

the large free energy decrease is consistent with the observed completeness of reaction at all three temperatures studied.

Little could be deduced concerning the kinetics of the reaction, for obviously the observed rate of pressure increase was a composite of a decrease due to absorption of the trioxide and an increase due to evolution of the dioxide and chlorine. Hence only near the end of reaction could the observed rate of pressure change serve as a measure of the rate of evolution of the gases. Actually, by using the times of 0.9 reaction for the usual $\log-1/T$ graph, a reasonably straight line was obtained from whose slope a value of 38,000 cal. was obtained for the apparent energy of activation.

Summary

1. In flow runs, the decomposition of a low temperature sulfur trioxide-sodium chloride addition complex has been shown to yield sulfur dioxide and chlorine in exactly equivalent proportions; this holds at all temperatures between 220 and 440° in a nitrogen or an oxygen atmosphere.

2. The reaction of sulfur trioxide with sodium chloride between 279 and 350° has been investigated by a static method. It was established that 1.5 moles of sulfur trioxide react with 1.0 mole of sodium chloride to produce 0.5 mole each of chlorine, sulfur dioxide, and sodium pyrosulfate. Thus: $\text{NaCl} + \frac{3}{2} \text{SO}_3 = \frac{1}{2} \text{Na}_2\text{S}_2\text{O}_7 + \frac{1}{2} \text{SO}_2 + \frac{1}{2} \text{Cl}_2$.

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[CONTRIBUTION FROM TUNGSRAM RESEARCH LABORATORY, UJPEST NEAR BUDAPEST]

Reaction of Tantalum, Columbium and Vanadium with Iodine

BY F. KÖRÖSY

The latest investigation on the reaction of tantalum with iodine is that of Moissan,¹ while the reactions of columbium and vanadium have never been investigated. Moissan briefly stated that tantalum powder and vapor of iodine do not react at 600°; this is the last reference to be found on the subject.² The direct reaction has never been described although van Haagen³ succeeded in preparing tantalum pentaiodide from the bromide and hydrogen iodide. The formula was confirmed by analysis and the color of both the condensed and gaseous compounds was described as resembling bromine. Barr⁴ prepared a crude, stable columbium iodide from the bromide. He was unable to obtain this material free from bromine and did not analyze it.

In search of a metal that would be resistant to iodine vapor at temperatures between 1500 and 2500° we tried tantalum, hoping that Moissan's statement would also be valid for these high temperatures. However, we soon noticed the formation of a black-brown solid that melted at 365° and could be distilled without decomposition at about 400°. The vapor had a characteristic brown color quite distinct from iodine. It

was soon identified as tantalum pentaiodide and we decided to investigate its physical properties and chemical reactions because scarcely anything was known about them.⁵ Further we studied a reduction product of this substance and the reactions between columbium and iodine and vanadium and iodine to some extent because the metals of this sub-group of the periodic system are the only ones that were hitherto not known to react with elementary iodine.

Whereas tantalum pentaiodide is stable at least up to 500° and had to be reduced in the vapor phase with incandescent tantalum wire, columbium and vanadium pentaiodides easily dissociate at their sublimation temperatures (about 400°). It may be that the greater stability of the tantalum compound is due to the fact that the Ta ion fills the "hole" between the large iodine ions ($\phi = 2.2 \text{ \AA.}$) more completely than the V and Cb ions [$V = 0.4 \text{ \AA.}$, $Cb = 0.70 \text{ \AA.}$, $Ta = 0.85 \text{ \AA.}$ (extrapolated)]. The "hole diameter" between five I ions in a regular pentagon is 1.5 Å. so that this configuration is less probable than a steric one.

The stoichiometric formula of the lower iodides is open to discussion; their chemistry seems complicated. The tantalum compound decomposes

(1) H. Moissan, *Compt. rend.*, **134**, 212 (1902).
 (2) Gmelin's "Handbuch der anorganischen Chemie," System No. 8, Jod, 1933, p. 180.
 (3) W. K. van Haagen, *THIS JOURNAL*, **32**, 729 (1910).
 (4) W. M. Barr, *ibid.*, **30**, 1668 (1908).

