ \rightarrow 30^+$ (-C ₆ H ₅ O) $77^+ \rightarrow 24^+$ (-C ₄ H ₅) $77^+ \rightarrow 27^+$ (-C ₄ H ₂) $77^+ \rightarrow 50^+$ (-C ₂ H ₃) $76^+ \rightarrow 50^+$ (-C ₂ H ₂) (RMU-6E)	NO_2^- is very intense; $C_6H_5O^-$ also observed along with $C_6H_5NO_2^-$ in rather large yields.

Table 9 A Short Catalog of Mass Spectra of Organophosphorus and Related Compounds.

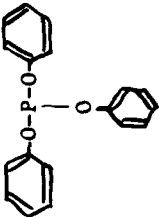
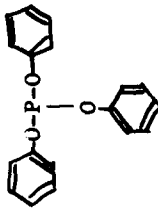
Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
<u>DDVP</u> $\begin{array}{c} \text{O} \\ \\ \text{Cl}-\text{C}-\text{H} \\ \\ \text{C}=\text{C}-\text{O}-\text{P}-\text{OCH}_3 \\ \\ \text{Cl} \quad \text{OCH}_3 \end{array}$	$\frac{109}{102}$	$\frac{185, 1}{33}$	$\frac{19}{27}$	$\frac{145, 1}{11}$	$\frac{220, 2, 4}{41}$	$\frac{41}{41}$	$\frac{60}{2}$				220+ 222+ 224+	10
<u>Metasystox</u> $\begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5-\text{SCH}_2\text{CH}_2-\text{S}-\text{P}-\text{OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	$\frac{88}{112}$	$\frac{60}{59}$	$\frac{109, 10, 11}{20}$	$\frac{142, 3, 4}{19}$	$\frac{19}{11}$	$\frac{59}{9}$	$\frac{75}{7}$	$\frac{230, 1, 2}{7}$	$\frac{45}{6}$	$\frac{125}{5}$	230+ 231+ 232+	10
<u>Malathion</u> $\begin{array}{c} \text{S} \\ \\ \text{C}_2\text{H}_5-\text{OC}-\text{CH}-\text{S}-\text{P}-\text{OCH}_3 \\ \quad \\ \text{C}_2\text{H}_5-\text{OOC}-\text{CH}_2 \quad \text{OCH}_3 \end{array}$	$\frac{173}{111}$	$\frac{127, 8}{91}$	$\frac{125, 6}{89}$	$\frac{93}{73}$	$\frac{158, 9, 60}{63}$	$\frac{99}{30}$	$\frac{55}{28}$	$\frac{143}{20}$	$\frac{43}{19}$	$\frac{79}{18}$	330+ 331+ 332	10
<u>Malathion</u> $\begin{array}{c} \text{S} \\ \\ \text{C}_2\text{H}_5-\text{OOC}-\text{CH}-\text{S}-\text{P}-\text{OCH}_3 \\ \quad \\ \text{C}_2\text{H}_5-\text{OOC}-\text{CH}_2 \quad \text{OCH}_3 \end{array}$	$\frac{29}{49}$	$\frac{173}{120}$	$\frac{127, 8}{97}$	$\frac{125, 6}{61}$	$\frac{93}{54}$	$\frac{158, 9, 60}{52}$	$\frac{99}{22}$	$\frac{27}{17}$	$\frac{63}{16}$	$\frac{47}{16}$	330+ 331+ 332	11

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
<u>Folithion</u> 	$\frac{109, 10, 11}{121.}$	$\frac{277, 8, 9}{106.}$	$\frac{125, 6}{102.}$	$\frac{260, 1, 2}{51.}$	$\frac{79}{38.}$	$\frac{47}{36.}$	$\frac{93}{31.}$	$\frac{63}{19.}$	$\frac{89}{10.}$	$\frac{121}{7.}$	277+ 278+ 279	10
<u>Folithion</u> 	$\frac{125, 6, 7}{121.}$	$\frac{109, 10, 11}{111.}$	$\frac{277, 8}{95.}$	$\frac{260, 1, 2}{60.}$	$\frac{79}{47.}$	$\frac{47}{41.}$	$\frac{93}{32.}$	$\frac{63}{34.}$	$\frac{51}{20.}$	$\frac{52}{17.}$	277+ 278	11
<u>Methyl Parathion</u> 	$\frac{109, 10}{106.}$	$\frac{125}{70.}$	$\frac{263}{52.}$	$\frac{79}{29.}$	$\frac{44}{29.}$	$\frac{47}{26.}$	$\frac{63}{26.}$	$\frac{93}{25.}$	$\frac{15}{15.}$	$\frac{43}{14.}$	263	11
<u>Parathion</u> 	$\frac{109}{100.}$	$\frac{29}{85.}$	$\frac{291}{84.}$	$\frac{97}{72.}$	$\frac{139}{62.}$	$\frac{137}{60.}$	$\frac{40}{49.}$	$\frac{125}{45.}$	$\frac{155}{34.}$	$\frac{43}{30.}$	291	11

