

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

RED PHOSPHORUS AS A REDUCING AGENT.

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In qualitative analysis all the group separations and by far the larger number of individual separations are based on the precipitation of relatively insoluble compounds. Such precipitation reactions are always reversible and the extent to which they proceed in the one direction or the other depends on the conditions under which the precipitation is carried out. Consequently we find many cases in which the qualitative separations by precipitation are imperfect and others in which useful results can only be obtained by strict adherence to narrowly limited conditions. On the other hand, reactions involving valence change as well as precipitation are very frequently of such a nature that broad conditions may be described under which they run to completion. For example, silver ion will react with metallic copper to give metallic silver and copper ion, and under the usual experimental conditions the precipitation of the silver is complete. Wherever such reactions can be used in qualitative analysis we may expect a sharp and unambiguous separation to a large measure independent of the experimental conditions.

With this thought in view the actions of a number of reducing agents on acid solutions of metallic salts were investigated.¹ Hydroxylamine, hydrazine, and hydrosulfurous acid were soon found to have only limited applicability; phosphorous and hypophosphorous acids gave more promising results; and it was finally found that red phosphorus, in a large number of cases, would react smoothly and completely as a reducing agent in acid solutions.

Red phosphorus as a reducing agent seems to have received little attention, although the action of yellow phosphorus and phosphine on neutral or alkaline solutions of metallic salts has been the subject of a number of investigations.² The reactions with red phosphorus, aside from their possible application to qualitative analysis, are interesting in themselves; in a number of cases metallic phosphides not previously observed are precipitated, and these phosphides, while entirely inactive toward hydrochloric acid, sulfuric acid, or alkali, are decomposed by *dilute* nitric

¹ A. A. Noyes has suggested the use of metallic silver as a reducing agent in qualitative analysis. He found that Hg, Pt, Pd, and Ru could be precipitated by shaking their acid solutions with precipitated silver. See *Z. Elektrochem.*, 9, 839-40 (1903).

² Granger, *Compt. rend.*, 117, 231 (1893); *Ann. chim. phys.*, [7] 14, 5 (1899); Cross and Higgins, *J. Chem. Soc.*, 35, 249 (1879); Rose, *Pogg. Ann.*, 6, 206 (1826); 14, 184 (1828); Rubenovitch, *Compt. rend.*, 127, 270 (1898); 128, 1398 (1899); 129, 336 (1899); Kulisch, *Ann.*, 231, 327 (1885); Oppenheim, *Ber.*, 5, 979 (1872); Sidot, *Compt. rend.*, 84, 1454 (1877).

acid, red phosphorus being one of the products of the reaction. It seemed desirable, therefore, to begin a systematic investigation of the action of red phosphorus on acid solutions of metallic salts.

This investigation is by no means complete. Some of the experiments need amplification and confirmation, and in none of the cases has the nature of the reactions received any adequate attention. Conditions are such that resumption of the work in the near future seems unlikely, so the observations, in rather fragmentary form, are presented in the hope that some one else may find them sufficiently interesting to continue.

Altogether about 120 experiments were performed; these will not be described in detail, but instead will be given a short summary of the findings under the heading of the respective ions. A large part of the experiments were performed by Mr. R. N. Donaldson in 1916, and I wish, in this place, to express my thanks to him for his faithful and painstaking work.

Of the omissions made necessary by lack of time or material, the author most regrets that experiments were not performed with ceric salts, uranyl salts, tungstates (meta and para) stable in acid solution, rhodium and ruthenium salts, thallic and thalious salts. From analogy with the cases studied it seems likely that ceric salts would be reduced to cerous; uranyl to uranol salts; meta and para tungstates probably unaffected; rhodic to rhodous salts; ruthenium salts to metal or a phosphide; and thallic to thalious salts.

Experimental Results.

The experimental results obtained will be described under 4 heads, namely: *Group A*, those ions reduced and precipitated by red phosphorus from acid or neutral solutions, Ag^+ , Cu^{++} , Hg^+ , Hg^{++} , Pd^{++} , Au^{+++} , Os^{+8} , SeO_4^{--} ; *Group B*, those ions reduced but not precipitated from acid solutions, Sn^{+4} , Fe^{+++} , Ir^{+4} , MoO_4^{--} , VO_3^- , $\text{Cr}_2\text{O}_7^{--}$, and MnO_4^- ; *Group C*, ions which were found not to react with red phosphorus in acid solutions, Bi^{+++} , Pb^{++} , Cd^{++} , Sb^{+++} , As^{+++} , AsO_4^{--} , Sn^{++} ; *Group D*, ambiguous cases, those ions with which the reduction, if any, was very slight, but for which the evidence of no reduction was not conclusive, Pt^{+4} , and TeO_4^{--} .

