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A Study of Reduction of Vanadate

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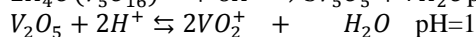
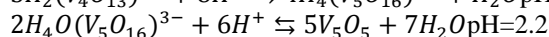
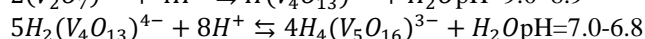
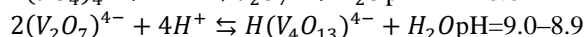
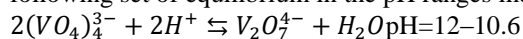
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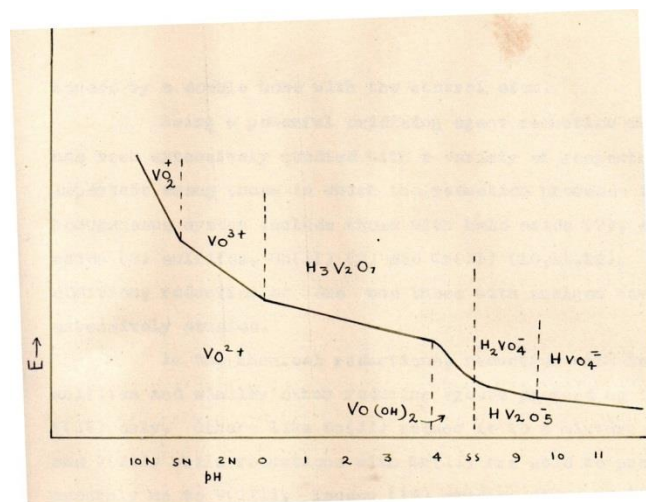
INTRODUCTION

Vanadates are salts corresponding to oxidation state V of vanadium. The salts are pretty strong oxidizing agents having a standard potential comparable to that of nitric acid. Their structures and nature of species present in solution have been extensively studied. The results show that in electronic configuration vanadates show resemblance with phosphate to the extent that none of them is left with any unshared electron and both exist in modifications like ortho, meta, para etc. differing essentially in the water content of the acid and also in the extent of polymerization. However, an important difference between the two is that whereas for phosphates the rate of interchange of different forms is quite slow, it is quite fast for vanadates. Hence any form of vanadate when put into solution rapidly comes to an equilibrium common for all. This divergence is further manifested in their behavior towards acids. The increase of acidity in the case of phosphate lead to simpler molecules but for vanadates as one passes from alkaline to acidic solutions the complexity of the vanadate ion raises leading ultimately to precipitation of (V_2O_5) in about N/100 acid. On further increase in acidity, the precipitate redissolves but now as a cation formulated variously as VVO_2^+ , $V(OH)_4^+$ or VO^{3+} . In this respect and in other chemical properties they are closer to chromates.

The variation in ionic species of V(V) with acidity has been studied in detail by Jander and Jahr (I) who give the following set of equilibrium in the pH ranges mentioned

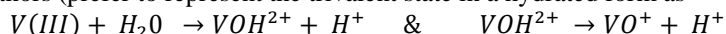


Additional evidence for the existence of vanadium as positively charged ion in acidic solutions of vanadate comes from transport number experiments by Dullberg. More exact formulation of the ion comes from diffusion measurements of Chilesotti who showed that ion contains only one atom of vanadium. However, the exact nature of the ion is not completely settled and carpenter advocates the use of the formula $V(OH)_4^+$ in preference to VO_2^+ or VO^{3+} . The situation is possibly best summed up in the following diagram from Kolthoff and Elving (showing the variation in vanadate ion structure with pH).



The next lower oxidation state of vanadium is V (IV) and in this, the ion mainly exists as vanadyl ion to which is attributed the structure

VO^{2+} . In the other two lower states the element behave essentially like a basic element and gives trivalent and bivalent simple cations though some authors (prefer to represent the trivalent state in a hydrated form as



The coordination number of all the states in the majority of cases is six. But in the vanadyl ion, the actual number of coordinated groups is only four as the oxygen in these ions is bonded by a double bond with the central atom.