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	MW	Ref.
<u>Paralaxan</u> 	$\frac{109.10}{114.}$	$\frac{29}{56.}$	$\frac{149}{47.}$	$\frac{81}{46.}$	$\frac{275}{40.}$	$\frac{139}{37.}$	$\frac{65}{32.}$	$\frac{75}{25.}$	$\frac{63}{25.}$	$\frac{64}{25.}$	275	11
<u>EA 1207</u> 	$\frac{99}{100.}$	$\frac{81}{31.6}$	$\frac{82}{17.2}$	$\frac{111}{15.4}$	$\frac{29}{10.1}$	$\frac{47}{6.8}$	$\frac{83}{6.7}$	$\frac{67}{6.0}$	$\frac{27}{5.6}$	$\frac{15}{4.6}$	126	12
<u>EA 1232</u> 	$\frac{82}{100.0}$	$\frac{67}{43.8}$	$\frac{81}{24.6}$	$\frac{47}{13.9}$	$\frac{15}{13.4}$	$\frac{83}{12.3}$	$\frac{112}{12.2}$	$\frac{97}{10.9}$	$\frac{29}{7.3}$	$\frac{31}{5.9}$	112	12
<u>GF</u> 	$\frac{99}{100.0}$	$\frac{67}{28.7}$	$\frac{41}{26.8}$	$\frac{54}{24.7}$	$\frac{39}{20.3}$	$\frac{27}{17.2}$	$\frac{29}{16.4}$	$\frac{81}{13.8}$	$\frac{55}{12.8}$	$\frac{82}{11.7}$	180	12

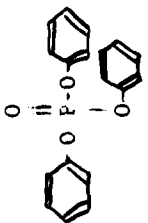
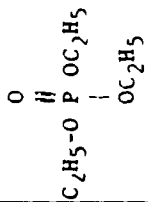
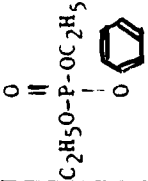
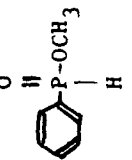
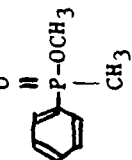
Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
	$\frac{277.8}{120.0}$	$\frac{278.9}{31.7}$	$\frac{201.2}{24.0}$	$\frac{199,200}{22.0}$	$\frac{183.4}{17.7}$	$\frac{77}{16.6}$	$\frac{185.6}{12.9}$	$\frac{152.3}{10.6}$	$\frac{51}{8.4}$	$\frac{154.5}{5.3}$	278	12
	$\frac{93.4}{119.5}$	$\frac{66}{28.2}$	$\frac{65}{19.7}$	$\frac{39}{18.3}$	$\frac{40}{10.3}$	$\frac{27}{7.8}$	$\frac{38}{7.7}$	$\frac{29}{7.0}$	$\frac{63}{6.5}$	$\frac{55}{6.3}$	234	12
	$\frac{93.4,5}{117.}$	$\frac{156.8}{31.}$	$\frac{83.5}{21.5}$	$\frac{126.8}{21.3}$	$\frac{47}{19.6}$	$\frac{56}{17.5}$	$\frac{63}{17.0}$	$\frac{31.}{14.7}$	$\frac{29}{11.0}$	$\frac{79}{11.0}$	156+ 158	12
	$\frac{41}{100.0}$	$\frac{57}{62.1}$	$\frac{39}{49.2}$	$\frac{79}{37.2}$	$\frac{81}{27.5}$	$\frac{80}{26.5}$	$\frac{58}{16.5}$	$\frac{121}{13.3}$	$\frac{55}{12.5}$	$\frac{67}{11.3}$	202	12
	$\frac{41}{100.0}$	$\frac{39}{21.3}$	$\frac{81}{14.8}$	$\frac{79}{13.1}$	$\frac{80}{9.5}$	$\frac{57}{9.0}$	$\frac{42}{6.3}$	$\frac{55}{5.1}$	$\frac{54}{4.5}$	$\frac{161}{4.3}$	202	12
	$\frac{41}{100.0}$	$\frac{57}{69.8}$	$\frac{39}{54.5}$	$\frac{121}{36.5}$	$\frac{58}{25.0}$	$\frac{80}{22.8}$	$\frac{42}{13.5}$	$\frac{29}{14.7}$	$\frac{27.}{12.9}$	$\frac{55}{10.9}$	162	12

Formula of compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\text{CH}_3\text{-P-Cl}_2$	$\frac{101}{100.0}$	$\frac{41}{84.2}$	$\frac{116}{70.2}$	$\frac{44}{22.4}$	$\frac{81}{21.6}$	$\frac{46}{9.0}$	$\frac{35}{8.1}$	$\frac{31}{5.5}$	$\frac{15}{5.3}$	$\frac{66}{5.3}$	$\frac{110+}{118+}$ 120	12
$\text{O} \parallel \text{Cl-P-Cl}$	$\frac{117}{100.0}$	$\frac{154}{44.2}$	$\frac{47}{37.3}$	$\frac{35}{23.7}$	$\frac{31}{12.6}$	$\frac{66}{6.9}$	$\frac{82}{4.1}$	$\frac{101}{2.0}$			$\frac{154+}{156+}$ 158	12
$\text{S} \parallel \text{CH}_3\text{-P-Cl}$	$\frac{113}{100.0}$	$\frac{148}{61.5}$	$\frac{45}{47.5}$	$\frac{77}{34.5}$	$\frac{63}{32.5}$	$\frac{44}{16.2}$	$\frac{31}{15.6}$	$\frac{15}{13.7}$	$\frac{133}{10.5}$	$\frac{43}{8.0}$	$\frac{148+}{150}$	12
$\text{O} \parallel \text{C}_2\text{H}_5\text{O-P-OC}_2\text{H}_5$	$\frac{111}{100.0}$	$\frac{93}{84.1}$	$\frac{31}{70.1}$	$\frac{65}{68.6}$	$\frac{139}{53.3}$	$\frac{81}{36.9}$	$\frac{166}{34.4}$	$\frac{45}{32.9}$	$\frac{82}{28.8}$	$\frac{78}{27.9}$	166	12
$\text{S} \parallel \text{C}_2\text{H}_5\text{O-P-OC}_2\text{H}_5$	$\frac{29}{100.0}$	$\frac{65}{64.0}$	$\frac{121}{59.3}$	$\frac{27}{56.4}$	$\frac{97}{56.4}$	$\frac{198}{47.7}$	$\frac{93}{45.3}$	$\frac{45}{37.2}$	$\frac{115}{32.6}$	$\frac{109}{30.2}$	$\frac{198+}{200}$	12
$\text{O} \parallel \text{CH}_3 \text{C}_2\text{H}_5\text{O-P-CH-COOC}_2\text{H}_5$	$\frac{109}{100.0}$	$\frac{193}{94.0}$	$\frac{165}{82.0}$	$\frac{137}{73.0}$	$\frac{29}{66.0}$	$\frac{81}{65.0}$	$\frac{155}{50.0}$	$\frac{99}{45.0}$	$\frac{138}{40.0}$	$\frac{27}{36.0}$	238	13

