

The product contains a small amount of water which is not expelled at 110°. This corresponds to slightly less than $\frac{1}{2}$ molecule. It is an amorphous powder, with a specific gravity, $15/4$ of 7.00. Crystallized trilead arsenate (anhydrous) prepared by fusion, had a specific gravity $15/4$ of 7.30.

Summary.

It has been shown that the action of dilute ammonia on dilead orthoarsenate proceeds as follows:

(1) Transposition to trilead orthoarsenate, $Pb_3(AsO_4)_2$, the supernatant solution remaining constant at the $(NH_4)_2HAsO_4$ stage until transformation is complete.

(2) Formation of solid solutions ranging from trilead arsenate to a basic arsenate, beyond which no further change occurs.

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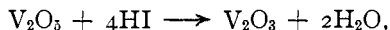
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA.]

THE REDUCTION OF VANADIC ACID BY HYDRIODIC ACID.

By GRAHAM EDGAR.

Received August 28, 1916.

In a recent paper by Ditz and Bardach¹ experimental results are given which indicate that the reduction of vanadic acid by hydriodic acid at room temperature and at considerable dilution proceeds irregularly, and that the iodine liberated in the course of the reaction corresponds approximately to that calculated for the reaction



or in some instances to an even greater amount. At the same time it is pointed out that tetravalent vanadium is relatively stable towards dilute hydriodic acid. In order to explain their results, Ditz and Bardach offer the hypothesis that the reduction of vanadic acid by hydriodic acid proceeds directly from the pentavalent to the trivalent state, without the formation of tetravalent vanadium as an intermediate product.

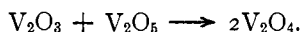
The results of Ditz and Bardach conflict with those of several earlier investigators. Numerous statements occur in the literature to the effect that reduction of vanadic acid by dilute hydriodic acid proceeds until the vanadium approximates the *tetravalent* condition,² and several investigators have defined conditions under which a quantitative reduction may be expected, and have based methods for the estimation of vanadium

¹ *Z. anorg. Chem.*, **93**, 97 (1915).

² Browning, *Am. J. Sci.*, [4] **2**, 185 (1896); Hett and Gilbert, *Z. öffentl. Chem.*, **12**, 265 (1906); Warynski and Mdivani, *Mon. Sci.*, **22**, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] **29**, 540; Rosenheim, *Inaug. Diss. Berlin* (1888).

upon the reaction.¹ The experimental conditions in most cases seem more favorable for reduction than those described by Ditz and Bardach.

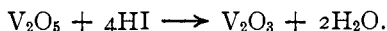
Furthermore it is stated by Rutter² that trivalent and pentavalent vanadium react with one another readily in acid solution, undergoing mutual oxidation and reduction in the sense of the equation



If this is true, then reduction of vanadic acid by hydriodic acid *must* pass through the tetravalent stage, even if the initial reduction involved the formation of trivalent vanadium, and since tetravalent vanadium is relatively stable towards dilute hydriodic acid,³ further reduction must proceed with great difficulty.

The conclusions of Ditz and Bardach seem, therefore, to warrant further investigation.

The experiments described by them are essentially as follows: (1) About 0.062 g. of vanadic acid (in solution as ammonium vanadate) was measured into a large bottle fitted with a separatory funnel and a trap valve. To it were added 1000 cc. of water, 75 cc. of conc. HCl, and 1.5 g. of KI. After vigorous shaking the bottle was allowed to stand for a few minutes and then titrated for iodine with dilute $\text{Na}_2\text{S}_2\text{O}_3$ solution, after the addition of starch. After the first titration the bottle was allowed to stand, and the continually reappearing blue color of "starch-iodide" was removed from time to time by further titration with thiosulfate. After several hours the amount of thiosulfate used corresponded in most cases to somewhat *more* than that calculated on the assumption that the reduction had proceeded according to the equation



(2) A solution containing V_2O_5 , HCl and KI in approximately the same concentrations as in the preceding experiments was shaken repeatedly in a separatory funnel with toluene, and the combined toluene extracts were titrated with thiosulfate as before. Here again the amount of thiosulfate used corresponded to a quantity of iodine somewhat greater than that calculated on the assumption that the reduction had proceeded until the vanadium was in the trivalent condition.