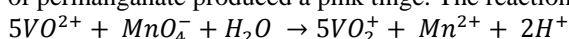
Being a powerful oxidizing agent reduction of vanadates has been extensively studied with a variety of reagents. Important among these in which the reduction proceeds in a homogeneous system include those with halo acids, amino acids, sulfites, Sn(II) and Cr(II)). In addition, reduction at dme and those with amalgam have been extensively studied.

In the chemical reductions, reduction with halo acids, sulfites, and similar other reducing agents proceed up to state V (IV) only. Others like Sn (II) reduce it to a mixture of V (IV) and V (III) while reductions with Cr(II) are said to proceed smoothly up to V(III). Tandon (8) studied it by adding an excess of Cr (II) to an acidified vanadate solution and back titrating the Cr(II) left over.

Kinetic of the reductions of different oxidation states of vanadium have also been studied (9, 10, 11). In these studies, it is reported that V (III) can further be reduced to V (II) by Cr (II). In the present work, therefore, attempts have been made to find conditions under which this step of reduction could be detected potentiometrically. The results obtained are compared with those obtained during reduction with V (II) and polarographic reduction.

As all the steps of reduction were found to be sufficiently fast to permit a direct titration the technique adopted for following the course of this reduction.

A M/25 solution of ammonium vanadate (Riedel) was prepared as a stock solution by weighing out accurately the required quantity of the salt and dissolving it in air free water. The solution was standardized by the procedure described by Scott and Furman. The vanadate solution acidified with sulfate acid was reduced with sodium sulfite to V(IV) stage and sulfur dioxide was boiled off the blue solution so obtained and its completion tested with acidified dichromate paper. The solution while still hot was then titrated with standard potassium permanganate till the blue color gave place to faint yellow and the first additional drop of permanganate produced a pink tinge. The reaction involved can be written as



And the strength of vanadate solution calculated accordingly.

An acidified solution of vanadate is light to deep yellow, the intensity of color increasing as the acidity decreases. When chromous chloride was added to this solution the color became greenish but on standing for a few minutes it changed to bluish. The blue tinge intensified as more and more of chromous chloride was added and reached a maximum at a point corresponding to the first inflection. Thereafter it was the green color that increased and this too reached a maximum at appointing corresponding to the second inflection. After this, no significant change in potential or color was observed in spite of additional quantities of $CrCl_2$ added. The sequence of color change narrated above was applicable to solutions more than 3N with respect to acid. But in the acidity range, 3N to N/2 the color of the solution remained bluish green up to the end and no pure green color was obtained. As still lower acid concentrations like N/10 or N/20, the color of the solution was found to be violet towards the end. The violet color was not due to any excess of Cr(II) or any V(II) formed as it remained stable even for days when exposed to air.

The sequence of color change was all the more interesting with vanadous chloride as the reductant. Here the addition of VCl_2 produced first a greenish tinge which on standing changed to blue. The blue color continued to grow till the first inflection point after which it became green in solutions at least 6N with respect to acid. But in the acidity range 3N-1N, the reaction mixture remained blue till the end. At still lower acidities there was the appearance of a brown color on addition of VCl_2 which on standing changed first to green and then to blue.

The behavior of the two electrodes throughout the course of titration remained almost similar except for small differences in the sizes of inflections. But in a solution of V(V) more than 3N in HCl, the gold film was found to get dissolved in about 20-30 minutes. This dissolution was found to occur even if no reductant was added to the system. Hence the study with gold electrode was restricted to solution less than 3N in acid. But the platinum electrode behaved satisfactorily even at higher acid concentrations. However, visible decomposition of vanadate solution occurred in solutions more than 6N in HCl as a starch iodide paper held just above a acidified vanadate solution turned blue in a short period indicating oxidation of HCl to chlorine by vanadate. The lower limit of acidity up to which the reaction could be studied conveniently was found to be N/20. Below this acidity long periods of waiting were required before a stable potential could be recorded. Precipitation of hydroxide etc was indicated by the turbid nature of the solution in this range. Alos the inflexions tended to lose their sharpness.

The polar graphic reduction of V(V) was studied with both HCl and KCl as supporting electrolytes. With KCl a maximum was observed in between the two waves. The waves were not well developed and the plateau corresponding to the limiting current was not well defined. The maximum could be suppressed with gelatin but the waves could not be improved upon.