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
	$\frac{94}{100.0}$	$\frac{66}{32.0}$	$\frac{65}{23.7}$	$\frac{39}{23.3}$	$\frac{95}{22.}$	$\frac{93}{21.}$	$\frac{43}{18.}$	$\frac{54}{15.}$	$\frac{38}{14.}$	$\frac{62}{14.}$	310	12
	$\frac{94}{100.0}$	$\frac{217}{55.}$	$\frac{77}{46.}$	$\frac{43}{35.}$	$\frac{66}{22.}$	$\frac{65}{21.}$	$\frac{39}{18.}$	$\frac{51}{15.}$	$\frac{310}{14.}$	$\frac{153}{14.}$	310	14
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{COOCH}_3 \end{array}$	$\frac{183}{100.}$	$\frac{123}{73.}$	$\frac{74}{48.}$	$\frac{155}{46.}$	$\frac{137}{40.}$	$\frac{95}{34.}$	$\frac{109}{33.}$	$\frac{29}{30.}$	$\frac{81}{29.}$	$\frac{42}{28.}$	210	13
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	$\frac{123}{100.}$	$\frac{197}{72.}$	$\frac{179}{71.}$	$\frac{151}{63.}$	$\frac{29}{63.}$	$\frac{109}{52.}$	$\frac{152}{48.}$	$\frac{81}{47.}$	$\frac{42}{41.}$	$\frac{88}{41.}$	224	13
$\begin{array}{c} \text{GA} \\ \text{O CH}_3 \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{N} \\ \quad \\ \text{CNCH}_3 \end{array}$	$\frac{43}{100.0}$	$\frac{44}{76.3}$	$\frac{70}{52.6}$	$\frac{42}{45.8}$	$\frac{15}{17.0}$	$\frac{133}{14.1}$	$\frac{45}{12.4}$	$\frac{47}{10.2}$	$\frac{162}{9.0}$	$\frac{18}{6.8}$	162	12

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	$\frac{15}{100.0}$	$\frac{110}{86.3}$	$\frac{29}{36.6}$	$\frac{109}{28.0}$	$\frac{79}{26.6}$	$\frac{95}{22.1}$	$\frac{47}{22.0}$	$\frac{80}{17.3}$	$\frac{31}{16.7}$	$\frac{140}{14.0}$	140	15
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O-P-OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	$\frac{99}{100.0}$	$\frac{81}{78.3}$	$\frac{155}{68.0}$	$\frac{109}{49.3}$	$\frac{127}{47.0}$	$\frac{82}{47.0}$	$\frac{45}{45.4}$	$\frac{182}{26.0}$	$\frac{29}{25.0}$	$\frac{125}{19.7}$	182	15
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{CH}_3 \end{array}$	$\frac{79}{100.0}$	$\frac{94}{88.0}$	$\frac{15}{82.5}$	$\frac{47}{47.6}$	$\frac{29}{39.8}$	$\frac{93}{38.6}$	$\frac{109}{28.3}$	$\frac{80}{21.7}$	$\frac{31}{16.9}$	$\frac{124}{15.7}$	124	15
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{CH}_3 \end{array}$	$\frac{79}{100.0}$	$\frac{94}{81.5}$	$\frac{47}{37.6}$	$\frac{15}{34.7}$	$\frac{109}{33.0}$	$\frac{93}{31.6}$	$\frac{63}{20.8}$	$\frac{124}{13.6}$	$\frac{29}{12.4}$	$\frac{31}{10.7}$	124	16
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-O-P-OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	$\frac{93}{100.0}$	$\frac{63}{64.}$	$\frac{109}{57.}$	$\frac{15}{42.}$	$\frac{79}{41.}$	$\frac{94}{36.}$	$\frac{47}{36.}$	$\frac{124}{36.}$	$\frac{80}{23.}$	$\frac{31}{20.}$	124	14
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O-P-OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	$\frac{65}{100.0}$	$\frac{82}{94.}$	$\frac{83}{76.}$	$\frac{111}{76.}$	$\frac{29}{56.}$	$\frac{139}{52.}$	$\frac{93}{46.}$	$\frac{81}{43.}$	$\frac{121}{37.}$	$\frac{166}{36.}$	166	14