An obvious source of possible error in these experiments is that of atmospheric oxidation. This is indeed admitted by Ditz and Bardach, but they do not seem to consider that this error can materially influence the results. In the present paper experiments are described which cover almost the same ground as those of Ditz and Bardach, but the influence

¹ Browning, *Am. J. Sci.*, [4] 2, 185 (1906); Warynski and Mdivani, *Mon. Sci.*, 22, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] 29, 540.

² *Z. anorg. Chem.*, 52, 368 (1907).

³ Ditz and Bardach, *Z. anorg. Chem.*, 93, 97 (1915); Muller and Diefenthaler, *Z. anal. Chem.*, 51, 21 (1912); Wegelin, *Ibid.*, 53, 80 (1914).

of atmospheric oxidation has been kept as low as possible, and very different results have been obtained in consequence.

Experimental.

Solutions of sodium vanadate, sodium thiosulfate, and iodine, each approximately 0.05 *N* were prepared and carefully standardized. An apparatus similar to that of Ditz and Bardach was prepared for the preliminary experiments. It consisted of a large bottle (Fig. 1) fitted with a tightly fitting paraffined cork, through which passed a separatory funnel, a trap valve, and a bent glass tube through which a current of carbon dioxide could be passed.

In the first experiment there were placed in the bottle 1000 cc. of distilled water, 75 cc. of conc. HCl, and about 0.1000 g. of V_2O_5 (added as sodium vanadate). The trap was charged with 10 cc. of 5% KI solution. Then a current of carbon dioxide was passed for some time through the solution to remove air from the bottle and to diminish the amount of dissolved oxygen. After the gas had been passed through the liquid for about 30 minutes, 30 cc. of 5% KI were added from the funnel, and the current of CO_2 was discontinued. At the end of an hour's time, starch was added and the solution was titrated with 0.05 *N* (approx.) thiosulfate solution, still without admission of air. This titration required 23.15 cc. of thiosulfate solution (calculated for reduction to *tetravalent* vanadium, 24.20 cc.). After a few minutes the blue color returned, and was discharged by the addition of more thiosulfate. This was repeated three times during the next six hours, resulting in a total consumption of 28.35 cc. of thiosulfate for all titrations. After the last titration the blue color of "starch-iodide" had not returned after *three days'* standing, thus exhibiting no further signs of reduction. At the end of that time the bottle was opened and air admitted, and after a few hours the blue color due to iodine had developed again.

In this experiment the amount of thiosulfate used corresponds to somewhat more than that calculated from the assumption that the reduction proceeds only to the tetravalent condition, but the evidence that this excess was caused largely at least by atmospheric oxidation seemed so strong that a set of experiments was devised to study the reaction under conditions more readily controlled.

For this purpose the apparatus shown in Fig. 2 was constructed. It consisted of a large separatory funnel (about 550 cc.) connected by means of a ground glass connection with a small separatory funnel, and a glass tube through which a gas could be admitted. The figure shows the de-

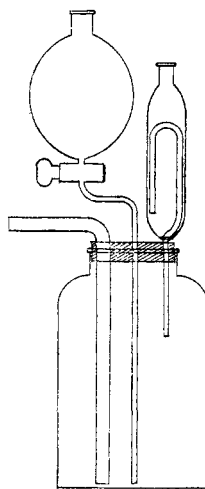


Fig. 1.

tails clearly. The technique involved in carrying out the experiments in this apparatus was as follows: The desired amounts of sodium vanadate solution, concentrated hydrochloric acid, and distilled water were run into the apparatus through the small separatory funnel, and a current of pure hydrogen gas was then bubbled through the liquid for about twenty minutes in order to remove air as far as possible. At the end of this time the desired amount of 5% potassium iodide solution was run in through the small funnel, and this was followed by 25 cc. of pure carbon bisulfide. All stopcocks were then closed, and the apparatus was shaken vigorously from time to time for perhaps half an hour. The carbon bisulfide was then drawn off through the lower stopcock, while hydrogen was admitted from the upper one. A fresh portion of carbon bisulfide was then admitted through the small separatory funnel, and the shaking was repeated as before.

