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THE REACTION OF ANHYDROUS HYDROGEN FLUORIDE WITH VARIOUS PHOSPHATES OF URANIUM

By

D. W. KUHN

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RESEARCH AND DEVELOPMENT DIVISION
Dr. E. D. Shipley, Director

CHEMICAL DEVELOPMENT DEPARTMENT
Mr. G. H. Clewett, Superintendent

THE REACTION OF ANHYDROUS HYDROGEN FLUORIDE WITH VARIOUS PHOSPHATES OF URANIUM

Abstract

The reactions of anhydrous hydrogen fluoride with uranyl ammonium phosphate, uranyl hydrogen phosphate, and uranous oxypyrophosphate at 400 - 500°C have been studied with the purpose of identifying the volatile reaction products. It has been found that in such hydrofluorination reactions the phosphorus is evolved as either PF_5 or HPF_6, and can be collected as an HPF_6 solution by cooling the effluent gases.

In addition, several experiments have been performed which were designed to show how much hydrogen fluoride can be recovered from the product gases for recycle. Data from distillation experiments for recovery of hydrogen fluoride are included in this report.

D. W. Kuhn

Oak Ridge, Tennessee
November 17, 1949

[redacted]

THE REACTION OF ANHYDROUS HYDROGEN FLUORIDE WITH VARIOUS PHOSPHATES OF URANIUM

INTRODUCTION

The problem of identifying the volatile products formed when uranyl ammonium phosphate reacts with anhydrous hydrogen fluoride was undertaken in this laboratory in November, 1948. The results of the early work were presented in report number Y-323[1]. Considerable additional information has been acquired over a period of eight months, and the results and conclusions to be obtained from this work are presented here.

The experiments will be divided into two categories:

I. Identification of products from the laboratory-scale reaction of HF with several uranium phosphates.

II. Distillation experiments concerning recovery of HF from the effluent gases of the pilot plant for the conversion of uranyl ammonium phosphate to uranium tetrafluoride.

EXPERIMENTAL RESULTS

I. Identification of Products from the Laboratory-Scale Reaction of HF with Several Uranium Phosphates

Most of the experiments concerned with identifying the products of a hydrofluorination reaction were carried out in similar fashion. The

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[1] Kuhn, D. W., "Identification of the Reaction Products in the Hydrofluorination of Uranyl Ammonium Phosphate", C&CCC - Y-12, Y-323, January 11, 1949.

uranium phosphate, contained in a gold boat, was placed within a horizontal monel tube in a tube furnace, and anhydrous hydrogen fluoride passed through the reactor. The effluent gases were passed through a series of traps which were maintained at various controlled temperatures. A detailed description of the apparatus may be found in report Y-323. In the first eight experiments, uranyl ammonium phosphate was employed as the charge material. Then twelve runs were completed in which uranyl hydrogen phosphate was used. In addition, three experiments were run in which the charge was the tetravalent uranium compound, $(UO)_2P_2O_7$.

In the earlier work on this problem, it was noted that a large percentage of the volatilized phosphorus was not recovered in the trapping system. With further experience in the handling of trap liquids, it was found that more than 90 percent of the phosphorus could be accounted for at the end of a carefully performed hydrofluorination run. The earlier losses of phosphorus probably occurred at the conclusion of the run, when the trap liquids were being transferred and diluted so as to be in a form easily handled by the analytical laboratory. Run No. 12 was carried out chiefly as an attempt to secure a good recovery of phosphorus. Following the reactor there were just two traps, the first immersed in a bath of boiling water and the second in a bath of liquid nitrogen. This latter trap was of stout construction, and was equipped with valves so that both inlet and outlet tubes could be closed off as desired. A concentrated solution of sodium hydroxide was placed in the bottom of the cold trap so that the liquid level was below the dip tube and hence did not block the flow of gas through the trap. The duration of the flow of HF was limited to one hour in order not to exceed the

capacity of the alkali in the trap. At the conclusion of the hydrofluorination, the cold trap was closed off tightly before being allowed to warm up to room temperature. The alkaline solution could then be washed out and diluted with no loss by fuming. The first trap was cooled to 0°C and crushed ice was added to the contents in order to dilute the sample without loss by fuming. The results obtained in this experiment are shown in the following table.