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\text{n-C}_3\text{H}_7\text{O-P-OC}_3\text{H}_7\text{-n}$ $\text{OC}_3\text{H}_7\text{-n}$	$\frac{83}{100.}$	$\frac{43}{42.}$	$\frac{82}{34.}$	$\frac{65}{27.}$	$\frac{125}{21.}$	$\frac{41}{17.}$	$\frac{107}{14.}$	$\frac{27}{12.}$	$\frac{167}{11.}$	$\frac{149}{10.}$	208	14
$\text{1-C}_3\text{H}_7\text{O-P-OC}_3\text{H}_7\text{-1}$ $\text{OC}_3\text{H}_7\text{-1}$	$\frac{82}{100.}$	$\frac{124}{62.}$	$\frac{43}{62.}$	$\frac{109}{49.}$	$\frac{83}{48.}$	$\frac{107}{47.}$	$\frac{65}{30.}$	$\frac{41}{29.}$	$\frac{45}{20.}$	$\frac{27}{15.}$	208	14
$\text{n-C}_4\text{H}_9\text{O-P-OC}_4\text{H}_9\text{-n}$ $\text{OC}_4\text{H}_9\text{-n}$	$\frac{83}{100.}$	$\frac{57}{30.}$	$\frac{138}{25.}$	$\frac{41}{20.}$	$\frac{29}{16.5}$	$\frac{56}{13.}$	$\frac{195}{9.}$	$\frac{31}{6.}$	$\frac{177}{5.}$	$\frac{65}{5.}$	250	14
$\text{C}_2\text{H}_5\text{O-P-OC}_2\text{H}_5$ C_2H_5	$\frac{111}{100.0}$	$\frac{93}{69.}$	$\frac{139}{47.}$	$\frac{65}{44.}$	$\frac{29}{35.}$	$\frac{109}{34.}$	$\frac{138}{30.}$	$\frac{82}{28.}$	$\frac{81}{23.}$	$\frac{83}{21.}$	166	14
$\text{1-C}_3\text{H}_7\text{O-P-1-OC}_3\text{H}_7$ H	$\frac{83}{100.}$	$\frac{109}{85.}$	$\frac{45}{39.}$	$\frac{43}{35.}$	$\frac{41}{19.}$	$\frac{27}{12.}$	$\frac{59}{11.}$	$\frac{39}{10.}$	$\frac{65}{10.}$	$\frac{42}{8.}$	166	14
$\text{1-C}_3\text{H}_7\text{O-P-OC}_3\text{H}_7\text{-1}$ CH_3	$\frac{97}{100.}$	$\frac{123}{65.}$	$\frac{45}{31.}$	$\frac{43}{27.}$	$\frac{79}{24.}$	$\frac{41}{22.}$	$\frac{28}{18.}$	$\frac{39}{15.}$	$\frac{27}{10.}$	$\frac{80}{9.}$	180	14

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W	Ref
	$\frac{326}{100}$	$\frac{325}{81}$	$\frac{94}{74}$	$\frac{11}{17}$	$\frac{170}{40}$	$\frac{169}{26}$	$\frac{233}{25}$	$\frac{215}{22}$	$\frac{168}{14}$	$\frac{232}{13}$	326	18
	$\frac{155}{100}$	$\frac{99}{93}$	$\frac{127}{56}$	$\frac{81}{43}$	$\frac{109}{41}$	$\frac{82}{31}$	$\frac{29}{19}$	$\frac{125}{18}$	$\frac{111}{15}$	$\frac{45}{15}$	182	17
	$\frac{94}{100}$	$\frac{104}{78}$	$\frac{65}{27}$	$\frac{77}{24}$	$\frac{230}{23}$	$\frac{81}{21}$	$\frac{174}{17}$	$\frac{187}{14}$	$\frac{66}{13}$	$\frac{202}{12}$	230	18
	$\frac{77}{100}$	$\frac{79}{96}$	$\frac{51}{88}$	$\frac{47}{74}$	$\frac{78}{69}$	$\frac{155}{56}$	$\frac{156}{42}$	$\frac{50}{35}$	$\frac{126}{33}$	$\frac{141}{22}$	156	19
	$\frac{155}{100}$	$\frac{77}{65}$	$\frac{47}{42}$	$\frac{170}{42}$	$\frac{51}{28}$	$\frac{169}{27}$	$\frac{140}{26}$	$\frac{91}{24}$	$\frac{125}{20}$	$\frac{139}{8}$	170	19

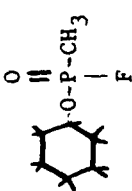
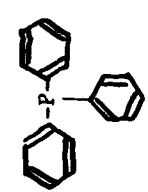
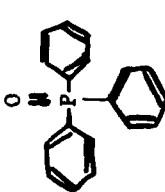
Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5 - \text{P} - \text{OCH}_3 \\ \\ \text{C}_2\text{H}_5 \end{array}$	$\frac{155}{100.}$	$\frac{77}{70.}$	$\frac{51}{40.}$	$\frac{47}{33.}$	$\frac{184}{27.}$	$\frac{78}{14.}$	$\frac{50}{13.}$	$\frac{79}{12.}$	$\frac{91}{12.}$	$\frac{141}{9.}$	184	19
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{OC}_4\text{H}_9(\text{n}) \end{array}$	$\frac{65}{100.}$	$\frac{109}{96.}$	$\frac{181}{88.}$	$\frac{138}{77.}$	$\frac{111}{65.}$	$\frac{166}{58.}$	$\frac{81}{54.}$	$\frac{137}{50.}$	$\frac{57}{35.}$	$\frac{139}{34.}$	238	20, 21
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 \end{array}$	$\frac{125}{100.}$	$\frac{81}{79.}$	$\frac{111}{75.}$	$\frac{82}{60.}$	$\frac{138}{55.}$	$\frac{29}{44.}$	$\frac{65}{38.}$	$\frac{109}{35.}$	$\frac{153}{34.}$	$\frac{137}{29.}$	210	21
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{OC}_3\text{H}_7(\text{n}) \end{array}$	$\frac{125}{100.}$	$\frac{81}{88.}$	$\frac{111}{80.}$	$\frac{138}{71.}$	$\frac{82}{55.}$	$\frac{65}{47.}$	$\frac{137}{46.}$	$\frac{109}{41.}$	$\frac{43}{39.}$	$\frac{139}{33.}$	224	21
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}=\text{CH}_2 \end{array}$	$\frac{91}{100.}$	$\frac{109-}{87.}$	$\frac{109+}{86.}$	$\frac{27}{61.}$	$\frac{29}{51.}$	$\frac{137}{47.}$	$\frac{136}{36.}$	$\frac{119}{19.}$	$\frac{45}{18.}$	$\frac{110}{8.}$	164	22
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{OCH}_3 \\ \\ \text{CH}_2\text{Cl} \end{array}$	$\frac{109}{100.}$	$\frac{79}{28.}$	$\frac{15}{13.}$	$\frac{158+60}{8.}$	$\frac{49+51}{5.}$	$\frac{31}{4.}$	$\frac{127+9}{2.}$				158+ 160	22

