

UNCLASSIFIED

AD NUMBER
AD803487
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; JUN 1966. Other requests shall be referred to Army Edgewood Arsenal, Attn: SMUEA-TSTI-T, Edgewood Arsenal, MD 21010.
AUTHORITY
Army Edgewood Arsenal ltr dtd 27 Jul 1972

THIS PAGE IS UNCLASSIFIED

803 487

AD-

REPORT NUMBER 2

ION PHENOMENA

Quarterly Progress Report

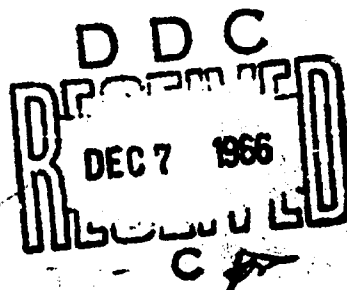
by

Robert W. Kiser

June, 1966

Physical Research Laboratory
RESEARCH LABORATORIES
Edgewood Arsenal, Maryland 21010

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



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, ATTN: SMJEA-TSTI-T, U. S. Army Edgewood Arsenal, Edgewood Arsenal, Maryland 21010.

KANSAS STATE UNIVERSITY
Department of Chemistry
Manhattan, Kansas 66502

BEST AVAILABLE COPY

FOREWORD

The work described in this report was authorized under Project 10022401A102, Chemical Agent Warning and Detection Techniques(U). This work was started in March of 1966 and completed in June of 1966. The experimental data are contained in notebooks KSU-182311-DLD-7 and KSU-182311-DLD-8.

Acknowledgments

Donald L. Dugger has been instrumental in obtaining the experimental findings reported herein.

Notices

Reproduction of this document in whole or in part is prohibited except with the permission of the U. S. Army Edgewood Arsenal CO, ATTN: SMUEA-RPR, Edgewood Arsenal, Maryland 21010; however, DDC is authorized to reproduce the document for United States Government purposes.

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

Reference to a company and/or product name in this report is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Disposition

When this document has served its purpose, DESTROY it.

A study of several simple phosphorus compounds containing alkyl, alkoxy, and halogen groups has been undertaken to obtain further fundamental information that will be of value in determining the processes which occur in more complex organophosphorus compounds.

In an effort to produce negative parent ions from these phosphorus compounds, a polonium-210 alpha particle source has been designed that will be employed in such studies.

70 ev positive ion mass spectra have been obtained for O-ethyl-N,N-dimethylphosphoramidocyanidate (Tabun, GA) and chloromethylphosphonic dichloride.

An attempt has been made to purify some simple phosphorus compounds for mass spectrometric analyses.

C-agents received for study have been properly transferred and await further investigation.

Energetic studies by either appearance potentials or clastograms have been made for the positive ions from O,O,O-triethyl phosphorothionate and methylthiophosphonic dichloride.

TABLE OF CONTENTS

STATEMENT OF PROBLEM	7
BACKGROUND	7
APPROACH TO THE PROBLEM	7
RESULTS	8
DISCUSSION	9
CONCLUSIONS	11
LITERATURE CITED	11
APPENDIX	13
DISTRIBUTION LIST	21
DOCUMENT CONTROL DATA - R & D DD FORM 1473, WITH ABSTRACT AND KEYWORD LIST	23

1. STATEMENT OF PROBLEM

This work was initiated in order (1) to obtain the mass spectra, (2) to make energetic studies by appearance potential and clastogram determinations for both positive and negative ions, and (3) 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 about 15 ev there is significant fragmentation of the parent molecule positive ion. However, the ionization and dissociation processes observed 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 the negative ions formed in the ionization and dissociation processes is important to understanding the fragmentation routes. 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 which would indicate possible routes of fragmentation.

3. APPROACH TO THE PROBLEM

3.1. Materials

The materials to be studied include GA, GF, CH_3PACl_2 , $\text{SP}(\text{CCl}_2)_3$, parathion, methyl parathion, methyl acid phosphate, chlorodiphenyl phosphine, benzenephosphorus oxychloride, benzenephosphorus dichloride, and chloromethylphosphonic dichloride.

