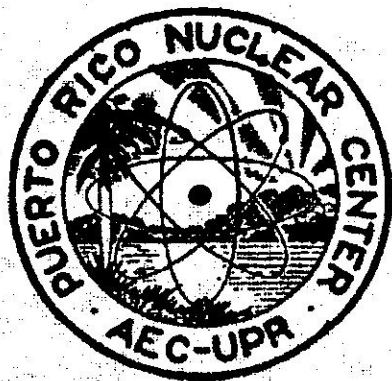


PUERTO RICO NUCLEAR CENTER

HOT-ATOM CHEMISTRY PROGRAM
PROGRESS SUMMARY REPORT NO. I
JULY, 1964 - MAY, 1966



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HOT-ATOM CHEMISTRY PROGRAM
PROGRESS SUMMARY REPORT NO. 1

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INTRODUCTION

While considerable attention has been paid to the chemical reactions accompanying nuclear transformations involving carbon atoms and tritium, very little work has been published on other atoms.

The initial purpose of this program was to study hot-atom reactions in organic compounds with multiple covalent bonds between carbon and activated atoms. Aromatic compounds were first used, since it was anticipated that they would prove more resistant to radiolysis.

Nuclear reactions of the n, γ type have been employed, the samples being activated in the PRNC swimming pool reactor. A number of analytical procedures were studied. These included column, paper, ion-exchange, thin-layer and vapor phase chromatography, and paper and thin-layer electrophoresis. Classical precipitation methods were also employed.

Our work in hot atom chemistry has been carried on at the academic level since July 1964. During this period, results were obtained which justified formalizing the research as a program. Support for the program from OS funds began in April 1966.

Phosphorus Compounds

Only brief and incomplete studies have been reported (1,2) on the hot-atom reactions in organic compounds with carbon-phosphorus bonds, during the reaction $^{31}\text{P} (n, \gamma) ^{32}\text{P}$. We have now completed

a detailed study of the products formed in the thermal neutron activation of triphenylphosphine, triphenylphosphine oxide and tetraphenylphosphonium chloride, irradiated in vacuo in the solid state.

The activated samples were dissolved in chloroform and the chloroform solution washed with an aqueous solution of inorganic phosphorus anion carriers to remove the inorganic phosphorus-32. The organic phase was then washed with dilute sodium hydroxide solution containing organic phosphorus acids as carriers. Aliquots of the solutions were counted (see Table I) in a dipping-type thin wall Geiger counter.

The inorganic fraction was analyzed (see Table I) by electrophoresis (3,4) (see Graph I). Good separations could not be obtained by ion-exchange chromatography or by precipitation techniques. The organic acid fraction was analyzed by paper chromatography (see Table III) using either n-butanol-ammonium hydroxide (1:1) (see Graph II), or collidine saturated with water (see Graph III). The mixture of acids could not be separated by electrophoresis or ion-exchange chromatography. Retention was determined by evaporating the organic residue in chloroform, and then subliming it. Retentions found were 1.8 ± 0.4 and $3.5 \pm 0.2\%$, for triphenylphosphine and its oxide. However, the irradiated triphenylphosphine contained triphenylphosphine oxide (7%) and the sublimed material may be a mixture of both.

Phosphite and hypophosphite can arise from the reaction of trapped species such as P^+ and PO^+ with water. However, orthophosphate and the polyphosphates must be formed through complex

reactions of trapped ^{32}P species. The increased proportion of phosphite given by triphenylphosphine oxide suggests the intervention of oxygen in the compound to form PO^+ intermediates. Similarly, the larger amounts of phosphite and hypophosphite formed from tetraphenylphosphonium chloride is consistent with participation of chloride ions to form PCl^{2+} and PCl intermediates. The higher percentage of inorganic anions formed from this last compound indicates that chloride ion is a more efficient scavenger than oxygen. The organic acids must arise from recombination of a hot phosphorus atom with the phenyl radicals in the "hot-zone", to form cations such as PhP^+ and Ph_2PO^+ , which are hydrolyzed to the phosphorus acids. The higher proportion of organic acids formed from triphenylphosphine oxide suggests that oxygen stabilizes the PhP type intermediates. Tetraphenylphosphonium chloride affords a larger amount of diphenyl acids, probably due to the higher ratio of phenyl groups to phosphorus atoms in this compound.