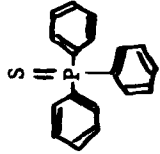
Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{Cl} \end{array}$	$\frac{138}{100.}$	$\frac{145+7}{80.}$	$\frac{109}{62.}$	$\frac{127+9}{60.}$	$\frac{29}{49.}$	$\frac{173+5}{44.}$	$\frac{91}{37.}$	$\frac{45}{25.}$	$\frac{137}{16.}$	$\frac{110}{15.}$	200+ 202	22
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{Cl} \end{array}$	$\frac{109}{100.}$	$\frac{159+161}{66.}$	$\frac{29}{43.}$	$\frac{131+3}{41.}$	$\frac{91}{40.}$	$\frac{137}{35.}$	$\frac{45}{26.}$	$\frac{113+5}{24.}$	$\frac{93}{15.}$	$\frac{141+3}{11.}$	186+ 188	22
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_3 \end{array}$	$\frac{97}{100.}$	$\frac{125}{90.}$	$\frac{79}{77.}$	$\frac{124}{26.}$	$\frac{107}{26.}$	$\frac{45}{10.}$	$\frac{109}{9.}$	$\frac{93}{8.}$	$\frac{137}{7.}$	$\frac{29}{6.}$	152	22
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{O}-\text{P}-\text{O}-\text{C}_6\text{H}_5 \\ \\ \text{CH}_2\text{Cl} \end{array}$	$\frac{125+7}{100.}$	$\frac{77}{83.}$	$\frac{282+4}{66.}$	$\frac{170}{30.}$	$\frac{165}{30.}$	$\frac{94}{24.}$	$\frac{215}{17.}$	$\frac{93}{5.}$	$\frac{49+51}{3.}$		282+ 284	22
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{O}-\text{P}-\text{O}-\text{C}_6\text{H}_5 \\ \\ \text{CH}_2\text{C}_6\text{H}_5 \end{array}$	$\frac{91}{100.}$	$\frac{167}{53.}$	$\frac{324}{51.}$	$\frac{77}{11.}$	$\frac{94}{6.}$	$\frac{93}{2.}$					324	22

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2-\text{C}_6\text{H}_5 \end{array}$	$\frac{91}{100.}$	$\frac{109}{25.}$	$\frac{228}{17.}$	$\frac{172}{14.}$	$\frac{29}{14.}$	$\frac{200}{6.}$	$\frac{93}{5.}$	$\frac{45}{3.}$	$\frac{173}{1.}$	$\frac{137}{1.}$	228	22
$\begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$	$\frac{125}{100.}$	$\frac{152}{87.}$	$\frac{111}{78.}$	$\frac{139}{70.}$	$\frac{138}{50.}$	$\frac{65}{46.}$	$\frac{97}{44.}$	$\frac{81}{38.}$	$\frac{82}{26.}$	$\frac{109}{34.}$	194	21
CF_3PCl_2	$\frac{101+3+5}{100.0}$	$\frac{170+2+4}{25.4}$	$\frac{85+7}{20.2}$	$\frac{66+8}{10.5}$	$\frac{69^+}{7.9}$	$\frac{69^-}{6.3}$	$\frac{151+3+5}{3.1}$	$\frac{50}{1.8}$	$\frac{31^+}{1.6}$	$\frac{31^-}{1.4}$	$\frac{170^+}{172^+}$ 174	23
CF_3PF_2	$\frac{69^+}{100.0}$	$\frac{69^-}{58.4}$	$\frac{31}{11.2}$	$\frac{138}{9.0}$	$\frac{119}{6.9}$	$\frac{50^+}{4.9}$	$\frac{50^-}{3.9}$				138	23
CF_3PH_2	$\frac{102}{100.}$	$\frac{69^+}{100.}$	$\frac{69^-}{49.5}$	$\frac{51^+}{16.8}$	$\frac{32}{11.7}$	$\frac{52}{12.8}$	$\frac{83}{11.4}$	$\frac{50}{11.0}$	$\frac{51^-}{8.4}$	$\frac{33}{8.1}$	102	23
$\text{CF}_3-\text{P}-\text{CF}_3$ CF_3	$\frac{69^+}{100.}$	$\frac{69^-}{24.8}$	$\frac{131}{16.4}$	$\frac{219}{9.0}$	$\frac{100}{8.8}$	$\frac{31}{7.8}$	$\frac{150}{5.7}$	$\frac{238}{4.8}$	$\frac{50}{4.6}$	$\frac{81}{3.6}$	238	23
$\text{CF}_3-\text{P}-\text{CF}_3$ Cl	$\frac{69^+}{100.}$	$\frac{85+7}{83.0}$	$\frac{204+6}{42.6}$	$\frac{69^-}{31.8}$	$\frac{116+8}{27.8}$	$\frac{66+8}{9.2}$	$\frac{31}{7.9}$	$\frac{50}{5.3}$	$\frac{135+7}{4.6}$	$\frac{100}{3.9}$	$\frac{204^+}{206}$	23