(5) F. Körösy, *Technikai Kurir*, **9**, 81 (1938) (Hungarian publication); see *C. A.*, **33**, 1615 (1939).

at the temperature necessary for the vaporization of tantalum penta-iodide and yields black powders of varying low iodine content and tantalum penta-iodide. The iodine content may decrease after prolonged heating even below the ratio of tantalum mono-iodide and the substance which remains consists mainly of metallic tantalum. This behavior of our new tantalum iodide perfectly agrees with that described on the reduction products of tantalum pentachloride and bromide by a series of authors. The pentahaloid and the metal residue are the stable components whereas the intermediate halides may be obtained in nearly any desired average composition. Only one deep green compound can be extracted therefrom with water. We too obtained a deep green solution from our raw mixture of lower iodides and the properties of this solution agreed with those of the corresponding chloride and bromide as described in publications of other authors. Chabrié⁶ reduced tantalum pentachloride with sodium amalgam and extracted a green compound from the mixture. It was oxidized easily with bromine and nitric acid and analysis gave the formula $TaCl_2 \cdot 2H_2O$. Chapin⁷ repeated the experiments with the chloride and with the bromide also. He improved the analytical method and found the composition $(Ta_6Cl_{12})Cl_2 \cdot 7H_2O$; it is especially interesting that he could only precipitate directly one-seventh of the halogen with silver nitrate. The molecular weight in water was 720 (three ions). The work on these compounds was resumed independently by Lindner and Feit⁸ and by Ruff and Thomas.⁹ They reduced the pentahaloids with aluminum powder at about 300° and extracted the residue with dilute acid. They isolated dark-green crystals, soluble in water and in some organic solvents. As to the analysis and its interpretation the various authors disagreed entirely. Lindner and Feit determined the valency of tantalum in the green compounds by titration with permanganate and assign to them the formula $H(Ta_3^{II}X_7 \cdot H_2O) \cdot 3H_2O$. Ruff and Thomas, on the other hand, derive the compound from trivalent tantalum and base their assumption on volumetric hydrogen determinations in course of the reaction with alkali. Their formula, $Ta_3X_7O \cdot 3H_2O$, cannot be

(6) M. C. Chabrié, *Compt. rend.*, **144**, 804 (1907).

(7) W. H. Chapin, *THIS JOURNAL*, **32**, 323 (1910).

(8) K. Lindner and H. Feit, *Ber.*, **55**, 1458 (1923); *Z. anorg. allgem. Chem.*, **137**, 66 (1924); **160**, 57 (1927).

(9) O. Ruff and F. Thomas, *Ber.*, **55**, 1473 (1923); *Z. anorg. allgem. Chem.*, **148**, 1, 19 (1925).

distinguished easily from the above one on the basis of elementary analysis. But analysis does not exclude the well-founded formula of Chapin either—a fact that seems to have been overlooked in this later discussion.

Our own experiments show conclusively that the green ion must be positively charged because it travels toward the cathode during electrolysis and so the formula of Lindner and Feit safely may be ruled out. We determined the Ta:I ratio and tried to establish a ratio between the iodine content and the quantity of permanganate consumed. The results are far from being definite because we had to operate with minimal quantities of the very poorly soluble green compound. They can be best interpreted as tantalum triiodide but until further evidence is available we would rather emphasize its analogy to Chapin's compound than our analysis. The separate existence of TaI_2 and TaI_3 in the reduction mixture, as postulated by Ruff, should be verified by actual separation or X-ray analysis.

The above-mentioned lower iodide of columbium is stable in vacuum up to 500–600° and therefore it is probably a definite compound. Its analysis can be explained by the formula Cb_2I_5 (molecular compound of CbI_2 and CbI_3 ?) or by Cb_6I_{14} in agreement with a series of complex columbium halides that were prepared by Harned¹⁰ in analogy to Chapin's⁷ tantalum compounds. Harned found the same constitution ($[Cb_6Cl_{12}]Cl_2 \cdot 7H_2O$), and he also prepared some compounds where one-seventh of the halogen was substituted ($[Cb_6Cl_{12}]X_2$). The solutions of this series are olive-green, but by precipitating the complex hydroxide, dissolving it in alkaline hydroxide solutions and precipitating this solution with concd. hydrochloric acid he obtained a brown solid that differed from the original formula by only two additional molecules of water. However, this brown solid differs from our brown compound in that it dissolves in water with the original olive-green color whereas our compound gave a coffee-brown aqueous solution. Brown solutions of reduced columbium were prepared electrolytically by Ott¹¹ and according to him they are characteristic of its trivalent state.