Retention was found to be 1.8 and 3.5%, expectively, in triphenylphosphine and its oxide. However, the calculated retention based on a random walk model is 0.8%, and the increased amounts must be due to recombination.

This work is being extended to studies of these compounds in benzene solution, with an without the addition of radical scavengers. Annealing effects are also being studied, as are the ^{31}Si products formed in the $^{31}\text{P} (n,p) ^{31}\text{Si}$ reaction.

SULFUR COMPOUNDS

No work has been published on the neutron activation of organic

sulfur compounds. We have investigated the sulfur-35 products formed in the activation of diphenyl sulfide, sulfoxide and sulfone, via the reaction $^{34}\text{S}(n,\gamma)^{35}\text{S}$. The irradiated samples were dissolved in chloroform and the chloroform solution washed with water. The organic solution was then washed with dilute sodium hydroxide, to isolate the organic acid fractions. Aliquots of each fraction were evaporated and counted (see Table IV). Activation of diphenyl sulfide (m.p. -50°) at -80° gave a similar distribution, but less activity was recovered from the walls of the vessel.

The inorganic anions were analyzed (see Table V) by dividing the extract into 5 fractions, adding the appropriate carrier, passing through activated charcoal to remove other anions, oxidizing with hydrogen peroxide and precipitating the sulfur-35 as barium sulfate. The elemental sulfur was determined by extraction with carbon disulfide in the presence of sulfur carrier, evaporating the extract and oxidizing the sulfur to sulfate with nitric acid. The decrease in the proportion of sulfite with an increase in the amount of sulfate or thiosulfate in the cases of the sulfoxide and sulfone is consistent with the initial formation of S^{4+} and SO^{2+} intermediates. These then react with water to afford sulfite, or are oxidized in the crystal to other intermediates (e.g. $\text{S}^{\ominus 4+}$ and SO_2^{2+}) which afford sulfate.

The organic acid fraction was analyzed by paper chromatography (see Table VI). Retention was found to be 3.4, 6.0 and 2.2%, respectively, for the sulfide, sulfoxide and sulfone, by distillation of the organic residue in the first case and sublimation in the others.

This work is being continued by investigating the inorganic phosphorus-32 anions formed via the $^{32}\text{S}(n,p)^{32}\text{P}$ reaction. Experiments in solution will also be carried out.

MERCURY COMPOUNDS

The neutron activation of diphenylmercury has been reported (3) to lead to 80% retention of the activity in the organic phase. Diphenylmercury, phenylmercuric chloride and phenylmercuric acetate were studied in detail. Diphenylmercury was activated for 10 minutes and the irradiated sample processed by dissolving in benzene and chromatography on alumina. Diphenylmercury-203 accounted for 83% of the activity and 0.2% was found as phenylmercuric acetate. Activation for 2 hours gave 34.3% inorganic 203-Hg. Of the organic fraction 88.5% of the activity was as diphenylmercury. However, if the sample was allowed to stand in benzene after activation for 2 hours, 17% of the activity was in an insoluble fraction, only 1% as diphenylmercury and 97% as radiochemically pure phenylmercuric acetate. Activation in benzene solution resulted in much activity (79%) on the walls of the vessel and the rest as diphenylmercury-203. These results suggest that high retention occurs in diphenylmercury, but that exchange occurs readily in the unpurified material.

Similarly, phenylmercuric chloride afforded 14.4% retention and 24.8% diphenylmercury, while phenyl mercuric acetate gave 97% retention.

Other Research Problems

Studies have been initiated the reaction $^{209}\text{Bi} (n, \gamma) ^{210}\text{Bi}$ in triphenyl bismuth, and diphenyl bismuth chloride, and on the reactions $^{124}\text{Sn} (n, \gamma) ^{125}\text{Sn} \xrightarrow{\beta} ^{125}\text{Sb}$ in tetraphenyl tin and related compounds. Other work concerns the $^{203}\text{Tl} (n, \gamma) ^{204}\text{Tl}$ reaction in diphenylthallium chloride and phenylthallium dichloride. The radioactive products were separated by chromatography on alumina.