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\text{CF}_3 \text{P}(\text{CF}_3)_2$ F	$\frac{69}{100.0}$	$\frac{69^+}{88.5}$	$\frac{31}{27.6}$	$\frac{100}{24.6}$	$\frac{188}{24.2}$	$\frac{119}{15.5}$	$\frac{50^-}{10.6}$	$\frac{81}{4.5}$	$\frac{169}{3.9}$	$\frac{50^+}{3.9}$	188	23
$\text{CF}_3 \text{P}(\text{CF}_3)_2$ H	$\frac{69^+}{100.0}$	$\frac{69^-}{31.8}$	$\frac{170}{25.6}$	$\frac{82}{24.4}$	$\frac{151}{11.2}$	$\frac{101}{10.4}$	$\frac{51^+}{10.4}$	$\frac{51^-}{7.9}$	$\frac{31}{7.9}$	$\frac{50}{4.8}$	170	23
F-P-F F	$\frac{69}{100.0}$	$\frac{88}{43.4}$	$\frac{50}{9.5}$	$\frac{31}{5.7}$	$\frac{19}{4.6}$						88	24
$\text{O} \parallel \text{F-P-F}$ F	$\frac{85}{100.0}$	$\frac{104}{87.0}$	$\frac{69}{17.7}$	$\frac{50}{4.4}$	$\frac{31}{3.6}$	$\frac{47}{2.2}$	$\frac{88}{1.1}$	$\frac{66}{1.1}$	$\frac{19}{1.1}$		104	24
$\text{O} \parallel \text{Cl-P-Cl}$ Cl	$\frac{117+9+21}{100.0}$	$\frac{152+4+6}{44.2}$	$\frac{47}{37.3}$	$\frac{35+7}{23.7}$	$\frac{31}{12.6}$	$\frac{66+8}{6.9}$	$\frac{82+4}{4.1}$				152+ 154+ 156	24
$\text{O} \parallel \text{Br-P-Br}$ Br	$\frac{205+7+9}{100.0}$	$\frac{47}{66.6}$	$\frac{284+6+}{288+90}$ 43.4	$\frac{79+81}{37.0}$	$\frac{126+8}{15.1}$	$\frac{31}{9.6}$	$\frac{110+12}{6.2}$		$\frac{189+91+}{193}$ 0.9		284+ 286+ 288+ 290	24

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{S} \\ \\ \text{F}-\text{P}-\text{F} \\ \\ \text{F} \end{array}$	$\frac{120+1+2}{100.}$	$\frac{32+3+4}{73.5}$	$\frac{101+2+3}{27.1}$	$\frac{69}{26.0}$	$\frac{88}{6.9}$	$\frac{50}{6.8}$	$\frac{63+4+5}{2.4}$				120+ 121+ 122	24
$\begin{array}{c} \text{CH}_3-\text{P}-\text{Cl} \\ \\ \text{Cl} \end{array}$	$\frac{101+3+5}{100.}$	$\frac{45}{84.2}$	$\frac{116+8+20}{70.2}$	$\frac{44}{22.4}$	$\frac{81+83}{21.6}$	$\frac{35+7}{8.1}$	$\frac{31}{5.5}$	$\frac{66+8}{5.3}$	$\frac{15}{5.3}$	$\frac{80+2}{4.6}$	116+ 118+ 120	24
$\begin{array}{c} \text{S} \\ \\ \text{CH}_3-\text{P}-\text{Cl} \\ \\ \text{Cl} \end{array}$	$\frac{113+4+5}{100.}$	$\frac{148+50+}{152}$ $\frac{61.5}{61.5}$	$\frac{45}{47.5}$	$\frac{77+8+9}{34.5}$	$\frac{63+4+5}{32.5}$	$\frac{44}{16.2}$	$\frac{31}{15.6}$	$\frac{15}{13.7}$	$\frac{133+5+7}{10.5}$	$\frac{43}{8.0}$	148+ 150+ 152	24
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{O}-\text{P}-\text{OCH}_3 \\ \\ \text{CH}_2\text{COOCH}_3 \end{array}$	$\frac{79}{100.}$	$\frac{80}{91.8}$	$\frac{15}{49.4}$	$\frac{47}{45.9}$	$\frac{31}{36.7}$	$\frac{29}{33.6}$	$\frac{110}{19.3}$	$\frac{94}{16.3}$	$\frac{109}{15.3}$	$\frac{95}{14.3}$	182	24
$\begin{array}{c} \text{S} \\ \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$	$\frac{29}{100.}$	$\frac{27}{59.2}$	$\frac{121}{56.3}$	$\frac{65}{54.3}$	$\frac{97}{51.8}$	$\frac{198}{42.7}$	$\frac{93}{41.4}$	$\frac{45}{33.5}$	$\frac{109}{26.4}$	$\frac{81}{23.3}$	198	24
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{O}-\text{P}-\text{F} \\ \\ \text{CH}_3 \end{array}$	$\frac{82}{100.0}$	$\frac{67}{43.8}$	$\frac{81}{24.6}$	$\frac{47}{13.9}$	$\frac{15}{13.4}$	$\frac{83}{12.3}$	$\frac{112}{12.2}$	$\frac{97}{10.9}$	$\frac{29}{7.3}$	$\frac{31}{5.9}$	112	24