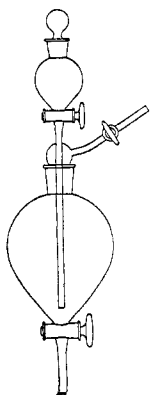


Fig. 2.

This process was continued until fresh portions of carbon bisulfide failed to extract any further amount of iodine even after standing for several hours. The time necessary for the reaction to become complete varied with the concentration of the different reagents, but was never less than an hour and a half nor greater than four hours. In all cases the apparatus was allowed to stand for twelve hours after apparent completion of the reaction, in order to make sure that no further separation of iodine took place, and in one case, after six weeks' standing under hydrogen, no further separation of iodine could be observed. The combined carbon bisulfide extracts were carefully titrated for iodine with 0.05 *N* sodium thiosulfate solution. The results of the experiments are given in Tables I and II. In Table I the concentration of reagents are approximately the same as those employed by Ditz and Bardach; in Table II the effect of certain variations in the concentrations has been studied.

TABLE I.

Total volume of solution in every case

500 cc. containing 0.06379 V_2O_5 .

Cc. conc. HCl.	Cc. 5% KI.	Cc. 0.05 <i>N</i> $Na_2S_2O_3$.	Cc. calc. for reduction to V_2O_4 .
37.5	15	14.10	14.00
37.5	15	14.05	14.00
37.5	15	14.20	14.00
37.5	15	14.10	14.00
37.5	15	14.10	14.00
37.5	15	14.05	14.00

TABLE II.

Total volume of solution in every case

500 cc. containing 0.0637 g. V_2O_5 .

Cc. conc. HCl.	Cc. 5% KI.	Cc. 0.05 <i>N</i> $Na_2S_2O_3$.	Cc. calc. for reduction to V_2O_4 .
37.5	30	14.20	14.00
37.5	30	14.15	14.00
37.5	60	14.15	14.00
75.0	15	14.05	14.00
75.0	15	14.10	14.00
110.0	15	14.15	14.00

The results given in Table I under conditions of concentration of acid and iodide almost identical with those used by Ditz and Bardach, show that the iodine liberated in the reaction corresponds almost exactly with

that calculated for reduction of the vanadium to the *tetravalent* condition, and not to that calculated for reduction to the *trivalent* condition, as found by Ditz and Bardach. Furthermore the color of the solution at the conclusion of the experiment was in every case the pure blue of tetravalent vanadium, and not the green trivalent. Obviously the large amounts of iodine which Ditz and Bardach found to be liberated in their experiments were caused partially by atmospheric oxidation. Further proof of this was given by an experiment carried out with the same concentration of reagents as those in Table I, and with the same technique, except that the air in the apparatus was not removed by hydrogen. In this case the amount of thiosulfate required for titration of the iodine after four hours' repeated extraction with CS_2 was 21.20 cc., an excess of 50+ % over that found necessary for the titrations given in Table I. Table II contains the results of experiments carried out with the same technique as that employed in the experiments of Table I, but the concentrations of acid have been varied in such a direction as to make the conditions more favorable for reduction than those studied in the previous experiments. The results show that even if the concentration of acid is made three times that employed by Ditz and Bardach, or if the concentration of iodide is increased to four times that used in their experiments, the amount of iodine liberated corresponds closely to that calculated for reduction of the vanadium to the tetravalent condition. Moreover, the solution at the completion of the experiment has the blue color of tetravalent vanadium, as in the experiments of Table I. The only noticeable effect caused by changing the concentrations of acid and iodide was that the time necessary for the reaction to come to completion was materially shortened by an increase in the concentration of either acid or iodide. The effect of the acid was more marked than that of the iodide, possibly because of the fact that carbon bisulfide does not extract the iodine as efficiently from a concentrated iodide solution as from a dilute one, and, therefore, the removal of the iodine from the solution was not so complete as in the experiments in which the acid concentration was high and that of the iodide low.