Table 1

Run: 12
Charge: UO_2HPO_4
Gaseous Reagent: HF

	Wt. P g	Wt. F g
1st trap	0.243	0.118
2nd trap	0.139	59.4
Residue in boat	0.595	1.60
Totals	0.977	61.1

Wt. P in original charge 1.06 g.

P recovery 92 %

The practice of cooling a trap to 0°C or below and adding ice before transferring trap liquids was used quite generally in later work.

Having shown that the phosphorus could be collected in the trapping system, there remained the problem of identifying the form in which the phosphorus appeared as a reaction product. The chief obstacle in the way of such a determination is the fact that the effluent gas from the HF reactor is principally unreacted hydrogen fluoride, and it was found

difficult to isolate a phosphorus-containing portion of the products without at the same time including considerable quantities of hydrogen fluoride. Several methods for separating the reaction product components were tried. The first method, that of fractional condensation, involved passing the reaction products through a series of traps, each at a given temperature, the first trap being the warmest and the last the coldest of the series. Several fractional distillation experiments were also attempted, in which all of the gases were first condensed, then fractionally distilled. A combination of these two methods was also tried. Another idea was to use KF or NaF to remove HF from the gas mixture, allowing only fluorides of phosphorus to pass through this KF absorber. Since water vapor is one of the reaction products, and since PF_5, POF_3, and the fluorophosphoric acids will react with water, attempts were made to dry the effluent gases with "Drierite" in order to minimize the hydrolysis reactions. Fractional condensation and distillation methods were found most helpful, while the use of KF, NaF and "Drierite" did not work out as planned. It had been hoped that KF or NaF would absorb all of the HF from a gas mixture, while absorbing none of the phosphorus fluorides. However, phosphorus compounds were absorbed by the alkali fluorides, and in addition some of the HF passed through unabsorbed so that the ratio of fluorine to phosphorus in the gas was actually increased by passing the gas through the alkali fluoride absorber. "Drierite" was found to absorb fluorine and phosphorus compounds along with water.

Results from five of the experiments involving fractional condensation and fractional distillation are given to show where the phosphorus

is ordinarily found in the trapping system.

Table 2

Run: 9
Charge: UO_2HPO_4
Gaseous Reagent: HF

Trap System: 1st trap, 100°C; 2nd trap, 0°C; 3rd trap, -196°C.
At conclusion of HF reaction, 3rd trap was warmed to 0°C and distillate from 3rd trap collected in a 4th trap at -196°C.

	Wt. P g	Wt. F g
1st trap, 100°C	0.570	1.53
2nd trap, 0°C	0.887	425.
3rd trap, -196°C	0.122	4.03
4th trap, distillate from 3rd trap	0.642	21.1
Reactor Flange and Tube Wash	0.357	2.69
Residue in Boat	0.691	6.55
Totals	3.269	461.

Wt. P in original charge 4.25 g

P Recovery 77 %

Table 3

Run: 18
Charge: UO_2HPO_4
Gaseous Reagent: HF

Trap System: 1st trap with no regulation of temperature; packed column, 18" long, 2-1/2" diameter, top of column operated at 15°C, liquid from column drained into 1st trap, vapor out top of column to 2nd trap; 2nd trap, -78°C. At end of run, last trap was replaced with a third trap at dry ice temperature, and the contents of 1st trap heated to 45°C. Column was not cooled during last distillation.

	Wt. P g	Wt. F g
1st trap (after distillation)	0.95	12.94
2nd trap, -78°C	0.007	1.98
3rd trap, (distillate from 1st trap)	0.021	83.2
Residue in boat	0.532	2.52
Totals	1.51	100.6

Wt. P in original charge 2.14 g

P recovery 71 %

Table 4

Run: 19
Charge: UO_2HPO_4
Gaseous Reagent: HF

Trap System: 1st trap at 50°C; 2nd trap at 0°C; packed column above 2nd trap, top of column maintained at 5°C; 3rd trap at -78°C.