The reaction of elementary vanadium and iodine has not been described previously either. From aqueous solutions Piccini and Brizzi¹² pre-

(10) H. S. Harned, *THIS JOURNAL*, **35**, 1078 (1913).

(11) F. Ott, *Z. Elektrochem.*, **18**, 349 (1912).

(12) Piccini and Brizzi, *Z. anorg. allgem. Chem.*, **19**, 394 (1899).

pared the compound $\text{VI}_3 \cdot 6\text{H}_2\text{O}$ which decomposed during desiccation. We found that the elements react at red heat and that the primary product sublimes at $400\text{--}500^\circ$ and forms a brown vapor which resembles exactly that of tantalum and columbium pentaïodides. This sublimation is accompanied by a decomposition into iodine and a lower, dark reddish-brown iodide which when analyzed in its crude state has the composition V_2I_3 . As no compounds of analogous composition are known, the formula should be accepted with reserve.

Experimental Part

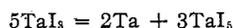
1. Tantalum and Iodine

The direct reaction of incandescent tantalum wire and iodine vapor and most of the physical and chemical properties of tantalum pentaïodide were described in the above-mentioned Hungarian publication.⁵

An attempt to saturate argon with iodine at $30\text{--}90^\circ$ and pass this gas over the incandescent tantalum filament in order to obtain the lower iodide also gave only tantalum pentaïodide but the yield was poor. In one experiment we sealed pieces of tantalum sheet and less than an equivalent quantity of iodine in a transparent quartz container, large enough to allow for complete vaporization of iodine at high temperature. The vessel was held in an electric furnace at about 1100° for two hours and then allowed to cool quickly. Free iodine remained beside tantalum iodides, so that we concluded that the temperature was higher than the dissociation temperature of the pentaïodide.

We found that tantalum pentaïodide is a semiconductor of electricity, a fact which is interesting in view of the results of Biltz and Vogt¹³ who examined the electric conductance of tantalum and columbium pentachloride in the liquid state at 230° and found that they were insulators with specific resistances 3×10^8 and 4×10^6 ohm cm., respectively.

Reduction of Tantalum Pentaïodide.—Tantalum wire of 0.3 mm. diameter was wound to a coil and mounted in a durane vessel containing less iodine than necessary for the formation of TaI_5 . The vessel was exhausted and the coil heated electrically to $1300\text{--}1600^\circ$; at the beginning all iodine is converted into tantalum pentaïodide. We found relatively the best yields of reduction when the temperature of the vessel was raised uniformly to about 500° in a furnace; at temperatures between 300 and 400° no reduced iodide is formed. But even at 500° the yield is always poor and there always remains much unreduced tantalum pentaïodide, presumably because the lower iodide decomposes at this temperature. The product of reduction is a black-brown solid which separates from the glass on gentle knocking and breaks up to form a black powder. It contains tantalum pentaïodide as can be seen from its reaction with water. When subjected to fractionation in high vacuum it always splits off tantalum pentaïodide anew, probably according to a reaction of the type



(13) W. Biltz and A. Vogt, *Z. anorg. allgem. Chem.*, **120**, 71 (1921).

This is in perfect analogy with the behavior of the lower tantalum chlorides and bromides as described in Ruff's and Lindner's papers.^{8,9} The black-brown powder, when free from tantalum pentaïodide, is resistant to air and moisture for days. It is oxidized by air slowly in the course of some weeks. It contains varying amounts of chemically bound iodine according to the length of the heat treatment it has received; *e. g.*, we found once 32.8% I, at another time 55.4% I, when the calculated values are 41.2% for TaI and 58.5% for TaI_2 . The fact that products with less iodine are formed than necessary for TaI proves that metallic tantalum must have been one product of the reaction.

The Green Tantalum Iodide Solution.—The black powder that consists of one or more lower tantalum iodides and metallic tantalum, gives a deep-green solution in cold water. The rate of solution is remarkably slow; one has the impression that it is determined by a process of hydration or internal rearrangement. Owing to the fact that different samples of the reduced mixture are different in composition and that the mixture seems to undergo some slow change in air, both velocity and extent of solution differ in different samples. The solubility is very low, it amounts to some tenth of a gram per liter. The intensity of color is about the same in this case as that of a 2 *N* nickel nitrate solution, so that the extinction coefficient must be very high. This agrees with Chapin's⁷ description of the respective chloride: he found that a 1% solution is practically black in a 1-cm. layer. The absorption spectrum contains, according to our spectrograms, a continuous absorption in the red and blue parts of the spectrum.