Some explanation seems necessary for the large increase in the amount of iodine liberated when air is admitted into the apparatus. Blank experiments carried out with dilute hydrochloric acid and potassium iodide, but without the V_2O_5 , showed that a little iodine is liberated when the solution is shaken with CS_2 in the presence of air but the amount is not nearly large enough to explain the results obtained in the presence of pentavalent vanadium under the same conditions. Likewise blank experiments carried out in the presence of tetravalent vanadium (previously prepared by reduction of pentavalent vanadium with sulfur dioxide) failed to show appreciable liberation of iodine after a few hours' extraction

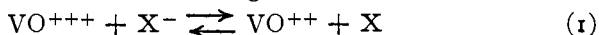
with CS_2 in the presence of air. Ditz and Bardach, in attempting to account for the fact that they found more iodine liberated than corresponded to reduction of the vanadium to the trivalent condition, offer the following explanation: (1) Pentavalent vanadium is reduced directly to the trivalent condition by dilute hydriodic acid; (2) in the presence of air the trivalent vanadium is oxidized to something (probably not tetravalent vanadium) which reacts further with the hydriodic acid to cause liberation of iodine. This explanation seems cumbersome and unnecessary. In the first place, the results given in this paper show that under the conditions of experimentation the iodine liberated corresponds to that calculated for formation of tetravalent vanadium, and the color of the solution is evidence that tetravalent vanadium is actually formed. There is no evidence that trivalent vanadium is formed, nor does it seem probable from the theoretical standpoint. A simpler and more plausible explanation of the excess of iodine liberated in the presence of air, is that pentavalent vanadium acts as a catalyst in accelerating the oxidation of hydriodic acid by the oxygen of the air, as certain other oxidizing agents are known to do.

Altogether there seems no reason to suppose that the nature of the reaction of hydriodic acid with pentavalent vanadium differs essentially from the similar reactions with the other halogen acids, or that tetravalent vanadium is not the primary product of reduction. This will be discussed further below.

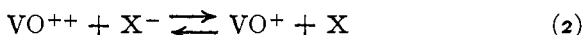
The Mechanism of the Reduction of Vanadic Acid by the Halogen Acids.

Numerous investigators have studied the reactions between the halogen acids and vanadic acid, and the apparent conflict between their results has in some cases led to considerable controversy. In view of the fact that even in some recent papers there appears to be some misconception of the mechanism of the reactions, and of the function of the different reacting substances, it may be well to give a brief discussion of the subject from the standpoint of the theory of electronic oxidation and reduction,¹ and to show how some of the conflicting views may be reconciled.

The most logical method of representing the reaction between vanadic acid and the halogen acids is the following:



and similarly for further reduction



where X represents the halogen (Cl, Br or I).

Obviously conditions which favor the progress of Reaction 1 from left to right are: (a) high concentration of the halogen ion; (b) high concentration of the VO^{+++} ion; (c) low discharging potential of the halogen

¹ Stieglitz, *Qual. Anal.*, Vol. I, p. 251.

ion; and (d) removal of the product of the reaction, X, from the solution (usually by boiling, by evaporation, by extraction, or by reaction with a metal).

Similar conditions will likewise favor the progress of Reaction 2.

The concentration of the halogen ion can of course be varied at will, and the discharging potential (c) will vary with the particular halogen used, being greatest with chlorine and lowest with iodine.