New Equipment

Transistorized scalers have been purchased to replace the older, worn-out vacuum tube equipment. A liquid scintillation system has also acquired.

A special laboratory reserved for work with radioactive gases has been equipped with a ~~four~~-~~daught~~ canopy. A radio-gas chromatographic system is being assembled under this canopy, and this will included a digital recording system.

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TABLE I

PHOSPHORUS-32 FRACTIONS

<u>Compound</u>	<u>Inorganic</u> ^a	<u>Organic Acids</u> ^b	<u>Residue</u> ^c
Ph ₃ P	7.9 ± 1.4	9.5 ± 1.3	82.6 ± 3.4
Ph ₃ PO	15.8 ± 4.8	31.1 ± 3.0	53.2 ± 4.7
Ph ₄ PCl	28.0 ± 0.9	15.0 ± 2.4	57.0 ± 1.6

^aExtracted with water. ^bExtracted with 5%NaOH. ^cResidue in chloroform.

TABLE II

ANALYSIS OF INORGANIC FRACTION^a

<u>Anion</u>	<u>Ph₃P</u>	<u>Ph₃PO</u>	<u>Ph₄POI</u>
Polyphosphate	14.3 ± 1.3	2.8 ± 0.7	11.5 ± 0.2
Orthophosphate	34.7 ± 1.0	38.5 ± 0.2	36.2 ± 1.3
Diphosphite	16.7 ± 0.3	20.3 ± 0.8	12.8 ± 2.3
Phosphite	5.9 ± 0.4	26.7 ± 0.4	21.8 ± 1.6
Hypophosphite	6.1 ± 1.6	9.7 ± 0.1	13.3 ± 1.1
Totals	77.7	98.0	95.6

1
∞
1

^a Separation by electrophoresis.

TABLE III
ANALYSIS ORGANIC ACID FRACTION^a

Acid	Ph ₃ P		Ph ₃ PO		Ph ₄ PCl	
	A	B	A	B	A	B
Phenylphosphonic	16.7 ± 0.4	17.4 ± 0.3	16.8 ± 0.5	19.4 ± 0.0	14.9 ± 0.9	16.8 ± 0.4
Diphenylphosphonous	14.6 ± 0.8	20.2 ± 0.9	15.9 ± 0.3	18.6 ± 0.5	17.8 ± 0.6	18.1 ± 0.2
Phenylphosphinic	18.6 ± 0.5	20.8 ± 0.8	23.1 ± 0.8	25.2 ± 1.1	13.6 ± 0.8	15.0 ± 0.1
Diphenylphosphinic	19.8 ± 0.7	23.4 ± 0.4	21.0 ± 0.1	23.6 ± 1.2	26.5 ± 0.3	27.1 ± 0.2
Totals	69.7	81.8	76.8	86.8	72.8	77.0

^a A in 1:1 n-butanol-ammonium hydroxide. B in collidine-water

TABLE IV
SULFUR-35 FRACTIONS

<u>Compound</u>	<u>Inorganic</u>	<u>Organic Acids</u>	<u>Residue</u>
Ph ₂ S	51	16	33
Ph ₂ SO	39	46	15
Ph ₂ SO ₂	48	17	35