3.2. Equipment

The equipment items discussed in section 3.2 of Quarterly Progress Report Number 1 were used to continue these studies. An additional item not included in the previous report is the polonium-210 alpha particle source for the time-of-flight mass spectrometer. The license required to handle polonium-210 has been approved by the appropriate agency within the State of Kansas and by the Kansas State University Radiation Safety Committee. After the source has been received, the Kansas State University Safety Control Officer will conduct wipe tests around the source at 3-month intervals to ascertain any leakage of the radioactive material.

... Corporation is requested to fabricate this source according to the specifications shown in the following description of this source is:

... more than 100 microcuries nor less than 50 microcuries of calcium-45 in a 0.25" to 0.40" diameter depression of 0.0825" in the center of a 1.00" x 1.50" stainless steel plate 0.01" thick. Construction of this plate is shown in Figure 1.) Overlay the plate with a thin layer of gold such that the emanating alpha particle energy is as close as is possible to 5.0 MeV. The resultant activity and alpha particle energy should be specified. Source: Monsanto Research Corporation, Dayton, Ohio.

The cost for the fabrication and testing of this item will be \$420.00. Approval was given to fabricate the source at this cost.

4.2. RESULTS

4.2.1. GA Studies

As noted in Quarterly Progress Report Number 1, the GA (Tabun, O-ethyl-S-(diethylphosphorothioate) sample appeared to contain significant impurities. Therefore, we requested and received a new sample of GA on 2 May, 1966.

4.2.2. GF

Thirty ml. of cyclohexyl methylphosphonofluoridate (GF) was received together with GA in the shipment from U. S. Army Edgewood Arsenal. The sample was removed from the shipping container and placed in the freezer compartment of the C-agent refrigerator preparatory to the necessary transfer operations.

4.3. O,O,O-Triethyl Phosphorothionate Studies

Appearance potentials of the most abundant ions in the mass spectrum of O,O,O-triethyl phosphorothionate are listed in Table 1 of the Appendix. Comparison of the mass spectrum of this compound with that obtained previously for triethyl phosphite will be discussed below.

4.4. Diethylthiophosphonic Dichloride Studies

The electron impact data for CH_3PSCl_2 has been determined using the Barron (1) and the semi-logarithmic plot (2) methods. These results differ slightly from those presented earlier and which were evaluated using only the energy compensation technique (3).

4.5. Parathion Studies

A few drops (less than 0.25 ml) of parathion was transferred to a glass storage bulb equipped with a stopcock. The transfer was carried out in a glove bag using an atmosphere of dry nitrogen. The results of this

the gas chromatograph and the mass spectrometer.

4.2.2. Sample Transfer Procedure

The procedure similar to that described above for transferring GA was employed for this compound.

4.2.3. Sample Ionization Source

This compound did not have sufficient vapor pressure to permit recording a mass spectrum by using the normal inlet system on the mass spectrometer. A sample of the material was introduced into the mass spectrometer by means of the sample boat and "hot" ionization source.

4.3. Other Compounds Studied

Other compounds investigated were chlorodiphenyl phosphine, chlorodiphenylphosphonic dichloride, benzene phosphorus oxychloride, and benzene phosphorus dichloride. The mass spectrum of each compound showed significant impurities. Attempts were made to purify these substances by means of gas chromatography.

5. DISCUSSION

5.1. GA Studies

A portion of the new sample of GA has been transferred into a sample vial ready for mass spectrometric investigation. A preliminary examination of this material indicated a mass spectrum very similar to the one obtained from the original sample of GA. The principal positively-charged ionic species found in the mass spectrum of GA are listed in Table 2, but no effort has been made to obtain either a clastogram or energetic data for this compound until the purity of the material has been established. There is reason to believe that the ions appearing at m/q values of 42, 43, 44, and 70 are due to one or more impurities rather than being formed from GA. The particular reason for this assignment is due to the very large relative intensities of these ions as compared to the parent and other ions in the mass spectrum.

5.2. GF Studies

About one ml of the liquid has been transferred into sample storage bulbs and stored in the freezer compartment of the G-agent refrigerator until it can be studied mass spectrometrically.