With hydrochloric acid as supporting electrolyte the waves were better developed and at the concentration of 0.1N acid as supporting electrolyte no maximum was observed. The mercury, in either case, was found to get oxidized supporting the earlier observations that mercury can reduce V(V) to V(IV). Hence following the suggestion of Lingane the two (Mercury and vanadate solution) were left in contact for as short a period as possible and readings completed in a short period.

The first wave appeared at zero applied potential while the second had the half-wave potential of -0.87 v with respect to saturated calomel electrode (S.C.E.). These corresponded to a reduction of V(V) to V(IV) and V(IV) to V(II) respectively.

The results obtained are as given in the table below:

Table – I

Reduction of V (V) with Cr (II).
Cell: 20ml M/50 (0.98) Ammonium vanadate in X N HCl.
Burette: Y N Chromous Chloride
One g molV(V) \equiv Z gmol Cr(II).

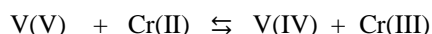
X	Platinum electrode			Gold electrode		
	Curve No.	Y	Z	Curve No.	Y	Z
6 (approx)	A	0.286	I infl. 1.07 II infl. 2.00	--	--	--
3.03	B	0.27	I infl. 0.99 II infl. 2.00	B	0.26	I infl. 1.06 II infl. 2.06
2.00	C	0.265	I infl. 1.02 II infl. 2.35	C	0.26	I infl. 0.996 II infl. 2.00
1.00	D	0.2	I infl. 0.97 II infl. 2.04	D	0.26	I infl. 1.06 II infl. 2.12
0.2	E	0.26	I infl. 0.996 II infl. 2.023	E	0.26	I infl. 1.06 II infl. 2.12
0.1	F	0.3126	I infl. 0.997 II infl. 1.99	F	0.23	I infl. 1.08 II infl. 2.11
0.05	G	0.3126	I infl. 0.997 II infl. 1.99	G	0.25	I infl. 1.02 II infl. 2.07 III infl. 3.22

Table – II

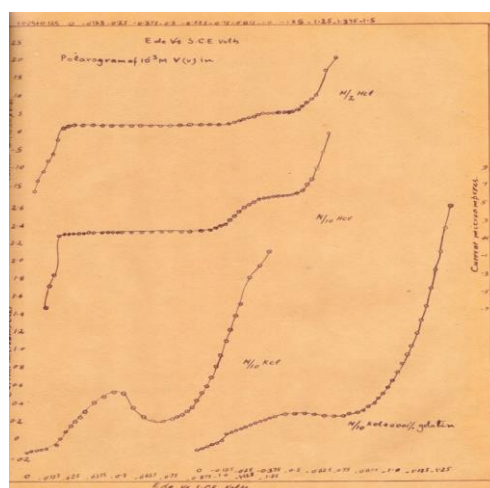
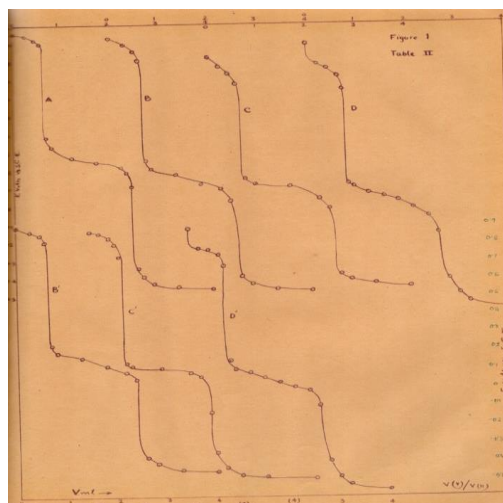
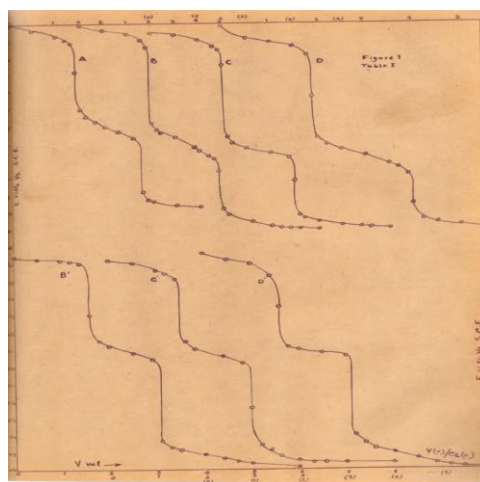
Reduction of V (V) with V(II).
Cell: 20ml M/50 (0.98) V (V) in X N HCl. .
Burette: Y N Chromous Chloride
One g molV(V) = Z g mol V(II).