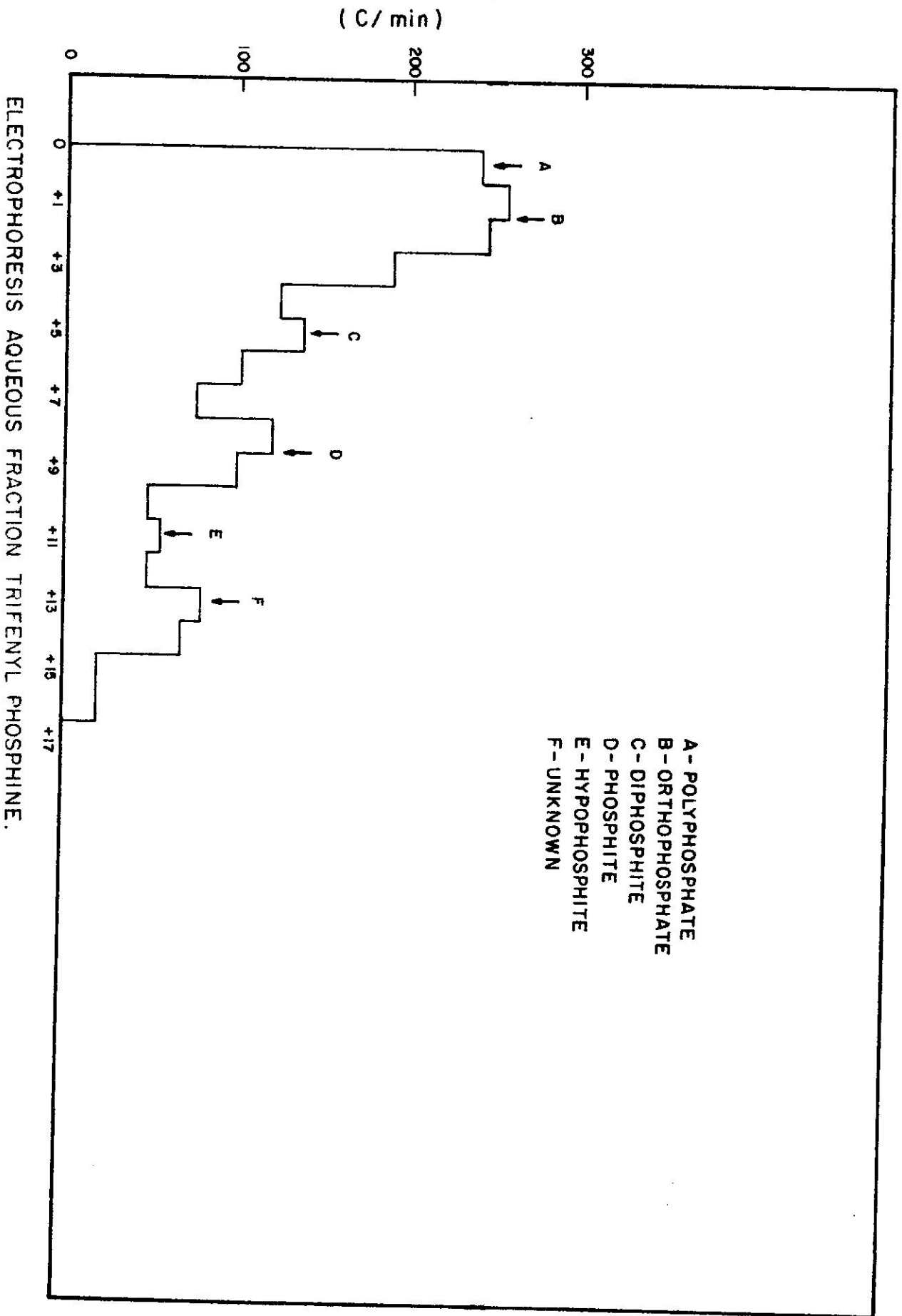
TABLE V
ANALYSIS OF INORGANIC FRACTION

<u>Anion</u>	<u>Ph₂S</u>	<u>Ph₂SO</u>	<u>Ph₂SO₂</u>
Sulfate	22	11	26
Sulfite	30	9	9
Sulfide	9	14	16
Thiosulfate	15	49	33
Sulfur	24	17	11