As soon as the cold aqueous solution forms it begins to decompose giving an apple-green precipitate of the consistency of aluminum or ferric hydroxide and perhaps in analogy with the formation of the latter in neutral solution.¹⁴ This neutral solution turns colorless on heating and the precipitate turns brown and later white, while minute gas bubbles evolve, probably hydrogen. The same process takes place at room temperature in one or two days. The green solution remains stable and clear even at its boiling point if it is slightly acidified with sulfuric acid. Alkali or ammonia turns the solution colorless without visibly precipitating anything. The reduction potential of trivalent (?) tantalum ion in alkaline solution is high enough to set hydrogen free and it is converted to the pentavalent state, in accordance with Ruff's experiments.⁹

The black reduced mixture behaves quite remarkably with dilute hydrochloric acid and ethyl alcohol. It is insoluble in both, a fact conspicuous in view of its solubility in dilute sulfuric acid. After standing in contact with dilute hydrochloric acid for a while and after this acid is removed, the black powder dissolves easily in alcohol (always leaving a residue, of course) and forms a solution many times deeper green than any aqueous solution that could be obtained. In the course of some hours this solution becomes turbid and overnight the whole substance settles as a muddy brown, voluminous precipitate. The same alcohol-soluble chloride may be obtained from

(14) A. B. Lamb and A. G. Jacques, *THIS JOURNAL*, **60**, 967, 1215 (1938).

the sulfuric acid solution. In this medium the green compound dissolves much better on heating than at room temperature and addition of hydrochloric acid precipitates the alcohol-soluble "complex chloride." The black powder, however, is hardly soluble in alcohol containing some dilute hydrochloric acid. It is insoluble in glacial acetic acid but dissolves slowly to some extent in dilute acetic acid. This green solution is converted into a brown precipitate on heating. The sulfuric acid solution forms apple-green precipitates with potassium chloride and iodide solutions, the former being insoluble, the latter soluble, in water. The complicated chemistry of this substance is by no means elucidated by our present work; we regard them as preliminary experiments that demonstrate only the existence of this group of complex iodides of lower valency. A thorough investigation will be possible only if the yield of reduction of the pentaiodide is improved.

The acid solution of the green compound (in sulfuric acid) is oxidized by hydrogen peroxide and by potassium permanganate but it is the iodide ion that is oxidized first: the first drop of the reagent sets free iodine which can be extracted with organic solvents. The solution thus freed from iodine remains green until nearly all the iodide is oxidized. Later the tantalum is oxidized also to tantalic acid. In agreement with these experiments we found that iodine does not oxidize the green solution.

A drop of the green solution was dried on an object plate *in vacuo* and examined under the microscope. We obtained beautiful dark green crystals: four-armed stars with arms subdivided like branches of a fir tree. Beside these there were, however, some light yellow, transparent six-sided plates and in the course of some days the green stars gradually disappeared and were transformed into the yellow plates. Neither of them showed optical anisotropy between crossed nicols. We do not know the chemical nature of the yellow crystals, they are probably oxidation products of the green ones. The black powder itself splits off some iodine after standing for weeks in the air.

A dark green aqueous solution of the green compound was placed in the bottom of a 2-mm. ϕ capillary U-tube and dilute alcoholic sulfuric acid was filled above it on both sides as a top layer; 60-v. d. c. current was applied through platinum electrodes and the resulting current of 20 m. a. displaced the green layer in five minutes totally into the cathode half of the U-tube. At the same time there appeared free iodine in the neighborhood of the anode. The importance of this experiment has already been treated in the general part of this paper.

Analysis of the Green Solution. (a).—A neutral solution was filtered quickly to remove undissolved black powder, but some of the above-mentioned green precipitate remained on the filter. The filtrate was acidified with sulfuric acid and divided in two equal parts. The first was evaporated to dryness in a miniature silica crucible, oxidized with nitric acid and ignited to tantalum penta-oxide. It was weighed on a micro balance (2.260 mg.). The second half was sealed in an exhausted U-tube with sulfuric acid, with a crystal of potassium permanganate and was heated gently while the other half of the inverted U-tube was cooled in liquid air. After the water distilled over the sulfuric acid was driven over with a free flame, taking with it some Mn_2O_7 in the other side of the tube.