	Wt. P g	Wt. F g
1st trap, 50°C*	1.02	7.70
2nd trap, 0°C	0.056	179.
3rd trap, -78°C	0.003	0.11
Residue in boat	0.776	1.94
Totals	1.86	189.

Wt. P in original charge 2.14 g

P Recovery 87 %

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* Nitron ppt. showed 0.16 grams of P in 1st trap as HPF_6.

Table 5

Run: 22
Charge: $(UO)_2P_2O_7$
Gaseous Reagent: HF

Trap System: 1st trap at 90°C; 2nd trap at 60°C; 3rd trap at 30°C. Effluent gases from 3rd trap were not collected.

	Wt. P Total g	Wt. P in Nitron ppt* g	Wt. P in Nitron ppt / Wt. P (total) x100	Wt. F g
1st trap, 90°C	1.06	0.374	35	5.94
2nd trap, 60°C	0.40	0.302	76	13.8
3rd trap, 30°C	0.07			30.5
Reactor Flange and Tube Wash	0.15			3.6
Residue in Boat	0.83			5.92
Totals	2.51			

Wt. P in original charge 2.76 g

P recovery 91 %

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* Analysis of nitron ppt. 90° trap 5.89% P, 22.8% F, F/P atom ratio 6.3.

Analysis of nitron ppt. 60° trap 5.53% P, 22.4% F, F/P atom ratio 6.6.

Theoretical for $C_{20}H_{16}N_4HPF_6$ 6.76% P, 24.9% F.

Table 6

Run: 24
Charge: $(UO)_2P_2O_7$
Gaseous Reagent: HF

Trap System: 1st trap, 100°C; 2nd trap, 50°C; 3rd trap, 0°C; at end of run, 3rd trap was connected to packed column with a 4th trap at -78°C for receiving distillate. 3rd trap heated in a water bath at 65 - 70°C for one hour.

	Wt. P Total g	Wt. P in Nitron ppt* g	Wt. P in Nitron ppt x100 / Wt. P (total)	Wt. F g
1st trap, 100°C	0.64	0.16	25	1.72
2nd trap, 50°C	0.11	0.064	58	24.3
3rd trap, 0°C (after distillation)	0.03			16.7
Distillate from 3rd trap	<0.001			53.8
Reactor Flange and Tube Wash	0.16			10.0
Residue in Boat	1.43			5.68
Totals	2.37			112.2

Wt. P in original charge 2.75 g

P Recovery 86 %

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* Analysis of nitron ppt., 100° trap 5.61% P, 25.4% F, F/P atom ratio 7.4.

Analysis of nitron ppt., 50° trap 5.56% P, 22.4% F, F/P atom ratio 6.6.

The "nitron precipitate" referred to in Tables 4, 5 and 6 is obtained by adding an acetic acid solution of nitron acetate (10 grams of nitron, $C_{20}H_{16}N_4$ + 90 grams of 5 percent acetic acid) to a neutralized portion of test solution. Nitron, a well known reagent for the determination of nitrate and perrhenate, will also form slightly soluble salts with hexafluorophosphoric acid and difluorophosphoric acid. According to Lange[1], the solubility of these precipitates is as follows: 9.2 mg of $C_{20}H_{16}N_4 \cdot HPF_6$ in 100 ml of water at 16.5°C, and 330. mg of $C_{20}H_{16}N_4HPO_2F_2$ in 100 ml of water at 18°C.

From the above and other data it has been found that HPF_6 was present in the trapping system. It is interesting to note the next to last column in Table 5 and Table 6. In Table 5, Run 22, it is seen that 35 percent of the P in the 90° trap solution was combined as HPF_6, while 76 percent of the P in the 60° trap solution was as HPF_6. Similar results are shown in Table 6. This trend might be interpreted in either of two ways. First, it might be supposed that there are two or more phosphorus-containing products entering the trapping system, one of which is more easily condensed than HPF_6, so that HPF_6 comes out in higher proportion at lower temperatures. A second inference might be that all of the phosphorus is initially condensed as an HPF_6 solution, but that hydrolysis within the trap proceeds faster at the higher temperature so that when the trap solutions are each cooled and sampled, less HPF_6 remains in the high temperature traps than in the low. The latter view is supported by data in the next section.