TABLE VI

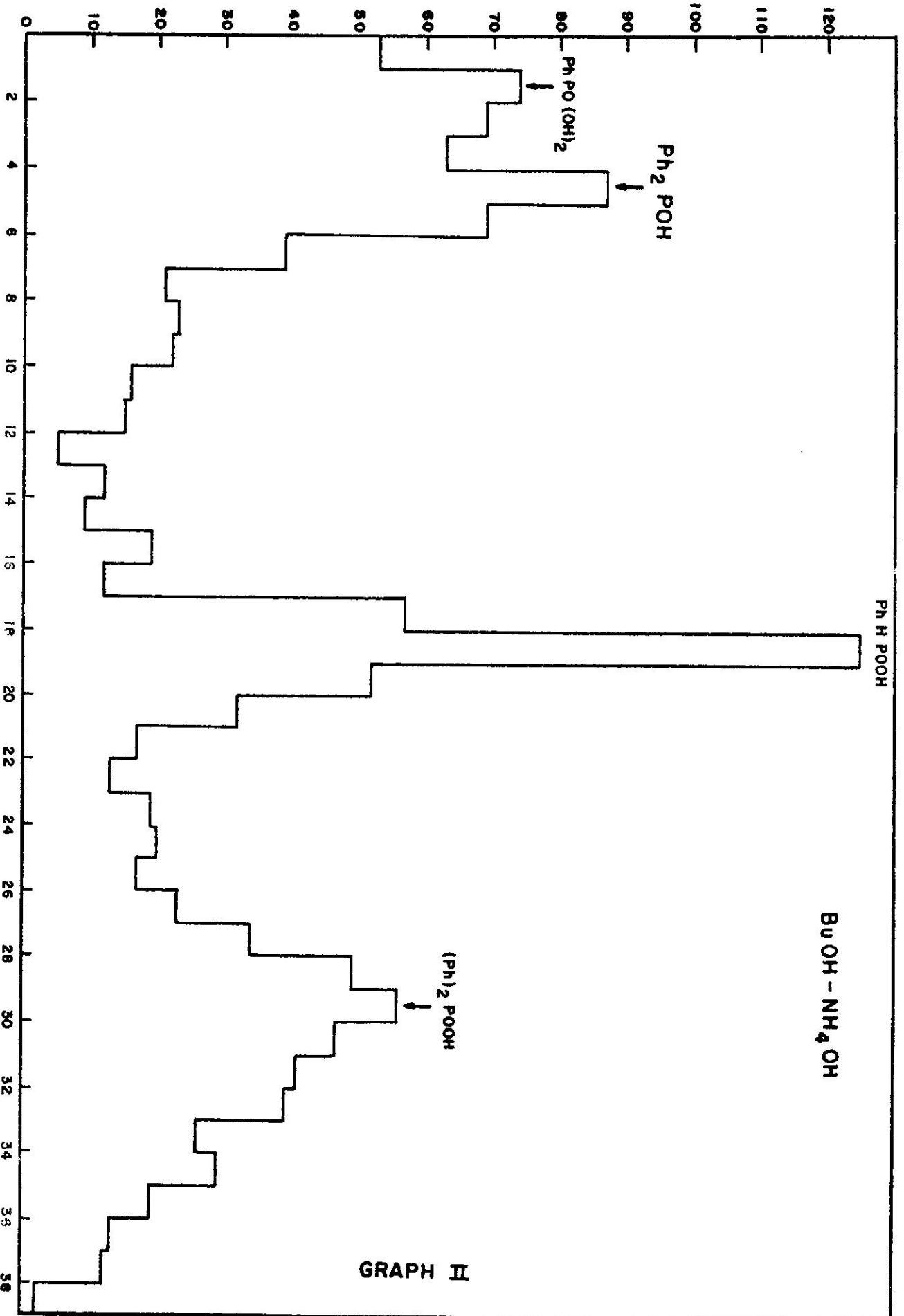
ANALYSIS OF ORGANIC ACID FRACTION

<u>Acid</u>	<u>Ph₂SO</u>	<u>Ph₂SO₂</u>
Benzenesulfinic	15	48 .
Benzenesulfonic	27	17
Phenylphosphinic	30	8
Phenylphosphonic	16	-
Totals	<u>78</u>	<u>73</u>