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{F} \\ \\ \text{CH}_3 \end{array}$	$\frac{99}{100.0}$	$\frac{81}{31.6}$	$\frac{82}{17.2}$	$\frac{111}{15.4}$	$\frac{29}{10.1}$	$\frac{47}{6.8}$	$\frac{83}{6.2}$	$\frac{67}{6.0}$	$\frac{21}{5.6}$	$\frac{15}{4.6}$	126	24
	$\frac{99}{100.0}$	$\frac{67}{28.3}$	$\frac{41}{26.2}$	$\frac{54}{24.0}$	$\frac{39}{20.0}$	$\frac{27}{17.2}$	$\frac{29}{16.4}$	$\frac{81}{12.7}$	$\frac{55}{11.5}$	$\frac{82}{11.3}$	180	24
$\begin{array}{c} \text{O CH}_3 \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{N} \\ \\ \text{CNCH}_3 \end{array}$	$\frac{133}{100.0}$	$\frac{47}{73.4}$	$\frac{162}{66.4}$	$\frac{108}{41.8}$	$\frac{117}{34.9}$	$\frac{107}{32.1}$	$\frac{134}{31.0}$	$\frac{106}{31.0}$	$\frac{65}{29.0}$	$\frac{135}{20.3}$	162	24
	$\frac{262}{100.0}$	$\frac{183}{44.0}$	$\frac{263}{23.0}$	$\frac{108}{21.0}$	$\frac{184}{10.0}$	$\frac{107}{10.0}$	$\frac{185}{7.0}$	$\frac{152}{5.0}$	$\frac{51}{5.0}$	$\frac{154}{3.5}$	262	25
	$\frac{277}{100.0}$	$\frac{278}{53.0}$	$\frac{77}{30.0}$	$\frac{201}{19.0}$	$\frac{183}{14.0}$	$\frac{199}{13.0}$	$\frac{51}{10.0}$	$\frac{185}{9.0}$	$\frac{47}{8.0}$	$\frac{152}{7.0}$	278	25

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
	$\frac{294}{100.}$	$\frac{183}{54.}$	$\frac{185}{47.}$	$\frac{293}{40.}$	$\frac{262}{32.}$	$\frac{295}{18.}$	$\frac{43}{15.}$	$\frac{152}{13.}$	$\frac{263}{11.}$	$\frac{139}{9.}$	294	25
$\begin{array}{c} \text{H-P-H} \\ \\ \text{H} \end{array}$	$\frac{32}{100.}$	$\frac{34}{75.2}$	$\frac{31}{24.1}$	$\frac{33}{21.8}$							34	26
$\begin{array}{c} \text{H-P-H} \\ \\ \text{H} \end{array}$	$\frac{32}{100.0}$	$\frac{31}{85.0}$	$\frac{33}{27.6}$	$\frac{31}{26.4}$							34	27
$\begin{array}{c} \text{H-P-H} \\ \\ \text{H} \end{array}$	$\frac{32}{100.0}$	$\frac{34}{68.0}$	$\frac{31}{40.2}$	$\frac{33}{25.4}$							34	28
$\begin{array}{c} \text{H-P-H} \\ \\ \text{H} \end{array}$	$\frac{32}{100.0}$	$\frac{34}{89.4}$	$\frac{33}{26.2}$	$\frac{31}{18.7}$							34	29
$\begin{array}{c} \text{H-P-H} \\ \\ \text{H} \end{array}$	$\frac{34}{100.0}$	$\frac{33}{33.1}$	$\frac{31}{32.1}$	$\frac{32}{12.7}$							34	30
$\begin{array}{c} \text{H-P-P-H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\frac{32}{100.0}$	$\frac{66}{74.6}$	$\frac{31}{65.3}$	$\frac{62}{57.3}$	$\frac{34}{52.0}$	$\frac{64}{50.7}$	$\frac{63}{44.0}$	$\frac{33}{21.3}$	$\frac{65}{9.3}$		66	26

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\begin{array}{c} \text{H-P-P-H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\frac{62}{100.0}$	$\frac{66}{8.4}$	$\frac{64}{5.8}$	$\frac{63}{5.6}$	$\frac{33}{5.1}$	$\frac{65}{1.3}$	$\frac{31}{1.2}$	$\frac{34}{0.4}$	$\frac{32}{0.2}$		66	28
$\begin{array}{c} \text{F} \\ \\ \text{F-P-F} \\ \wedge \\ \text{F} \quad \text{F} \end{array}$	$\frac{107}{100.}$	$\frac{88}{21.0}$	$\frac{50}{10.3}$	$\frac{69}{6.0}$	$\frac{31}{3.2}$	$\frac{19}{2.0}$					126	26
$\begin{array}{c} \text{Cl-P-Cl} \\ \\ \text{Cl} \end{array}$	$\frac{101+3+5}{100.}$	$\frac{35+7}{48.3}$	$\frac{136+8+}{140}$ $\frac{31.5}{31.5}$	$\frac{66+8}{29.2}$	$\frac{31}{20.9}$						136+ 138+ 140	26
$\begin{array}{c} \text{O} \\ \\ \text{Cl-P-Cl} \\ \\ \text{Cl} \end{array}$	$\frac{117+9+}{121}$ $\frac{100.0}{100.0}$	$\frac{47}{87.5}$	$\frac{35+7}{49.5}$	$\frac{152+4+6}{37.8}$	$\frac{31}{21.0}$	$\frac{66+8}{20.8}$	$\frac{82+4}{7.4}$	$\frac{101+3+5}{6.2}$			152+ 154+ 156	26
$\begin{array}{c} \text{S} \\ \\ \text{Cl-P-Cl} \\ \\ \text{Cl} \end{array}$	$\frac{133+4+}{135+6+7}$ $\frac{100.0}{100.0}$	$\frac{168+9+}{170+1+2+4}$ $\frac{51.3}{51.3}$	$\frac{63}{47.1}$	$\frac{31}{27.3}$	$\frac{35+7}{25.5}$	$\frac{101+3+5}{18.5}$	$\frac{66+8}{11.2}$	$\frac{98+9+100}{8.0}$			168+9+ 170+1+2 +174	26
$\begin{array}{c} \text{CH}_3\text{-P-CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\frac{61}{100.0}$	$\frac{76}{78.2}$	$\frac{59}{66.2}$	$\frac{45}{56.4}$	$\frac{57}{32.8}$	$\frac{75}{20.0}$	$\frac{15}{15.2}$	$\frac{44}{12.1}$	$\frac{58}{11.8}$	$\frac{47}{11.4}$	76	26