In all experiments, except where it is otherwise stated, red phosphorus was added in excess. Usually from 100 to 200 mg. was used.

In all these experiments both silver and copper were precipitated as phosphides and red phosphorus was oxidized to an acid lower than orthophosphoric. The pure phosphides of silver and copper were prepared by boiling red phosphorus with excess of silver nitrate and copper sulfate, respectively. The silver phosphide was grayish brown while the copper

TABLE I.

Group A. Silver and Copper Salts.—Volume 10 cc.

Salt.	Solvent.	Weight. Mg. Ag.	Time of boiling.
AgNO ₃	H ₂ O	100	5 min.
AgNO ₃	H ₂ O	10	5 min.
AgNO ₃	H ₂ O	1	5 min.
Ag ₂ SO ₄ ^a	H ₂ O	150	5 min.
Ag ₂ SO ₄ ^a	H ₂ O	1	5 min.
Ag ₂ SO ₄ ^a	6 <i>N</i> H ₂ SO ₄	150	5 min.
Ag ₂ SO ₄ ^a	12 <i>N</i> H ₂ SO ₄	150	5 min.
CuSO ₄	H ₂ O	500	15 min.
		Mg. Cu.	
CuSO ₄ ^b	H ₂ O	1	15 min.
CuSO ₄	3 <i>N</i> H ₂ SO ₄	500	15 min.
CuSO ₄	6 <i>N</i> H ₂ SO ₄	1	15 min.

Reduction complete in all experiments.

^a Ag₂SO₄ largely in suspension.^b Precipitation of minute traces of copper by yellow phosphorus has been observed by W. N. Ray. THIS JOURNAL, 38, 887 (1916).

phosphide¹ was metallic gray. With hydrochloric or sulfuric acids neither compound reacted, but *dilute* warm nitric acid decomposed them giving red phosphorus.

TABLE II.

Group A. Mercurous and Mercuric Salts.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.	Reduction.	Remarks.
HgCl ₂	H ₂ O	10	...	15	None	Sat. solution
	0.23 <i>N</i> HNO ₃	26	...	7	Complete	
	Dil. HPO ₂	25	...	5	Complete	5 drops HPO ₂ added
Hg ₂ SO ₄	6 <i>N</i> H ₂ SO ₄	10	100	5	Complete	
	6 <i>N</i> H ₂ SO ₄	10	10	5	Complete	
	6 <i>N</i> H ₂ SO ₄	10	1	5	Complete	
HgNO ₃	H ₂ O	10	...	10	Complete	Sat. solution. Acid with HNO ₃ . Vigorous evolution of oxides of nitrogen.

The first 2 experiments recorded in Table II suggested that the reduction of mercuric chloride by red phosphorus is unusually slow and is apparently catalyzed by an oxidizing agent. It seemed probable that the true catalyzer was the metaphosphorous acid (HPO₂) formed by the action of nitric acid on red phosphorus, and the third experiment confirmed this supposition.

¹ Granger (*loc. cit.*) prepared a similar phosphide of copper by heating an ammoniacal solution of copper sulfate with red phosphorus.

TABLE III.
Group A. Palladous and Auric Salts.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.
PdCl ₂	H ₂ O	10	10 Pd	5
	H ₂ O	10	1	5
	6 <i>N</i> HCl	10	1	5
AuCl ₃	0.01 <i>N</i> HCl	30	1 Au	8
	3 <i>N</i> HCl	20	1	10

Reduction was complete in all experiments.

When red phosphorus was treated with an excess of auric chloride solution a brown-black substance was formed which was unreactive towards hydrochloric and sulfuric acids, but liberated red phosphorus when treated with warm dil. nitric acid. After the action of nitric acid a reddish brown residue remained which proved to be metallic gold. The gold was, therefore, precipitated as a phosphide.