5.3. O,O,O-Triethyl Phosphorothionate Studies

The appearance potentials given in Table 1 represent data taken only with the energy compensation technique. A more detailed energetic analysis is needed in order to supplement the clastogram data; this will provide a test of the proposed fragmentation scheme given in Quarterly Progress Report Number 1.

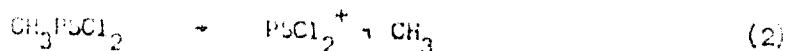
It is interesting to note the marked contrast in the relative abundances of similar fragment ions between triethyl phosphate and O,O,O-triethyl phosphorothioate (see Table 3). From a comparison of the two spectra, it appears to be a tendency for the thio compound to dissociate into more abundant lower mass fragments. Although the relative abundances differ, the two spectra reveal the same general type of ions with hydrogen atom rearrangement species quite prevalent in both materials.

Methylthiophosphonic Dichloride Studies

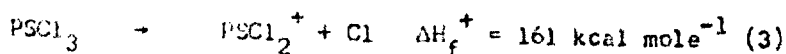
From the energetic data and the heats of formation of the ions, some interesting results have come about because of the study of this compound. Some investigators, working with halogenated compounds, have assumed that the process of removing a halogen from the parent ion involves an ion-pair formation as the major ionic gas phase process. For example, Halmann and Klein (4) have proposed the following reaction:



There is some doubt that this is the major reaction process because of the investigation of methylthiophosphonic dichloride. From Table 5, we have written the process:



The heat of formation of PSCl_2^+ is calculated to be $167 \text{ kcal mole}^{-1}$. The only means of obtaining agreement with the heat of formation of PSCl_2^+ in the PSCl_3 studies is by writing the following reaction:



If a chloride ion is used instead of the neutral chlorine atom, the heat of formation differs by approximately $87 \text{ kcal mole}^{-1}$. A similar comparison is observed using the PCl_2^+ ion from PCl_3 and CH_3PCl_2 . From these two studies there appears to be some doubt as to the validity of writing ion-pair processes as the major ionic processes occurring upon electron impact. Ion-pair processes do indeed occur, since other investigators have measured appearance potentials of the ion pairs and found them to be the same. From our results we must assume that the cross section for the ion-pair process is small in comparison to that for the reaction producing a neutral halogen atom.

Negative ion studies of this compound using the Hewlett-Packard system also have been made. The results are presented in Table 4 and shown in Figure 2. The chloride ion is the only significant negative ion present over a wide range of electron energy.

5.5. Parathion Studies

A sample of parathion was connected to the inlet system of the TOF mass spectrometer. Due to the low volatility of the compound it was not possible to obtain a mass spectrum. Because of the toxicity of parathion,

material was made to handle this material in the manner required to load sample into the sample cell of the "high temperature" ionization source.

5.6. Methyl Parathion Studies

As expected from the results with parathion, methyl parathion was also too non-volatile to be studied in our mass spectrometer with the general inlet system.

5.7. Methyl Acid Phosphate Studies

The introduction of this substance into the mass spectrometer by means of the "high temperature" ionization source sample boat created much difficulty. It appeared to possess sufficient vapor pressure to distill out of the sample cell while sealed inside the flight tube of the mass spectrometer, thereby preventing the diffusion pump from attaining a sufficiently low vacuum required for the proper operation of the mass spectrometer. Considerable amounts of hydrolyzed material had to be removed from the inside of the spectrometer flight tube after these attempted experiments. No further attempts were made to obtain a mass spectrum of this compound.

5.8. Other Compounds Studied

The mass spectra of chlorodiphenyl phosphine, chloromethylphosphonic dichloride, benzenephosphorus oxychloride, and benzenephosphorus dichloride all exhibited large quantities of impurities such as PCl_3 and POCl_3 . Attempts to design gas chromatographic techniques to permit the purification of these materials did not yield satisfactory results. An example of the problem encountered is illustrated in Table 5. The sample of chloromethylphosphonic dichloride contained large amounts of PCl_3 and POCl_3 which could not be separated from the desired compound. As a result, no further data has been taken on these systems at the present time.

