[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Reduction of +5 Vanadium in the Silver Reductor

BY JAMES J. LINGANE AND LOUIS MEITES, JR.

In their original study of the silver reductor Walden, Hammett and Edmonds[1] found that +5 vanadium was reduced only to the +4 state from its solutions in 1 *M* hydrochloric acid. These authors observed partial reduction to the +3 state only when the solution contained 5 *M* hydrochloric acid, or 1 *M* hydrochloric acid and 5 *M* sulfuric acid.

From the recent careful measurements of the vanadic ion–vanadyl ion potential by Jones and Colvin[2]

$$V^{+++} + H_2O = VO^{++} + 2H^+ + e^-;\ E^0_{298} = -0.337\text{ v.} \qquad (1)$$

When this half-reaction is combined with that of the silver–silver chloride couple of the silver reductor,[3] *viz.*

$$Ag + Cl^- = AgCl + e^-;\ E^0_{298} = -0.2225\text{ v.,} \qquad (2)$$

we obtain

$$VO^{++} + Ag + 2H^+ + Cl^- = V^{+++} + AgCl + H_2O;\ E^0_{298} = 0.115\text{ v.} \qquad (3)$$

from which $\Delta F^0_{298} = -2650$ cal., and

$$K = \frac{(V^{+++})}{(VO^{++})(H^+)^2(Cl^-)} = 87.9 \qquad (4)$$

Thus if equilibrium were attained +4 (and hence +5) vanadium should be reduced almost completely to the +3 state in 1 *M* hydrochloric acid at 25°.

The fact that Walden, Hammett and Edmonds[1] observed no reduction below the +4 state from 1 *M* hydrochloric acid indicates that, although reduction of +5 vanadium to the +4 state occurs rapidly, the reduction of +4 vanadium according to reaction 3 is so slow that equilibrium is not reached during the relatively rapid passage of the solution through the silver reductor. Without information on the influence of variations in the experimental conditions, and especially possible catalytic activity of accompanying elements, a determination based on such a metastable situation is subject to considerable uncertainty.

This investigation was undertaken to determine the influence of the following variables on the reduction of +5 vanadium in the silver reductor: (a) rate of flow of the solution, (b) hydrogen ion concentration, (c) chloride ion concentration, (d) temperature, and (e) presence of elements commonly associated with vanadium which might act as catalysts. Information has also been obtained on the rate of attainment of equilibrium in reaction 3. The conditions which lead to an accurate determination of vanadium via reduction to the +4 state in the silver reductor and titration with permanganate have been definitely established.

Experimental

Silver reductors were prepared as described by Walden, Hammett and Edmonds.[1] The silver columns were approximately 3.5 cm. in diameter and 4.0 cm. high, and the volume of solution retained in the column was 7.5 to 8.0 cc. To minimize the effect of variations in the active height of the column, the reductors were regenerated by contact with a zinc rod in dilute sulfuric acid[1] when the dark silver chloride zone had progressed downward about one-fifth the height of the column. It was later found that this precaution was unnecessary, and reductors in which the silver chloride zone occupied as much as two-thirds the height of the column gave identical results as the freshly regenerated reductors.

Standard solutions of +5 and +4 vanadium were prepared from purified ammonium vanadate as previously described.[4]

The concentration of +5 vanadium was usually 0.1 *M*, and the concentrations of hydrogen and chloride ions were adjusted by suitable additions of perchloric acid and sodium chloride. Usually 25 cc. of the solution was passed through the reductor at room temperature (23–27°) at the rate of 30 cc./minute, and the reductor was washed with three to five 25-cc. portions of the appropriate acid solution. Since +3 vanadium is rapidly oxidized by atmospheric oxygen, air was removed from the solutions and reductor with pure hydrogen, and the reduced solutions and washings were collected under carbon dioxide.

The amount of +3 vanadium formed was determined directly by potentiometric titration to the +4 state with 0.0075 *N* permanganate. A platinum indicator electrode, saturated calomel reference electrode and ordinary potentiometric equipment were used. Carbon dioxide was bubbled through the solution to exclude air and provide stirring. Manganous sulfate (*ca.* 0.03 *M*) was added to the solution to catalyze the reaction and stabilize the potential. Even with manganous ion present it was necessary to wait about five minutes after each addition of permanganate solution until the potential became reasonably constant. The potential break at the end-point was usually in the neighborhood of 90 mv. per 0.1 cc. of 0.0075 *N* permanganate. The equivalence point potential was approximately 0.43 v. positive to the saturated calomel electrode.

Results and Discussion

In a series of experiments at room temperature in which the concentrations of hydrogen and chloride ions were separately varied between 0.2 and 2 *M*, the amount of +3 vanadium found in the reduced solutions varied only between 0.090 and 0.102% with no systematic trend. Evidently reaction 3 is remarkably slow, and its rate is not sensibly affected by wide variations in the hydrogen and chloride ion concentrations in the range 0.2 to 2 *M*. Substitution of sulfuric acid for perchloric acid was without effect.

Decreasing the rate of flow through the reductor from 30 to 9.7 cc./min. produced no change in the small amount of +3 vanadium formed.

---

[1] G. H. Walden, Jr., L. P. Hammett and S. M. Edmonds, THIS JOURNAL, **56**, 350 (1934).

[2] Grinnell Jones and J. H. Colvin, THIS JOURNAL, **66**, 1563 (1944).

[3] H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932).

[4] J. J. Lingane and L. Meites, *ibid.*, **68**, 2443 (1946).

Furthermore, no significant change was observed when the height of the silver column was increased from 4 to 12 cm., the diameter remaining constant at 3.5 cm.