The latter was decomposed by heating it for some minutes to 100°. The iodine passed only when the dry substance was heated with a flame; it was titrated with 0.01 *N* sodium thiosulfate and gave 4.13 mg. of iodine. Thus the Ta:I ratio was 31:69. For TaI_5 the calculated ratio is 32.2:67.8, for Ta_5I_{14} (Chapin) 37.3:62.7.

(b).—The solution was decanted from the black powder to save the green precipitate. One part was evaporated to dryness and the tantalum determined as above. The other part was acidified with sulfuric acid and shaken with successive quantities of 0.01 *N* potassium permanganate and carbon tetrachloride in a separating funnel until all iodine was extracted. The carbon tetrachloride solution was titrated directly with 0.01 *N* sodium thiosulfate using the rose color of the solution as indicator. Two determinations gave 26.7:73.3 and 26.3:73.7 for the Ta:I ratio. We tried to determine the valency of tantalum in the green ion by adding successive quantities of potassium permanganate solution to the green solution in the separatory funnel after the iodine had been removed. However, the end-point of this titration was extremely uncertain; the result was a valency between 3 and 4.

Evidently a substance should be isolated in the solid state and in macro-quantity before definitive analysis. Even then it will be difficult to decide beforehand whether the relatively soluble sulfuric acid extract—that is, possibly a complex sulfate—or the original iodide should be analyzed for this purpose.

2. Columbium and Iodine

Reaction of the Elements.—One and one-half grams of columbium wire from the Fanco Corporation was wound to a coil, its ends soldered to molybdenum wire and the latter sealed in a 3-cm. ϕ durane-glass tube. The tube ended on one side in two glass bulbs which contained the iodine (8 g.) and where the superfluous iodine was collected after the reaction. The other end of the reaction tube was connected to a small durane vessel ending in a capillary within a surrounding glass tube: the product of reaction was brought into this part and sealed off; the capillary served to open this container in any desired vacuum apparatus. The whole vessel was exhausted to high vacuum and sealed off before the reaction.

The reaction started, as in the case of tantalum also, at the beginning of red heat and with iodine vapor at its saturation tension of room temperature; under these conditions a dark deposit was formed. The reaction was completed here also by heating the columbium electrically to 1300–1500° and the whole vessel with a free flame to about 200°: the reaction product emerged in thick clouds from the filament, which burned out after having lost in a few minutes more than two-thirds of its weight. The pentaiodide could be distilled away from the wall of the tube, its vapor had the same red-brown color as tantalum pentaiodide only without having the greenish-brown tint at the lowest concentrations. We heated the main part of the vessel in a furnace to 200° so that all free iodine condensed in the side bulb. There always remained, however, some iodine vapor in the main vessel, as we first thought, in solid solution. We decided, therefore, to seal off the side bulb with the bulk of the iodine and purify the iodide through distillation, but failed. On heating the iodide to

300–400° a considerable quantity of iodine was evolved and a new compound appeared: a black-brown solid that did not sublime until 600° and that ceased to split off further iodine after a time. Evidently the iodide that formed by combination of the elements is not stable above 200° and dissociates into iodine and a lower iodide. Both substances were isolated, the higher could be prepared only by distillation in an iodine atmosphere, whereas the lower was heated as long as all iodine that was capable of being split off departed.

Analysis of Columbium Pentaiodide.—The columbic acid was precipitated with ammonia and ammonium sulfate and the iodine determined in the filtrate as silver iodide. We found 11.7% Cb and 88.3% I, whereas the calculated value is 12.8% Cb and 87.2% I for columbium penta-iodide. The excess of iodine probably was caused by the fact that excess iodine vapor had to be present at the final distillation of the penta-iodide in order to prevent its dissociation. Analysis and behavior of the compound leave no doubt about the formula CbI_5 .

Properties of Columbium Penta-iodide.—Its melting point cannot be determined because it dissociates at temperatures below melting. The color of columbium penta-iodide is the same as that of tantalum penta-iodide, red-brown like bromine vapor. The difference mentioned above that its dilute vapor is not greenish-brown but also red-brown may be due to the presence of free iodine vapor. It reacts with water like tantalum penta-iodide and with atmospheric oxygen even more quickly than the former; the end-products are I_2 and Cb_2O_5 .