X	Platinum electrode			Gold electrode	
	Y	Curve No.	Z	Curve No.	Z
6(approx)	0.30	A	I infl. 0.514 II infl. 1.9	--	--
3.03	0.3	B	I infl. 0.497 II infl. 1.95	B	II infl. 0.497 II infl. 1.87
1.02	0.31	C	I infl. 0.514 II infl. 1.98	C	I infl. 0.514 II infl. 1.90
0.1	0.28	D	I infl. 0.536 II infl. 1.93	D	I infl. 0.5 II infl. 1.93

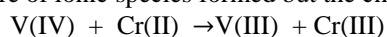
An examination of the potential versus volume graphs that were plotted show that for the titration with CrCl₂ the first inflexion corresponds to the addition of one mole of Cr (II) per mole of vanadate taken in the cell. As the color of the solution at this stage under all the conditions studied is blue which is typical of the vanadyl ion (VO²⁺) and the first higher oxidation state of Cr(II) is Cr(III) the reaction responsible for the first inflexion can be written as



Yellow Deep Blue Blue Green or Violet

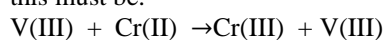


Further addition of Cr(II) gave one more inflexion at the total addition of two moles of Cr(II) for every mole of V(V) and the color of the solution at this stage was green at higher acidities but blue at lower. The change in color is possibly due to some change in the nature of ionic species formed but the chemical reaction responsible for the inflexion may be written as



Blue Green Green or Violet

After this, the curve was found to be quite smooth at higher acidities. But at lower acidities like N/10 or N/20 just at the point corresponding to the addition of the third mole of Cr(II) an inflexion could just be detected. This became definite when dE/dV value was considered. With a gold electrode, a definite though small inflexion was obtained. The reaction responsible for this must be.

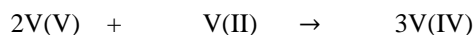


Greenblue Green or violet Violet

The first two inflexions were quite sharp. The size changed but little with a change in the acidity of the medium. But the third one which was obtained with gold electrode only and that too at quite low acidities was small.

With V(II) as the reductant, the first inflexion was obtained after addition of only one mole of V(II) per moles of V(V). The solution at this stage under all the conditions was blue and so vanadium must be in the oxidation state V(IV). This means that up

to this inflexion V(V) is reduced by one equivalent to giving V(IV) while V(II) is oxidized by two equivalents to reach the stage V(IV). This can be represented by the equation



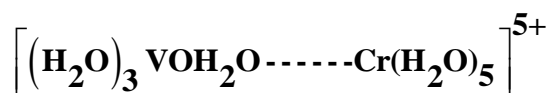
and fits well with the experimentally observed quantities and the color changes of the two reactants involved up to this point. The second inflexion that was observed required addition of an additional one and a half mole of V(II) for each mole of V(V) originally present. As due to the first step of reaction every mole of V(V) leads to one and a half mole of V(IV), this inflexion fits well with the reduction of V(IV) to V(III) and simultaneous oxidation of V(II) to V(III)



After this, the curve remained quite smooth and no indication of any further reaction was observed nor was any possible except for exchange reactions which can not affect potentiometric values.