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[1] Lange, Ber., 61, 799-801 (1928)

II. Distillation Experiments Concerning Recovery of HF from the Effluent Gases of the UAP Pilot Plant

In estimating costs for large scale hydrofluorination work, it is important that some quantitative information be available on recovery of hydrogen fluoride from off-gases. Since large quantities of hydrofluorination off-gases were available from the uranyl ammonium phosphate (UAP) pilot plant operations carried on in Y-12 under the supervision of John Reece, this problem could be studied using the knowledge gained in the work described in the previous section. The latter had indicated that the bulk of the phosphorus-containing product can be condensed out of the off-gas in the neighborhood of room temperature, and that HF would be the principal component of the gas remaining uncondensed. It was assumed that such uncondensed HF might be suitable for recycle with no further treatment. Our phase of the investigation, therefore, centered about the recovery of HF from the condensate. The off-gases from the HF reactor in the pilot plant were passed through a water-jacketed pipe, cooled by running tap water. The temperature of the gas leaving the condenser was in the range 30 - 50°C. Samples of the condensate from this condenser were furnished to us on four occasions. In each case, a number of analytical tests were carried out and a sample of the liquid was subjected to fractional distillation.

The analytical data obtained for the four batches of condensate are given below.

Composition (percent)	Pilot Plant Run # 1 Condensate	Pilot Plant Run # 2 Condensate	Pilot Plant Run # 3 Condensate	Pilot Plant Run # 4 Condensate
P	5.86	4.96	6.09	8.38
F	63.9	54.8	52.0	59.6
H^+	2.43	2.25	1.88	2.15
HPF_6	26.5	23.4	23.5	36.7
H_3PO_4	<0.1	<0.1	1.43	<0.03

Using these figures, the composition of the condensate samples may be estimated as follows:

Composition (percent)	Pilot Plant Run # 1 Condensate	Pilot Plant Run # 2 Condensate	Pilot Plant Run # 3 Condensate	Pilot Plant Run # 4 Condensate
HF	45	38	35	32
HPF_6	27	23	24	37
$H_2PO_3F + HPO_2F_2$	<1.0	-	2.1	1.9
H_3PO_4	<0.1	<0.1	1.4	<0.03
H_2O (by difference)	27	39	38	29

It is seen that virtually all of the phosphorus in these solutions is combined as HPF_6. Furthermore, there were only two places for volatilized phosphorus compounds to appear in the pilot plant system, either in the condensate or in the uncondensed off-gas which was absorbed in a caustic scrubber. To show the relative amounts of phosphorus to be found in the condensate and in the caustic scrubber solution data for the 24-hour period during which pilot plant Run # 4 condensate was obtained are as follows: 450 grams P found in condensate, 52 grams

P in scrubber solution. This means that 90 percent of the volatilized phosphorus appeared in the condensate, and 93 percent of the phosphorus in the condensate was combined as HPF_6. This is the best evidence that we have to show that there is essentially just one phosphorus-containing reaction product, namely HPF_6. This conclusion is not incompatible with the findings of the laboratory work, since, in the pilot plant operation, the gases leaving the HF reactor were immediately cooled and the condensate was stored at room temperature. The high HF content of the condensate solution prevented hydrolysis of HPF_6, which would hydrolyze partially if dissolved in pure water, according to the following system of reversible reactions, until an equilibrium mixture was obtained.