Formula of Compound	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	M.W.	Ref.
$\text{C}_2\text{H}_5\text{-P-C}_2\text{H}_5$ C_2H_5	$\frac{62}{100.0}$	$\frac{90}{75.6}$	$\frac{61}{73.0}$	$\frac{118}{52.7}$	$\frac{57}{46.9}$	$\frac{59}{45.7}$	$\frac{45}{29.0}$	$\frac{103}{22.8}$	$\frac{58}{20.7}$	$\frac{75}{19.5}$	118	26
$\text{CH}_3\text{-P-H}$ H	$\frac{46}{100.0}$	$\frac{15}{79.7}$	$\frac{48}{63.7}$	$\frac{45}{56.6}$	$\frac{44}{42.6}$	$\frac{47}{15.8}$	$\frac{43}{8.3}$				48	26
$\text{C}_2\text{H}_5\text{-P-H}$ H	$\frac{62}{100.0}$	$\frac{34}{53.2}$	$\frac{57}{50.7}$	$\frac{58}{35.2}$	$\frac{45}{35.2}$	$\frac{43}{25.3}$	$\frac{47}{19.7}$	$\frac{59}{19.4}$	$\frac{60}{18.7}$	$\frac{44}{14.4}$	62	26
$\text{CH}_3\text{-O-P-OCH}_3$ OCH_3	$\frac{93}{100.0}$	$\frac{15}{93.6}$	$\frac{63}{51.7}$	$\frac{109}{48.9}$	$\frac{47}{43.0}$	$\frac{124}{38.7}$	$\frac{94}{28.3}$	$\frac{79}{17.0}$	$\frac{29}{16.5}$	$\frac{45}{13.9}$	124	26
$\text{C}_2\text{H}_5\text{O-P-OC}_2\text{H}_5$ OC_2H_5	$\frac{29}{100.0}$	$\frac{65}{68.1}$	$\frac{82}{62.9}$	$\frac{27}{61.3}$	$\frac{83}{35.0}$	$\frac{81}{31.1}$	$\frac{111}{23.1}$	$\frac{47}{20.1}$	$\frac{139}{17.7}$	$\frac{79}{17.1}$	166	26
$\text{CH}_3\text{O-P-OCH}_3$ OH	$\frac{79}{100.0}$	$\frac{80}{91.8}$	$\frac{47}{54.6}$	$\frac{15}{51.5}$	$\frac{31}{41.6}$	$\frac{29}{25.8}$	$\frac{49}{18.9}$	$\frac{110}{18.4}$	$\frac{95}{15.9}$	$\frac{48}{12.7}$	110	26
$\text{C}_2\text{H}_5\text{C-P-OC}_2\text{H}_5$ OH	$\frac{111}{100.0}$	$\frac{83}{99.4}$	$\frac{65}{86.5}$	$\frac{45}{79.7}$	$\frac{29}{65.3}$	$\frac{31}{59.3}$	$\frac{27}{49.9}$	$\frac{93}{31.5}$	$\frac{66}{31.3}$	$\frac{110}{19.0}$	138	26

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) KANSAS STATE UNIVERSITY Department of Chemistry Manhattan, Kansas 66502		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE ION PHENOMENA			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report - December 1965-July 1967			
5. AUTHOR(S) (First name, middle initial, last name) Kiser, R. W.			
6. REPORT DATE May 1968		7a. TOTAL NO. OF PAGES 57	7b. NO. OF REFS 30
8a. CONTRACT OR GRANT NO. DA-18-145-AMC-718(A)		8b. ORIGINATOR'S REPORT NUMBER(S) FR	
b. PROJECT NO. 1062.401A102			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		N/A	
10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010			
11. SUPPLEMENTARY NOTES Chemical agent warning and detection techniques		12. SPONSORING MILITARY ACTIVITY Edgewood Arsenal Research Laboratories Edgewood Arsenal, Maryland 21010 (CE Block, Project Officer, Ext. 6294)	
13. ABSTRACT Mass spectrometric studies of trimethyl phosphorothionate, triphenyl phosphite, diallyl phosphite, diallyl allylphosphonate, triallyl phosphite, triallyl phosphate, and diphenyl phosphite were made to obtain more fundamental information for use in determining the ionization and dissociative ionization processes that occur upon electron impact with these organophosphorus compounds. Mass spectra, appearance potentials, clastograms, and metastable transitions obtained in these studies are reported. These results are discussed in relation to a better understanding of the fragmentation pathways in this class of compounds. A summary table of all results determined under this contract is included, and a brief catalog, with literature references, of the mass spectra of organophosphorus compounds summarizes much of the available literature. Future correlative activities are suggested.			
14. REFERENCES: Appearance potentials Biologically-active compounds Clastograms Diallyl allyl-phosphonate Diallyl phosphite Diphenyl phosphite Fragmentation processes		G agents Mass Spectra Metastable transitions Organophosphorus compounds Triallyl phosphate Triallyl phosphite Trimethyl phosphorothionate Triphenyl phosphite	

DD FORM 1473

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