In terms of the known structure of various oxidation states of vanadium the course of the reaction can be pictured as follows:

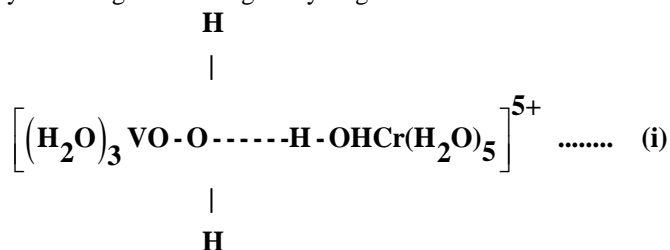
In passing from V(V) to V(IV) the structure of the vanadyl remains basically unaltered nor does any change occur in the coordination number of the two. This is particularly true in the acid range in which the reaction has been studied for which the two ions (excluding the water molecules associated with them) in aqueous solution can be written as VO^{+++} and VO^{++} respectively. This satisfies at least one of the requirements for the outer sphere mechanism of electron transfer. This mechanism may be operative with chromous ion as a reducing agent at low acidities where violet, fully aquated chromic ion is the reaction product. This gets some support from the fact that the inert character of chromic ion requires that the hydrated ion is formed as such, any subsequent aquation of any other primary product being very slow. However, due to the labile nature of aqueous chromous ion, this looks less probable than the path involving a water molecule as the bridging ligand. The bridged complex so formed can be written as



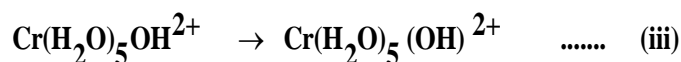
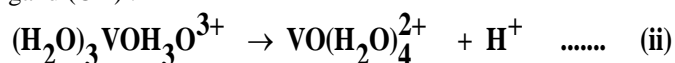
After the electron transfer from Cr to V labile V-OH₂ bond breaks transferring water molecules to chromous ion. The vacant place of the ligand on vanadium is however taken up by water which is in far more excess than any other landing group. The distinction between the two mechanisms can be made only with the use of labeled reactants.

At higher acid concentrations, however, the Cr(III) species formed is the green one indicating the participation of same ligand other than water in the coordination sphere of Cr(III). A plausible reaction sequence would be as follows:

The two aquated ions may come together through a hydrogen bond

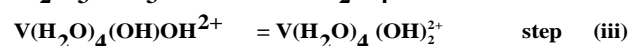
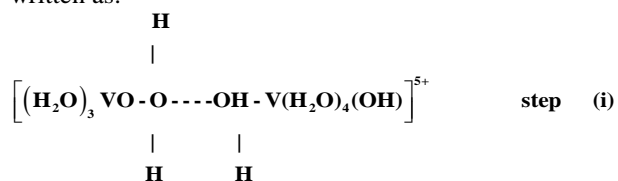


A hydrogen atom may be transferred from Cr(II) to V(V) by the homolytic fission of the O-H bond of water molecule attached to Cr(II) nucleus. This leads to the products $(H_2O)_3 VOH_3O^{3+}$ and $Cr(H_2O)_5 (OH)^{++}$. The hydrogen atom transferred to vanadium releases its electron to vanadium and reverts to the solution as a hydrogen ion. The OH radical left behind on Cr(II) acquires an electron from it and become the ligand $(OH)^-$.



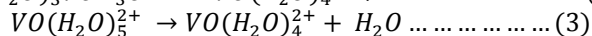
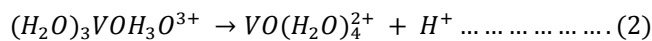
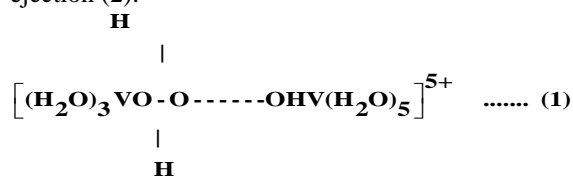
The reaction with vanadous ion can also be understood on the same lines, steps (i), (ii) and (iii), in which Cr (II) may be replaced by V (II).

The V (III) so formed may react with another vanadate ion in a similar manner and transfer a hydrogen atom to V (V) which may stabilize itself by a similar procedure. The V(IV) coming from the oxidation of V(III) in this step will have two OH⁻ groups in its coordination sphere and this structure is similar to the one proposed by Carpenter for V(V). The sequence can be written as:



The second stage of reaction may also proceed via hydroxyl bridge contributed by the V(III) ion (I). A hydrogen atom transfer may occur from V(III) to V(V) and the V(IV) formed from V(III) may stabilize itself by ejection of a water molecule and

conversion of the single bonded oxygen to a doubly bonded one (3). The V(IV) coming from V(V) may be stabilized by H^+ ion ejection (2).