TABLE IV.
Group A. Osmic and Selenic Acids.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.	Remarks.
OsO ₄	2 <i>N</i> H ₂ SO ₄	12	10 Os	15	Solutions were entirely free from Se.
H ₂ SeO ₄	H ₂ O	20	50 Se	25	
H ₂ SeO ₄	3 <i>N</i> HCl	20	50 Se	5	
H ₂ SeO ₄	3 <i>N</i> HCl	20	5 Se	5	

Reduction was complete in all experiments.

In experiments with osmiates care was taken to heat on the water bath before actually boiling to prevent the volatilization of osmic acid. This preliminary heating effected nearly complete reduction.

TABLE V.
Group B. Stannic, Ferric and Iridic Chlorides.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.	Reduction.
SnCl ₄	1 <i>N</i> HCl	30	200 Sn	30	Incomplete to Sn ⁺⁺
	3 <i>N</i> HCl	30	20	30	Incomplete to Sn ⁺⁺
FeCl ₃	1 <i>N</i> HCl	10	500 Fe	15	Complete to Fe ⁺⁺
	3 <i>N</i> HCl	10	10	15	Complete to Fe ⁺⁺
IrCl ₃	2 <i>N</i> H ₂ SO ₄	30	10 Ir	21	Solution became colorless. Reduction complete to Ir ⁺⁺ . No evidence of reduction to metallic Ir or a phosphide.

The experiments with chromium compounds showed that the hexavalent chromium is reduced to trivalent and that the action was accelerated by the addition of metaphosphorous acid. In the final solution ammonium hydroxide produced almost no precipitation of chromium hydroxide in the cold. In this solution the chromium was, therefore, not present as

chromic ion. It may have been present as a chromic phosphite complex ion, as the solution contained phosphites.

TABLE VI.

Group B. Molybdate, Vanadate, Dichromate and Permanganate.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.	Reduction.	Remarks.
MoO ₃	N HCl	25	50 Mo.	5	To deep blue solution.	
	N HCl	25		15	To light yellow solution, which gives red color with KSCN	The reaction with KCNS is indicative of tetravalent Molybdenum
	4N HCl	25		2	To deep blue solution	
	4N HCl	25		7	To light yellow solution, which gives red color with KSCN	
V ₂ O ₅	3N H ₂ SO ₄	20	50 V.	8	Solution bluish green	
	3N H ₂ SO ₄	20		25	Solution bright emerald green	From this solution NH ₄ OH + NH ₄ Cl produced a dirty green flocculent precipitate. The filtrate from this showed only a trace of vanadium.
V ₂ O ₅	3N H ₂ SO ₄	20	10	25	Solution bright emerald green	Results the same as above
K ₂ Cr ₂ O ₇	1N H ₂ SO ₄	10	10 Cr		Slow reduction to Cr ⁺⁺⁺	
	N H ₂ SO ₄	10	10	5	Solution bright green	5 drops conc. HPO ₂ added
	2N H ₂ SO ₄	20	100 Mn	1	Immediate reduction to Mn ⁺⁺	
KMnO ₄	2N H ₂ SO ₄	20	10		Same as above	

Group C.—Solutions containing the following ions in *N* acid, Pb⁺⁺, Bi⁺⁺⁺, Cd⁺⁺, Sb⁺⁺⁺, As⁺⁺⁺, AsO₄⁻⁻⁻, Sn⁺⁺, were boiled with red phosphorus for 2 hours and then heated on a steam bath for 12 hours, without evidence of reaction. The experiments were tried both with and without the addition of metaphosphorous acid.

Discussion.

As no experiments with mixtures of salts were performed, it is only possible with the results in hand to suggest their application to qualitative analysis. Further work is necessary to determine the extent to which several ions present in the same solution will modify the reactions. It may be, for example, that in the presence of cupric or silver ions platonic and iridous salts will be reduced smoothly to the metals. It is very likely that the reduction of telluric and arsenic acids by red phosphorus is possible, but very slow under the experimental conditions here described,

and that the presence of other substances may act catalytically causing reduction in these cases also.

It does appear, however, that the introduction of red phosphorus will make possible the complete elimination of the silver group, and a considerable simplification of the analysis of the aluminum and iron groups because of the reduction of the higher valence forms. The absence of cupric and mercuric sulfides from the hydrogen sulfide precipitate will also be a considerable advantage. The plan which suggests itself for beginning the analysis, assuming that the reactions proceed as indicated, is as follows:

To the solution containing the unknown substance in dil. nitric or sulfuric acid add excess of red phosphorus and boil 30 min.