$$HPF_6 + H_2O \rightleftharpoons PF_5 + HF + H_2O$$

$$PF_5 + H_2O \rightleftharpoons POF_3 + 2HF$$

$$POF_3 + H_2O \rightleftharpoons HPO_2F_2 + HF$$

$$HPO_2F_2 + H_2O \rightleftharpoons H_2PO_3F + HF$$

$$H_2PO_3F + H_2O \rightleftharpoons H_3PO_4 + HF$$

Since HF is a product of each of these reactions in the forward direction, an initially high concentration of HF would mean that only small amounts of the other hydrolysis products would be present in the equilibrium mixture. Referring again to Table 5 and Table 6, it is seen that 35 percent and 25 percent of the P in the hot traps (90° and 100°C) were later found to be HPF_6. The original product in both cases may have been just HPF_6, which was partially hydrolyzed during the experiment. There are two factors which make the rate of hydrolysis in these solutions greater than in the pilot plant liquids. First, the

trap solutions were maintained at 90°C for two hours in Run 22 (see page 10), and 100°C for 1-1/2 hours in Run 24 (see page 11), while the pilot plant condensates were at room temperature, and of course the rate of hydrolysis increases with temperature. Also, the concentration of HF in the material condensed at high temperatures is less than in the pilot plant condensates.

Although HPF_6 is the phosphorus compound found in the traps or condensate, the question is still open as to the identity of the phosphorus compound formed in the reactor. According to the literature, HPF_6 is known only in aqueous solution, and it is reported that HPF_6 cannot be distilled as such. It might be that PF_5 is the correct formula for the gas which enters the trapping system, where it combines with moist HF to condense as an HPF_6 solution. Once the phosphorus has been condensed in this way, the phosphorus ordinarily will not be volatilized from the container by subsequent heating or distillation. Instead, the fluorophosphoric acids are hydrolyzed, HF is volatilized off and H_3PO_4 remains in the residue. Exceptions to this rule have been noted on two occasions, when small but significant amounts of HPF_6 were found in the distillate.

Further information on the hydrolysis of HPF_6 in solution was obtained as a result of the distillation experiments with pilot plant condensates. For example, in Pilot Plant Run 4 condensate, 93 percent of the phosphorus in the original condensate was as HPF_6. After distilling HF from this solution at 90 - 98°C for three hours, it was found that 13 percent of the P in solution was combined as HPF_6, while 81 percent was as H_3PO_4.

The object of the distillation experiments, as has been stated, was to learn how much HF could be made available from the HF condensate for recycle. Each of the four condensate samples was placed in an all-metal still, fitted with a fractionating column packed with fluorothene rings. In the case of the first two condensate solutions, the aim was simply to collect as much anhydrous HF as possible, preventing the higher-boiling water-HF mixtures from coming over. In the last two experiments using condensates 3 and 4, this separation of anhydrous HF was carried out first, followed by a second distillation at higher temperatures so that aqueous HF was collected as a second fraction. Results are as follows:

Pilot Plant Condensate No.	Percent of Total Fluorine Recovered		Total Recovery of Fluorine (percent)
	As Anhydrous HF	As Aqueous HF	
1	61	-	61
2	44	-	44
3	29	63 (as 64% HF)	92
4	77	26 (as 56% HF)	103

CONCLUSIONS

1. The reaction of $(UO)_2P_2O_7$ with anhydrous HF at 400 - 500°C results in the formation of HPF_6, which may be found by cooling the gaseous reaction products. The existence of HPF_6 in the gases before cooling has not been established. The equation for the chemical reaction may be either of the following:

$$(UO)_2P_2O_7 + 20\ HF = 2\ UF_4 + 2\ HPF_6 + 9\ H_2O$$

$$\text{or}\ (UO)_2P_2O_7 + 18\ HF = 2\ UF_4 + 2\ PF_5 + 9\ H_2O$$

2. Distillation experiments have shown that at least 90 percent of the fluorine present in HF condensate can be distilled off as hydrogen fluoride plus water. Probably at least one-half of this hydrogen fluoride can be collected as anhydrous HF.

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The experimental work reported herein was performed by Miss P. M. Brown and Mr. F. L. Daley. The chemical analyses were done by the Technical Service Laboratory, under the direction of Mr. C. D. Susano.

Approved by: G. H. Clewett D. W. Kuhn

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