GRAPH I

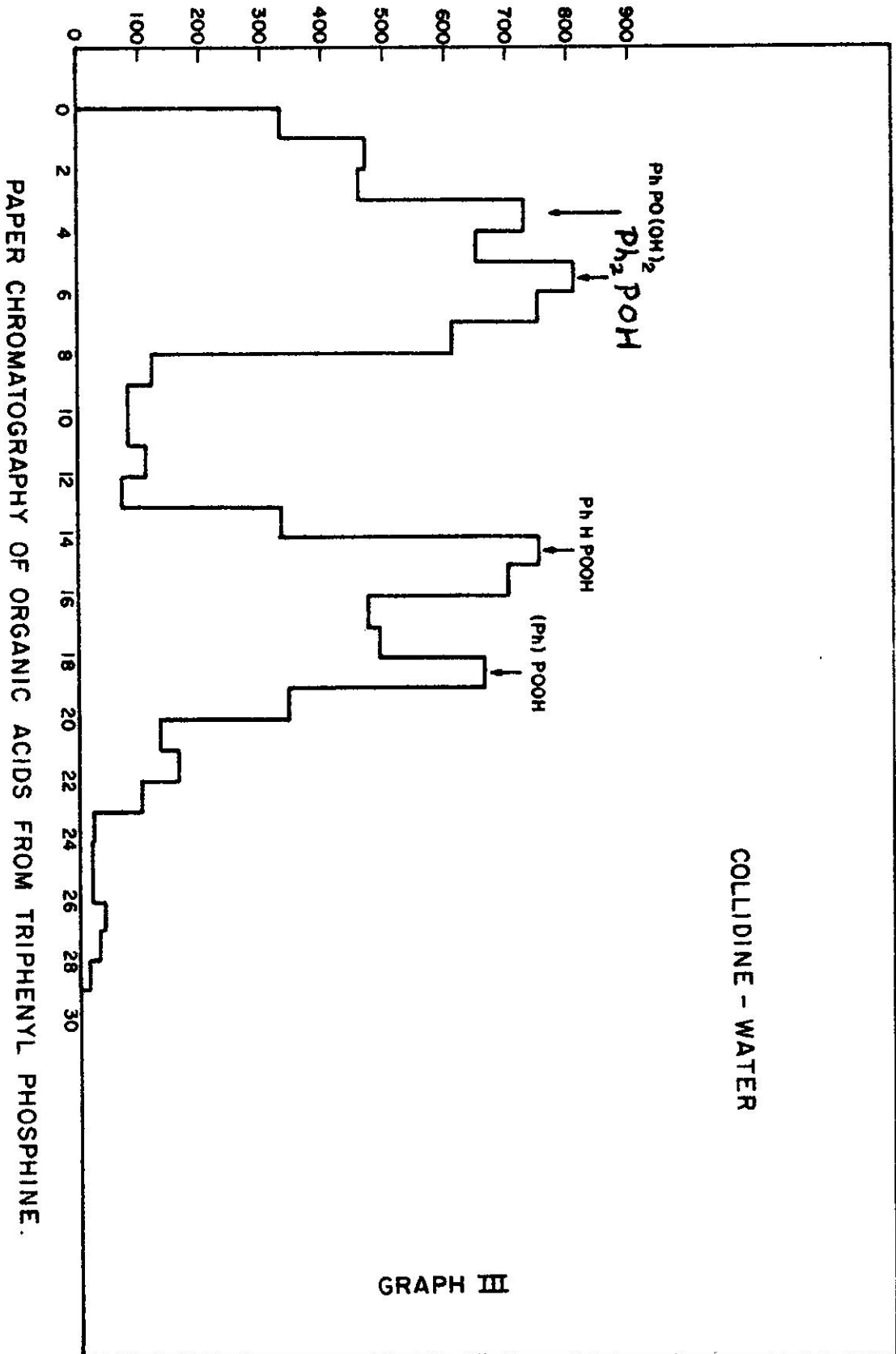
-14- (C/min)



PAPER CHROMATOGRAPHY OF ORGANIC ACIDS FROM TRIPHENYL PHOSPHINE.

GRAPH II

-15-
c/min.



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