Residue:

Ag, Cu, Hg, Au, Pd, Os, Se as metals or phosphides. Add excess of red phosphorus. Dissolve by repeated boiling with aqua regia, adding KClO_3 , if necessary. Evaporate. Take up with N HNO_3 .

Solution:

Bring to proper acid concentration and pass in H_2S

Residue:

AgCl

Solution:

Cu^{++} , Hg^{++} ,
 AuCl_4^- , Pd^{++} ,
 Os^{+8} ,^a SeO_4^{--}

Residue:

PbS , Bi_2S_3 , CdS ,
 SnS_2 , SnS , As_2S_3 ,
 As_2S_5 , Sb_2S_3 , sul-
fides of Mo, Ir,
Pt and Te.

Solution:

Ions of the iron and aluminum groups in their lower valence forms; alkaline earths, rare earths and alkalis. Also phosphites and phosphates.

^a Osmic acid may be completely volatilized. See A. A. Noyes, *Tech. Quart.*, 16, 103 (1903).

The introduction of phosphite and phosphate into the solution is no serious disadvantage. In a large number of cases phosphates are originally present, and in any case the scheme to include phosphates is little more complicated than the scheme for solutions free from them.

Summary.

1. The reactions between red phosphorus and acid solutions of various salts have been studied and their application to qualitative analysis has been indicated.

2. The following ions in acid solution are reduced by red phosphorus as indicated: Ag^+ to insoluble phosphide; Hg^{++} to Hg ; Hg^+ to Hg ; Cu^{++} to insoluble phosphide; Pd^{++} to metal or insoluble phosphide; Os^{+8} to metal or insoluble phosphide; Au^{+++} to insoluble phosphide; Sn^{++++} to Sn^{++} , partially; Fe^{+++} to Fe^{++} ; Ir^{+++} to Ir^{++} ; SeO_4^{--} to metal or insoluble phosphide; MoO_4^{--} to tetravalent form; VO_3^- to trivalent form; $\text{Cr}_2\text{O}_7^{--}$ to trivalent form; MnO_4^- to Mn^{++} .

3. The following ions in acid solution do not react with red phosphorus: Bi^{+++} , Pb^{++} , Cd^{++} , Sb^{+++} , As^{+++} , AsO_4^{--} , Sn^{++} .

4. The following ions are reduced only very slowly or not at all: TeO_4^{--} , PtCl_6^{--} .

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CRYSTALLIZATION OF A RADIUM-BARIUM SOLUTION.

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Radium of any degree of purity may be obtained by fractional crystallization of a radium-barium solution. The crystal fractions are progressively enriched with radium while the mother liquor fractions are progressively impoverished as the number of crystallizations increases. A system containing several fractions can be divided into 2 parts: first the increasing of the radium and the decreasing of the barium content commonly called the positive series (direction) and second the increasing of the barium and the decreasing of the radium content commonly called the negative series (direction). In such a system the original material enters the system at some point between the ends while high grade radium (low grade barium) comes out the positive end and high grade barium (low grade radium) comes out the negative end. The size of the different fractions decreases gradually toward the positive end and increases toward the negative end. Any soluble impurity occurring in the system stays in the mother liquor and finally passes out of the system with the barium without causing any disturbance. Any insoluble impurity present is occluded in the crystals and is carried toward the positive end with the crystals.

The negative ion usually employed in the system is the chloride or the bromide. The bromides of radium and barium are more soluble than the chlorides. About 50% of the total chlorides crystallize out upon cooling a neutral solution from 100 to 0°, while only about 33% of the total bromides crystallize out under like conditions; yet the quantity of crystals obtained from the same volume of either a chloride or a bromide solution is approximately the same which suggests that the bromide system would be more efficient than the chloride system.

Theoretical.

The concentration of the radium in any dish in the positive direction may be calculated from the equation

$$C = AK^n,$$

where n is the number of crystallizations, A the known concentration of some dish to start with and K the factor of enrichment—the relative concentration of radium in the crystals to radium in the original material.

Thus if the concentration of radium in the original material be taken as 1.0 and the concentration of radium in the crystals is 1.6 times the