6. CONCLUSIONS

70 ev positive ion mass spectra have been obtained for O-ethyl-N,N-dimethylphosphoramidocyanidate (Tabun, GA) and chloromethylphosphonic dichloride. An attempt has been made to purify other simple phosphorus compounds for mass spectrometric analyses.

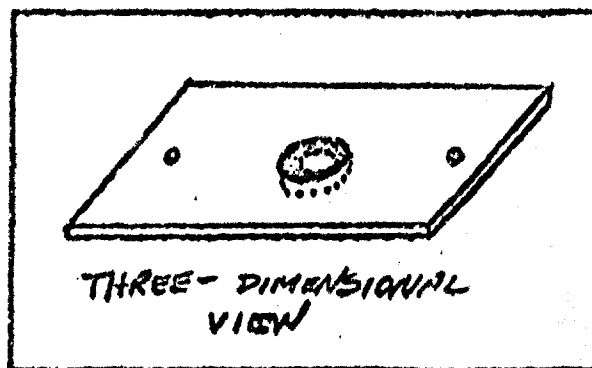
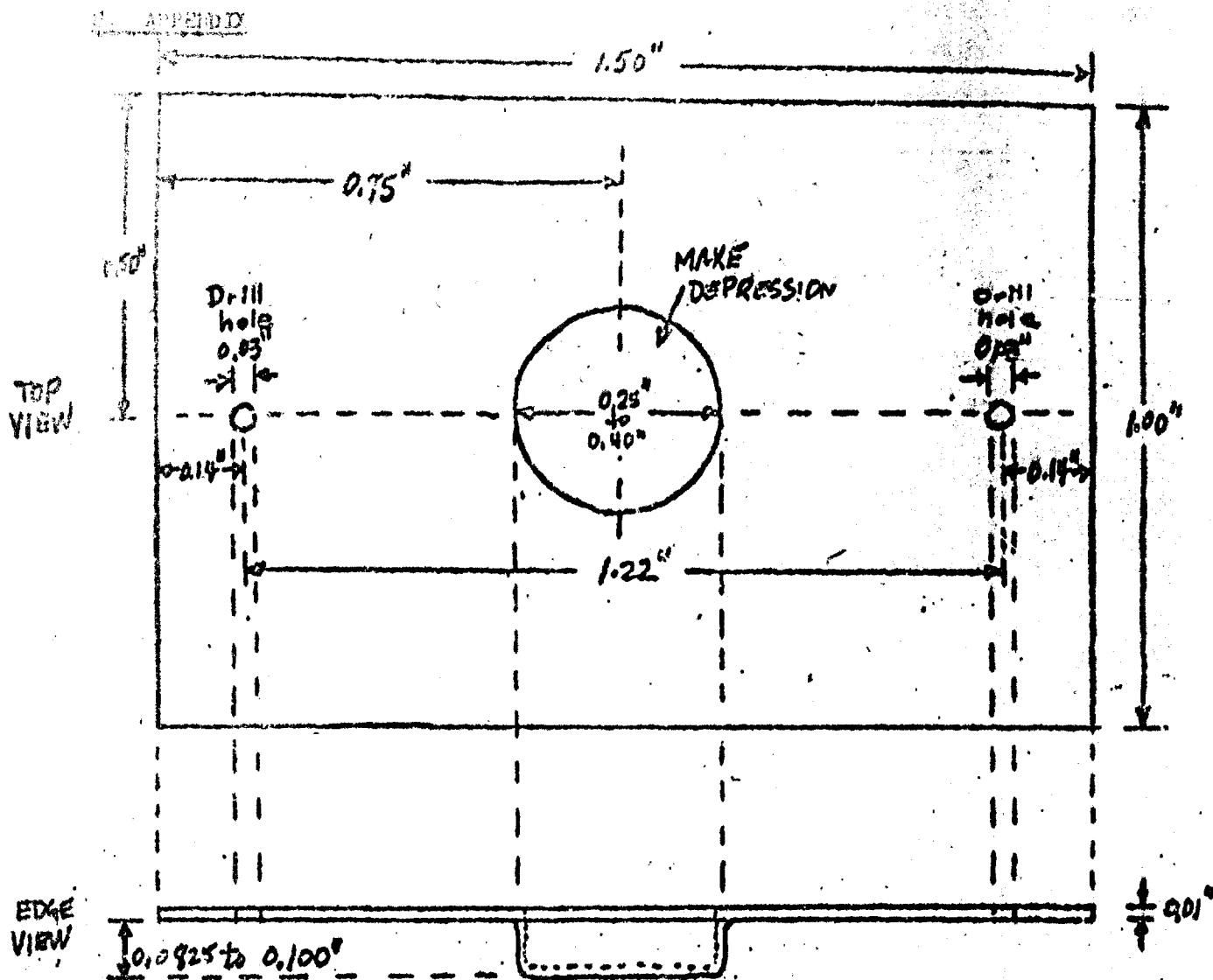
G-agents received for study have been properly transferred and now await detailed investigations.