Analysis of the Lower Columbium Iodide.—The substance stood under water for a time and seemed not to react with it. Very slowly a minute quantity dissolved and formed a light coffee-brown solution; heating did not accelerate this process. On adding dilute sodium hydroxide a brown precipitate was formed, resembling manganic hydroxide. Both the original substance and the precipitate evolved hydrogen at room temperature and on the water-bath. On the water-bath the whole substance gradually was transformed to the brown precipitate and after a time this was peptized to a brown solution that evolved gas and lost its color in the course of some hours. This sodium columbate solution was filtered from traces of columbium wire that remained undissolved, and columbic acid was precipitated with sulfuric acid and ammonium sulfate and then made alkaline with ammonium hydroxide. It was filtered and ignited to Cb_2O_5 , the iodine was precipitated in the filtrate with silver nitrate. Results: 23.2 and 24.0% Cb and 76.8 and 76.0% I. Calculated for Cb_2I_5 ($CbI_2 \cdot CbI_3$): 24.9% Cb and 75.1% I; for Cb_2I_4 (Harned's compound without crystal water) 23.9% Cb and 76.1% I. Both possible explanations of the analysis seem strange at the moment but they are not without precedent in the complicated chemistry of less than pentavalent columbium compounds. At present we cannot decide between the two explanations.

Properties of the Lower Columbium Iodide.—It neither melts nor vaporizes under 600°. Its density was determined under carbon tetrachloride in the state used for analysis, that is, slightly contaminated with metallic Cb, to be d_{16} 5.63. Its specific electric resistivity in form of hand-compressed powder was 50 ohm. cm. at room

temperature and 25 ohm. cm. in a boiling water-bath. Some of its chemical reactions were described above, with its analysis. It splits off some iodine while standing for days in the air. It also seems to undergo some sort of aging because the above-mentioned coffee-brown solution could not be reproduced a few days later. It does not dissolve in organic solvents but reacts in an extraordinary manner with xylene: in a state that was sufficiently free from iodine to show not the least color with carbon tetrachloride, xylene was tinted strawberry red in contact with the substance. The color never became any deeper, that is, it seemed to be in equilibrium, but new quantities of xylene always showed this color anew. It was identified as iodine. It may be that the xylene was contaminated by traces of an oxidizing agent. An analogous behavior was observed with the lower tantalum and vanadium iodides also, using benzene, xylene and carbon disulfide as solvents.

3. Vanadium and Iodine

Reaction of the Elements.—One-half gram of vanadium powder (from Schuchardt, Görlitz) was placed with 6.2 g. of iodine in an exhausted silica-glass tube. The vanadium was in the bottom of the V-shaped tube and was heated steadily to red heat while iodine was distilled over it by heating one end of the tube and cooling the opposite one. Very soon there appeared a brown vapor, distinct from iodine, that possessed a greenish tint at low concentrations. It condensed to small crystals of yellow-brown metallic luster. On heating it decomposed even more easily than columbium penta-iodide into free iodine and a lower iodide that could be heated to red heat without further decomposition. The compound that formed the brown vapor was not isolated in pure state but its analogy with tantalum and columbium penta-iodides leaves hardly any doubt about its being vanadium penta-iodide. The reaction of vanadium and iodine was continued until visibly all vanadium was converted into the low iodide and the excess of iodine was driven off and sealed in one end of the tube.

Analysis of the Low Vanadium Iodide.—The substance was dissolved in ammonium hydroxide and ammonium persulfate, care being taken not to lose any iodine as vapor. The process of solution was very slow and there remained an undissolved residue, probably metallic vanadium. The solution was reduced with sodium sulfite and sulfuric acid to iodide and tetravalent vanadium and the undissolved residue was filtered off and ignited. Iodine was precipitated with silver sulfate (nitrate had to be excluded because it would have made the oxidimetric titration of vanadium impossible), the solution decanted into a Schott glass filter and decanted several times with water. The silver iodide was freed from reduced metallic silver with nitric acid, washed and weighed. The blue vanadyl solution was boiled while bubbling through it a stream of argon until all sulfur dioxide was expelled and then titrated with 0.1 N potassium permanganate. Result: 21.0% V and 79.0% I. Calculated for VI_2 : 16.75% V and 83.25% I; for VI: 28.62% V and 71.38% I; for V_2I_3 : 21.1% V and 78.9% I. The last formula agrees surprisingly well with the analysis, but no definite compounds containing univalent vanadium are known. If we add the undissolved "metallic" vanadium to our analysis we arrive at

26.3% V and 73.7% I, that is, at a result that is no easier to explain. There seems to be, however, no justification for adding this residue. Here again X-ray analysis could help a good deal in elucidating the problem.