The concentration of positively charged vanadium ions (V^{++++} , or more correctly, VO^{+++}) will depend almost entirely upon the hydrogen ion content of the solution. Just as in the case of any other element whose oxide exhibits amphoteric properties the acidic ionization of vanadic acid will be diminished and its basic ionization increased, by increasing the hydrogen ion content of the solution.

Bearing these four different factors in mind, and their influence on the reaction, the apparent conflict in the results of different investigators is readily explained.

Reduction by Hydrochloric Acid.—In this case we have to overcome the high discharging potential of the chlorine ion, and for complete reduction of pentavalent vanadium to tetravalent all of the other factors mentioned above must be favorable. Thus dilute hydrochloric acid is practically without reducing action upon vanadic acid solutions² and even the ordinary process of boiling vanadic acid with concentrated hydrochloric acid³ fails to produce completion of Reaction 1.⁴ It is only when the highest concentration of hydrogen ion and halogen ion is maintained⁵ or when the solution is repeatedly evaporated to dryness with concentrated acid,⁶ that complete reduction can be effected. Even then the results are not always of the highest degree of uniformity.⁷ In no case do we have evidence that Reaction 2 takes place even to the slightest extent.

Reduction by Hydrobromic Acid.—In this case the discharging potential is much lower than in the case of the chlorine ion, and in consequence reduction takes place more readily. Thus it has been shown that for solutions whose hydrogen ion content is rather high (4–6 molar) the concentration of bromine ion need not be excessive to effect complete reduc-

¹ Ephraim, *Z. anorg. Chem.*, **35**, 66 (1903); Dullberg, *Z. physik. Chem.*, **45**, 129 (1903).

² Ditz and Bardach, *Z. anorg. Chem.*, **93**, 97 (1915).

³ Berzelius, *Pogg. Ann.*, **22**, 49 (1831); Bunsen, *Ann.*, **86**, 305 (1853); Gibbs, *Am. Chem.*, **J.**, **5**, 370 (1883).

⁴ Milch, *Inaug. Diss. Berlin* (1887); Holverscheit, *Ibid.* (1890); Rosenheim, *Ibid.* (1888); Gooch and Stookey, *Am. J. Sci.*, [4] **14**, 369 (1902).

⁵ Gooch and Stookey, *Am. J. Sci.*, [4] **14**, 369 (1902); Bèard, *Ann. chim. anal.*, **10**, 41 (1905).

⁶ Campagne, *Ber.*, **36**, 3164 (1903); Auchy, *J. Ind. Eng. Chem.*, **1**, 455 (1907).

⁷ Müller and Diefenthaler, *Z. anal. Chem.*, **51**, 21 (1912).

tion of pentavalent vanadium to the tetravalent condition, provided the bromine is removed from the solution by boiling.¹ If the acid concentration is still higher, Reaction 1 goes to completion with relatively low concentration of bromine ion, even at room temperature.² Several accurate volumetric processes for the estimation of vanadium have been based upon this reaction, as there is a rather wide range of conditions under which Reaction 1 goes to completion, and Reaction 2 does not begin to take place. On the other hand, if *all* of the factors influencing reduction are made favorable (for example, by boiling vanadic acid with concentrated hydrobromic acid, in which *both* hydrogen and bromine ion are present in very high concentration) Reaction 2 begins to take place, and a considerable amount of trivalent vanadium may be formed.³

Reduction by Hydriodic Acid.—It is in this case that much of the difference of opinion in regard to the reaction of vanadic acid with the halogen acids is found. Methods for the quantitative estimation of vanadium have been proposed, based upon the reduction of vanadium from pentavalent to tetravalent condition,⁴ from pentavalent to trivalent condition,⁵ and from tetravalent to trivalent condition⁶ by the action of hydriodic acid under various conditions. On the other hand, numerous investigators have obtained very irregular results with the reaction, and have raised objections to its use for quantitative purposes.⁷ This is probably partially due to failure to eliminate the error due to atmospheric oxidation of the acid iodide solutions, and partially to the fact the range of conditions under which Reaction 1 is complete and Reaction 2 not occurring is more limited than in the case of the reduction involving hydrobromic acid. A careful study of the literature shows that if the concentration of hydrogen ion is kept moderate and that of the iodide ion small, reduction of pentavalent vanadium to tetravalent takes place readily, if the iodine set free is removed by boiling,⁸ by extraction with a solvent (see above), or by reaction with a metal.⁹ Oxidation of the acid iodide solution must be