Energetic studies by either appearance potentials or cleavage patterns have been made for the positive ions from O,O,O-triethyl phosphorothionate and methylthiophosphonic dichloride.

7. LITERATURE CITED

- (1) J. W. Warren, Nature, **165**, 810 (1950).
- (2) F. P. Lossing, A. W. Tickner, and W. A. Bryce, J. Chem. Phys., **19**, 1254 (1951).

- (3) R. W. Kiser and E. J. Gallegos, J. Phys. Chem., **66**, 947 (1962).
- (4) M. Haimann and Y. Klein, J. Chem. Soc., **1964**, 4324.
- (5) Y. Wada, Doctoral Dissertation, Kansas State University, 1964.
- (6) D. A. Bafus, E. J. Gallegos and R. W. Kiser, J. Phys. Chem., **70**, 2614 (1966).



MATERIAL OF CONSTRUCTION:
STAINLESS STEEL

FIGURE 1.
POLONIUM-210 SOURCE PLATE FOR USE IN MASS SPECTROMETER.

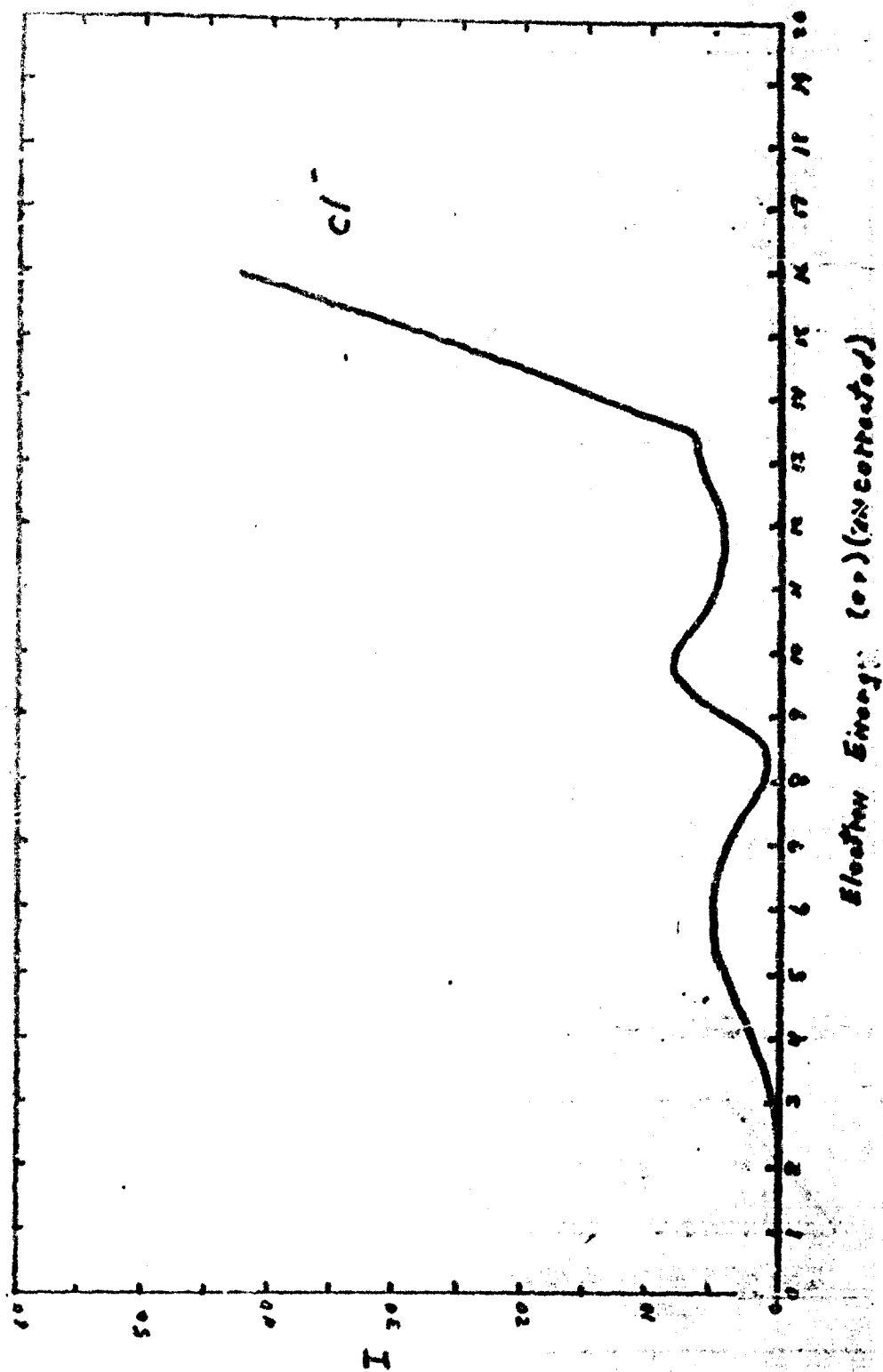


Figure 2. Ionization Efficiency Curve for Cl^- from $\text{CH}_3\text{P(S)Cl}_2$.

Table 1. Preliminary Electron Impact Data for the Positively-Charged Ions from O,O,O-Triethyl Phosphorothionate.

<u>Ion</u>	<u>m/q</u>	<u>Relative Abundance</u>	<u>Appearance Potential (ev)*</u>
$C_2H_3^+$	27	56.4	19.0
$C_2H_5^+$	29	100.0	17.5
$OC_2H_5^+$	45	37.2	15.2
$P(OH)_2^+$	65	64.0	15.2
$OP(OH)_2^+$	81	26.7	15.7