Properties of the Low Vanadium Iodide.—It neither melts nor vaporizes at red heat. Its density was determined under carbon tetrachloride in the same state as used for analysis, that is, slightly contaminated with metallic vanadium, to be $d_{15} 5.30$. Its specific electric resistivity in the form of hand compressed powder was 10^6 ohm cm. at room temperature and 10^4 ohm. cm. in a boiling water-bath. It consists of garnet-red crystalline lamellae, resembling chromium trichloride in its consistency. It does not dissolve in water but evolves hydrogen slowly when treated with alkali; the low speed of this reaction may be partly due to the fact that it is moistened very slowly. It does not dissolve in organic solvents but splits off traces of iodine in contact with some of them (see above under Cb_2I_5). After standing for about one-fourth hour in the air it splits off some iodine and becomes moist.

Summary

1. Tantalum, columbium and vanadium react with iodine vapor at the temperature of dull red heat; the primary reaction products are the pentaiodides.

2. Tantalum pentaiodide vapor is reduced by incandescent tantalum. One product of this reaction dissolves in water to a deep green solution and is probably an analog of Chapin's green chloride and bromide.

3. Columbium and vanadium pentaiodide dissociate on heating and form compounds that gave the formulas $Cb_6I_{14}(Cb_2I_5?)$ and V_2I_3 on preliminary analysis. Some of their physical properties and chemical reactions are described.

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[CONTRIBUTION No. 148 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

The Catalytic Hydrogenation of Some Organic Acids in Alkaline Solution

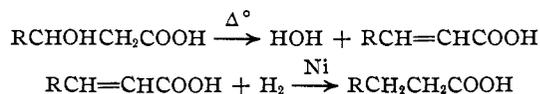
BY BRUCE B. ALLEN,¹ B. WOODROW WYATT² AND HENRY R. HENZE

During the course of another investigation identification of certain acidic substances, obtained as end-products of the high temperature-high pressure catalytic hydrogenation of cellulose suspended in alkaline solution,³ necessitated attempts to hydrogenate some of the more common hydroxy acids in alkaline solution. The results of such experiments were of interest and importance sufficient to warrant the inclusion in this study of the behavior of keto acids and unsaturated acids under the same conditions.

The conditions of hydrogenation imposed upon the acids in alkaline solution were such that the temperature was not to exceed 250° , and the pressure at this temperature to be not more than 330 atmospheres. From the study made has come definite and quite interesting information. Thus, if the behavior of lactic acid be accepted as typical of the α -hydroxy acids, then it may be concluded that acids of this structure are not affected by catalytic hydrogenation under the conditions imposed. Apparently, γ -hydroxy

acids, too, are stable toward hydrogenation under our conditions since γ -hydroxyvaleric acid was identified as the primary reduction product of levulinic acid.

In contrast with the behavior of the α - and γ -hydroxy acids is that exhibited by the examples of β -hydroxy acids studied. Thus, hydracrylic acid, entirely typical of this class of compound, readily underwent hydrogenation at 175° to form propionic acid in excellent yield. Likewise, subjecting malic acid to the same conditions of alkali and hydrogen and also at 175° resulted ultimately in the replacement of the hydroxyl group by hydrogen, succinic acid being the product. In view of the ease with which β -hydroxy acids are known to become dehydrated at elevated temperatures, the following series of equations represent the reactions involved in the catalytic hydrogenation of β -hydroxy acids in alkaline solution



This mechanism of reaction⁴ was substantiated in the instance of malic acid which was converted

(4) In discussing the possible mechanism involved in the hydrogenolysis of certain organic compounds oxygenated in 1,3-positions, Connor and Adkins, *THIS JOURNAL*, **54**, 4678 (1932), consider the mechanism here formulated as a possibility in the instances which they studied, but conclude it to be not a probability.

(1) Cotton Research Foundation Post-Doctorate Fellow, The University of Texas.

(2) Cotton Research Foundation Fellow, The University of Texas.

(3) We have found Raney nickel to catalyze hydrogenation in alkaline aqueous solution (5-10% sodium hydroxide); in this connection cf. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, 1937, p. 25 and Covert, Connor and Adkins, *THIS JOURNAL*, **54**, 1661 (1932).