¹ Holverscheit, *Inaug. Diss. Berlin* (1890); Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Bèard, *Ann. chim. anal.*, 10, 41 (1905).

² Ditz and Bardach, *Z. anorg. Chem.*, 93, 97 (1915).

³ Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904).

⁴ Browning, *Am. J. Sci.*, [4] 2, 185 (1896); Warynski and Mdivani, *Mon. Sci.*, 22, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] 29, 540.

⁵ Friedheim and Euler, *Ber.*, 28, 2067 (1895).

⁶ Edgar, *Am. J. Sci.*, [4] 27, 174 (1908); Friedheim and Euler, *Ber.*, 28, 2067 (1895).

⁷ Ditz and Burdach, *J. anorg. Chem.*, 93, 97 (1915); Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Mülle rand Diefenthaler, *Z. anal. Chem.*, 52, 11 (1912); Wegelin, *Ibid.*, 53, 80 (1914); Ditte, *Compt. rend.*, 102, 1310 (1886); Rosenheim, *Inaug. Diss. Berlin* (1888).

⁸ Browning, *Am. J. Sci.*, [4] 2, 185 (1896); Gooch and Curtis, *Ibid.*, [4] 17, 41 (1904); Warynski and Mdivani, *Mon. Sci.*, 22, II, 527 (1908),

⁹ Perkins, *Am. J. Sci.*, [4] 29, 540.

guarded against and the proper conditions carefully observed, however, if accurate results are to be obtained. Further reduction of the tetravalent vanadium to trivalent (Reaction 2) does not take place appreciably in solutions in which the concentrations of hydrogen and iodide ion are kept low, but it is possible by making these two factors favorable to effect a complete reduction of tetravalent to trivalent vanadium.¹ Naturally, pentavalent vanadium can be reduced to trivalent by the use of high concentrations of acid and iodide,² but the evidence does not justify the assumption that the tetravalent condition is not reached as an intermediate stage. The conditions for effecting a quantitative reduction must be more sharply defined than in the case of hydrobromic acid, but there seems to be no evidence that the mechanism of the reaction is different from that occurring in the case of the other halogen acids.

Summary.

(1) The reaction between vanadic acid and hydriodic acid at room temperature and at considerable dilution has been investigated. Within the limits of concentration covered by this investigation the reaction results in the formation of tetravalent vanadium, and not trivalent. This is contrary to the observations of Ditz and Bardach. A probable source of error in the results of Ditz and Bardach has been pointed out.

(2) The mechanism of the reactions between vanadic acid and the halogen acids, and the influence of various factors upon the equilibrium, has been discussed.

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[COMMUNICATION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

ANALYSIS OF CERTAIN TUNGSTEN DERIVATIVES.

BY ORLAND R. SWEENEY.

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The analysis of "complex inorganic acids" and their salt derivatives has been a subject of interest to analysts. Peculiar difficulties have been frequently encountered, and the impression exists that none of the methods proposed for the various separations are satisfactory. In passing, it may be observed that these doubts are particularly strong in connection with the separation of phosphoric and vanadic acids from molybdic and tungstic acids. In this laboratory where, for many years, "complexes" have received attention, numerous opportunities have arisen to test the proposals made from time to time, and as it was given me to inquire more closely

¹ Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Friedheim and Euler, *Ber.*, 28, 2067 (1895); Edgar, *Am. J. Sci.*, [4] 27, 174 (1908).

² Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Friedheim and Euler, *Ber.*, 28, 2067 (1895).