$P(OH)(OC_2H_5)^+$	93	45.3	13.0
$SP(OH)_2^+$	97	56.4	15.3
$PO(OH)(OC_2H_5)^+$	109	30.2	12.7
$P(OC_2H_5)_2^+$	121	59.3	11.4
$SP(OC_2H_5)_3^+$	198	47.7	7.5

*) Determined by the energy compensation technique (3).

Table 2. Principal Positively-Charged Ionic Species Found in the Mass Spectrum of O-Ethyl-N,N-dimethylphosphoramidocyanidate.

m/g	Ion	Relative Abundance	m/g	Ion	Relative Abundance
15	CH_3^+	25.3	90	$\text{P(O)N(CH}_3)(\text{CH}_2)^+$	2.0
26	C_2H_2^+	4.6	91	$\text{P(O)N(CH}_3)_2^+$	1.8
27	C_2H_3^+	22.2	92	$\text{P(OH)N(CH}_3)_2^+$	2.0
29	C_2H_5^+	24.5	93	$\text{HP(OH)N(CH}_3)_2^+$	1.8
31	P^+	2.0	106	$\text{P(O)}_2\text{N(CH}_3)(\text{CH}_2)^+$	4.8
41		3.6	107	$\text{P(O)}_2\text{N(CH}_3)_2^+$	4.8
42		50.0	108	$\text{P(O)(OH)N(CH}_3)_2^+$	7.9
43		100.0	117	$\text{P(O)(CN)N(CH}_3)_2^+$	5.4
44		85.7	133	$\text{PO}_2(\text{CN)N(CH}_3)_2^+$	14.5
45		14.5	134	$\text{PO(OH)(CN)N(CH}_3)_2^+$	5.1
47	PO^+	12.0	135	$\text{P(OH)}_2(\text{CN)N(CH}_3)_2^+$	3.3
65	P(OH)_2^+	4.3	136	$\text{P(OH)}_2(\text{HCN)N(CH}_3)_2^+$	2.3
69		4.1	147	$\text{C}_2\text{H}_5\text{OPO(CN)N(CH}_3)_2^+$	1.3
70		45.9	162	$\text{C}_2\text{H}_5\text{OPO(CN)N(CH}_3)_2^+$	9.7
71		5.6			