A distinction between the two mechanisms is difficult to find and it is also difficult to say whether the complex is an inner sphere or outer sphere type.

The particle VO^{++} may reduce to V(III) by another H atom absorption (leading to $\text{V}(\text{OH})^{2+}$ which by further absorption may be converted into V(II), a hydroxyl perhaps eliminating as water. This last possibility has been realized with Cr (II) as already stated.

For all these steps we must assume that both H_2O and (OH) bridges are present but the proportion changes as proton concentration are changed. At low proton concentration, the hydroxyl bridge which is regarded as more effective for electron conduction must prevail. Indeed it is only in nearly neutral solutions that the reduction of V (III) to V(II) is observed by us.

Further as the last step of reduction (reduction to V(II) is observed only at low acidities where the Cr(II) product is violet the oxidation-reduction must proceed without any net transfer of group to the chromous ion so that its fully aquated nature remains unchanged. This should happen irrespective of the nature of complex (inner sphere or outer sphere) formed. An example of similar behavior where oxidation- reduction proceeds by an inner sphere complex but without any transfer of the bridging group to the reductant has been reported by Taube who reports that the reduction of IrCl_6^{2-} by CrCl_2 proceeds via an inner sphere complex involving Cl^- bridge but no transfer of Cl^- occurs.

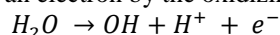
An interesting observation is the nature of vanadium species formed which is much more obvious in the titration with V(II) as a reductant. Examination of the graphs shows that the final oxidation state of V(V in this titration is V(III). However, the solution at the end point is found to be blue though green is the color in which V(III) is most frequently found. A blue species of V(III) is reported by Sidgwick and also by Alvarez and Pino who found that V(V), when reduced by gaseous hydrogen under catalytic effect of Pd salts, gives V(III) as the reduction product and the solution is blue.

However, none of them points out to the factors which make the two forms of V(III) differ. It is a well-known fact that Cr(III), when fully aquated, is violet but green when any other group also participates in the coordination sphere. A similar explanation may apply for V(III) as well and the blue form observed may be the fully aquated form of the ion which becomes green when another molecule also participates in the coordination sphere. The fact that the two isoelectronic ions V_{aq}^{2+} and Cr_{aq}^{3+} are both violet under similar conditions and the formation of the latter from its lower oxidation state involve shift in color towards shorter wave lengths (blue to violet). While oxidation of the former (V_{aq}^{2+}) changes the color in the reverse direction (violet to green or blue) shows that other factors like polymerization etc should also be responsible. It has been reported that aerial oxidation of V(II) gives a hydrated form of V(III), possibly a dimer, which is brown and formulated as $(\text{VOV})^{4+}$. This brown product when dissolved in sulphate acid was found to give a green solution but in hydrochloric acid the solution was very close to blue. Thus the situation seems to be quite complex and factors like polymerization; hydration and nature of ligands must be taken into consideration. The labile nature of V(III) ion makes the situation even more confusing and puts more weight on the composition of the medium which will determine the nature of the predominating form of V(III) ion particularly as to the composition of its coordination sphere.

It is interesting to note that this brown product was also observed during titrations with V(II) particularly at low acidity and after the first inflection. As at this stage the solution contains only V(IV) it seems reasonable to say that the brown product is some of V(III), stable under these conditions but decomposed at higher acidities, and so may be a dimer at least.

Another point that requires consideration is the dissolution of gold in acidified vanadate solution. This can occur due to several factors. The first and simplest is that vanadates are reduced by hydrochloric acid producing nascent chlorine which attacks gold. This gets some support from the reports that the oxidation of HCl by V(V) proceeds at elevated temperature and high concentration of the acid. But platinum too is susceptible to such chlorine and the salts formed like those of gold are soluble. Hence some corrosion should be observable on the surface but we could not. Perhaps a protective oxide layer comes into existence on the platinum surface which prevents corrosion although oxidation potential values make it more prone to attack than gold.

Still another possibility is the extraction of an electron by the oxidizing agent from the solvent according to the equation



and the free radical (OH) so produced can attack metal films. No doubt the formation of free radical by this mechanism requires too high a potential (calc. 2.8 V) still it cannot be ignored as a possibility.

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