Table 3. Comparison of the Mass Spectra of Triethyl Phosphate (6) with O,O,O-Triethyl Phosphorothionate.

OP(OC ₂ H ₅) ₃			SP(OC ₂ H ₅) ₃		
m/q	Ion	Relative Abundance	m/q	Ion	Relative Abundance
29	C ₂ H ₅ ⁺	25.0	27	C ₂ H ₃ ⁺	56.4
45	C ₂ H ₅ ⁺	45.4	29	C ₂ H ₅ ⁺	100.0
81	PO(OH) ₂ ⁺	78.3	45	C ₂ H ₅ O ⁺	37.2
82	P(OH) ₃ ⁺	47.0	47	PO ⁺	16.3
83	HP(OH) ₃ ⁺	14.4	65	HPO(OH) ⁺	64.0
99	P(OH) ₄ ⁺	100.0	81	PO(OH) ₂ ⁺	26.7
109	OP(OH)(OC ₂ H ₅) ⁺	49.3	93	P(OH)(OC ₂ H ₅) ⁺	45.3
110	P(OH) ₂ (OC ₂ H ₅) ⁺	9.2	97	SP(OH) ₂ ⁺	56.4
111	OP(OH) ₂ (OC ₂ H ₅) ⁺	10.4	109	OP(OH)(OC ₂ H ₅) ⁺	30.3
125	PO ₂ (OH)(OC ₂ H ₅) ⁺	19.7	114	SP(OH) ₃ ⁺	24.4
126	PO(OH) ₂ (OC ₂ H ₅) ⁺	5.7	115	HSP(OH) ₃ ⁺	32.6
127	P(OH) ₃ (OC ₂ H ₅) ⁺	47.0	121	P(OC ₂ H ₅) ₂ ⁺	59.3
137	PO(OC ₂ H ₅) ₂ ⁺	11.4	137	PO(OC ₂ H ₅) ₂ ⁺	6.7
138	P(OH)(OC ₂ H ₅) ₂ ⁺	10.6	143	(HS)P(OH) ₂ (OC ₂ H ₅) ⁺	18.6
149	HP(OH)(OC ₂ H ₅) ₂ ⁺	8.3	153	SP(OC ₂ H ₅) ₂ ⁺	9.9
155	P(OH) ₂ (OC ₂ H ₅) ₂ ⁺	68.0	154	SP(H)(OC ₂ H ₅) ₂ ⁺	14.5
167	PO(OCH ₂)(OC ₂ H ₅) ₂ ⁺	6.1	170	SP(OH)(OC ₂ H ₅) ₂ ⁺	17.4
182	PO(OC ₂ H ₅) ₃ ⁺	26.0	198	PS(OC ₂ H ₅) ₃ ⁺	47.7

Table 4. Partial Electron Impact Data for Positive and Negative Ions
Produced from Methylthiophosphonic Dichloride.^a

Ion	m/g	Relative Appearance		Probable Process	$\Delta H_f(\text{ion})$ (kcal/mole)
		Abundance	Potential (ev)		
CH_3^+	15	13.7	16.92 ± 0.20	$\text{CH}_3\text{PSCl}_2 \rightarrow \text{CH}_3^+ + \text{PS} + \text{Cl}_2$	267
P^+	31	15.6			
PC^+	43	8.0			
PCH^+	44	16.2			
PCH_2^+	45	47.5	15.49 ± 0.18	$\rightarrow \text{PCH}_2^+ + \text{SH} + \text{Cl}_2$	235
PCH_3^+	46	6.3			
PS^+	63	32.5	15.45 ± 0.32	$\rightarrow \text{PS}^+ + \text{CH}_3 + \text{Cl}_2$	233
PCl^+	66	5.5			
CH_2PS^+	77	34.5	13.83 ± 0.29	$\rightarrow \text{CH}_2\text{PS}^+ + \text{HCl} + \text{Cl}$	221
CH_3PCl^+	81	4.2			
SPCl^+	98	4.3			
PCl_2^+	101	6.4			
CH_3PSCl^+	113	100.0	11.87 ± 0.28	$\rightarrow \text{CH}_3\text{PSCl}^+ + \text{Cl}$	154
SPCl_2^+	133	10.5	12.57 ± 0.28	$\rightarrow \text{SPCl}_2^+ + \text{CH}_3$	167
$\text{CH}_3\text{PSCl}_2^+$	146	61.5	9.95 ± 0.36	$\rightarrow \text{CH}_3\text{PSCl}_2^+$	158
Cl^-	35	100.0 ^b			
PCl^-	43	13.0 ^b			
PCH_2^-	44	1.1			

(a) An estimated $\Delta H_f[\text{CH}_3\text{PSCl}_2(\text{g})] = -91 \text{ kcal mole}^{-1}$ has been employed in these calculations.

(b) These values are related to each other, but not to the others in this column.

Table 5. Principal Positively-Charged Ionic Species Found in the Mass Spectrum of Chloromethylphosphonic Dichloride.

m/z	Ion	Relative Abundance (70 eV)
12	C^+	6.2
13	CH^+	10.4
14	CH_2^+	?
31	P^+	29.8
35	Cl^+	?
43	PC^+	7.6
44	PCH^+	21.8
45	PCH_2^+	11.4
47	PO^+	?
66	PCl^+	45.6
67	$HPCl^+$	6.3
82	$POCl^+$	18.8
83	$POHCl^+$	25.0
101	PCl_2^+	46.2
117	$POCl_2^+$	79.2
130	$HCPOCl_2^+$	11.6
131	$H_2CPOCl_2^+$	31.4
136	PCl_3^+	100.0
166	$ClH_2CPOCl_2^+$	80.6

1. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
2. GROUP N/A		
3. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
4. GROUP N/A		
5. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
6. GROUP N/A		
7. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
8. GROUP N/A		
9. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
10. GROUP N/A		
11. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
12. GROUP N/A		
13. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
14. GROUP N/A		
15. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
16. GROUP N/A		
17. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
18. GROUP N/A		
19. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
20. GROUP N/A		
21. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
22. GROUP N/A		
23. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
24. GROUP N/A		
25. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
26. GROUP N/A		
27. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
28. GROUP N/A		
29. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
30. GROUP N/A		
31. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
32. GROUP N/A		
33. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
34. GROUP N/A		
35. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
36. GROUP N/A		
37. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
38. GROUP N/A		
39. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
40. GROUP N/A		
41. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
42. GROUP N/A		
43. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
44. GROUP N/A		
45. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
46. GROUP N/A		
47. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
48. GROUP N/A		
49. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
50. GROUP N/A		
51. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
52. GROUP N/A		
53. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
54. GROUP N/A		
55. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
56. GROUP N/A		
57. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
58. GROUP N/A		
59. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
60. GROUP N/A		
61. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
62. GROUP N/A		
63. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
64. GROUP N/A		
65. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
66. GROUP N/A		
67. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
68. GROUP N/A		
69. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
70. GROUP N/A		
71. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
72. GROUP N/A		
73. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
74. GROUP N/A		
75. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
76. GROUP N/A		
77. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
78. GROUP N/A		
79. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
80. GROUP N/A		
81. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
82. GROUP N/A		
83. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
84. GROUP N/A		
85. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
86. GROUP N/A		
87. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
88. GROUP N/A		
89. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
90. GROUP N/A		
91. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
92. GROUP N/A		
93. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
94. GROUP N/A		
95. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
96. GROUP N/A		
97. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
98. GROUP N/A		
99. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		
100. GROUP N/A		

DD FORM 1473

UNCLASSIFIED
Security Classification