When the concentrations of hydrogen and chloride ions are very great reduction to the +3 state does occur fairly rapidly. In a typical experiment in which a solution containing 0.1 *M* ammonium vanadate, 4.5 *M* sulfuric acid and 7.5 *M* hydrochloric acid was passed twice through the reductor in the absence of air, 95% of the vanadium was reduced to the +3 state.

Increasing temperature greatly increases the rate of reaction 3, and hence the amount of +3 vanadium formed, as shown by the following data obtained with a 0.1 *M* ammonium vanadate solution in 1 *M* hydrochloric acid.

t°, C.	25	45	65	80	95
V^{+3}, %	0.10	0.99	1.99	3.62	31.9

Note that the amount of +3 vanadium formed increases very rapidly at temperatures above 80°. It is evident that the temperature should not be higher than 25° in the practical determination of vanadium with the silver reductor.

The possible catalytic effect of elements commonly associated with vanadium was investigated. Iron, cobalt, nickel, manganese, chromium, titanium, molybdenum, uranium and tungsten, in amounts approximately equal to that of the vanadium, produced no detectable change in the amount of +3 vanadium formed (0.08 to 0.16%), when the reduction was carried out by the usual technique at room temperature in 1 *M* hydrochloric acid. Molybdenum, uranium, and tungsten are of course reduced under these conditions to Mo(V), U(IV), and W(V), which are subsequently reoxidized to the +6 states by permanganate, and hence their amounts must be known, and corrected for, when vanadium is being determined.

In order to obtain an idea of the rate of reaction 3, 400 cc. of 0.1 *M* ammonium vanadate solution originally containing 1.96 *M* hydrogen ion (as sulfuric and hydrochloric acids) and 1.14 *M* chloride ion was agitated with 50 g. of finely-divided silver until equilibrium was attained. Air was excluded from the reaction flask with a steady stream of carbon dioxide, and the flask was kept in a water thermostat at 25.00°. Efficient mechanical stirring was employed. Samples were withdrawn at intervals, with precautions to prevent air-oxidation, and the concentration of +3 vanadium was determined by potentiometric titration to the +4 state with standard permanganate. An exactly similar experiment, except that the concentration of hydrogen ion was 2.27 *M*, was performed with 0.1 *M* vanadyl sulfate instead of ammonium vanadate. The results are shown in Table I.

TABLE I

RATE OF FORMATION OF +3 VANADIUM BY REDUCTION OF +4 AND +5 VANADIUM WITH SILVER AT 25°

Time, min.	V^{+3}, %
(a) 0.1 *M* Ammonium vanadate originally containing 1.14 *M* chloride and 1.96 *M* hydrogen ion	
45	32.1
120	52.0
284	73.0
431	83.0
1192	97.5
1326	98.7
(b) 0.1 *M* Vanadyl sulfate originally containing 1.14 *M* chloride and 2.27 *M* hydrogen ion	
16	42.7
117	95.0
191	98.8

From these data, which demonstrate the remarkable slowness of reaction 3, it is clear why only a very slight amount of +3 vanadium is formed during the relatively rapid flow of vanadate solution through the silver reductor. The more rapid approach to equilibrium with the vanadyl solution (*ca.* three hours) than with the vanadate solution (*ca.* twenty-two hours) may have been due to the considerably larger concentration of hydrogen ion in the former case; in the reduction of the vanadate solution the actual concentrations of hydrogen and chloride ions after the initial rapid reduction to the +4 state were 1.76 and 1.04 *M*, compared to 2.27 and 1.14 *M* at the start of the experiment with the vanadyl solution. In both cases the equilibrium concentrations of vanadic ion agree well with the values predicted by equation 4.

Since +5 vanadium (probably pervanadyl ion, VO_2^+, under these conditions) is reduced rapidly to the +4 state (probably vanadyl ion, VO^{++}) it appears that the primary reactions between either the VO_2^+ ion or the VO^{++} ion and the silver are so rapid that they are diffusion controlled. Hence the slow, rate-controlling step in the reduction of the VO^{++} ion to V^{+++} must be a secondary reaction.

A direct comparison of the silver reductor technique with the classical sulfur dioxide method[5] was made with the results shown in Table II.

TABLE II

PERMANGANIMETRIC DETERMINATION OF VANADIUM AFTER REDUCTION BY SULFUR DIOXIDE AND BY THE SILVER REDUCTOR

	Normality of ammonium vanadate solution	
	Sulfur dioxide method	Silver reductor
	0.07481	0.07487
	.07485	.07480
	.07479	.07479
	.07482	.07486
Av.	0.07482	0.07483
Av. dev.	±0.03%	±0.04%

The same ammonium vanadate and permanganate solutions, and the same calibrated volu-

---

[5] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 359.

metric apparatus, were used in the comparisons of Table II. The permanganate solution was standardized against sodium oxalate. The reduction procedure with sulfur dioxide was essentially that described by Hillebrand and Lundell[5] and Campbell and Woodhams.[6] In the determinations via the silver reductor the solutions contained 1 *M* hydrochloric acid, they were poured through the reductor at a rate of 30 cc./minute, and the reductor was washed with four 25-cc. portions of 1 *M* hydrochloric acid. Since Fryling and Tooley[7] demonstrated by specific tests that significant amounts of hydrogen peroxide are produced when hydrochloric acid solutions containing dissolved oxygen are passed through the silver reductor, air was removed from the reductor, ammonium vanadate solutions, and wash solutions, with hydrogen. The reduced solutions were diluted with an equal volume of water and 0.2 mole (*ca.* 0.08 mole excess) of sodium acetate was added to buffer the solution at a *p*H of about 4.5. The solutions were then allowed to stand in contact with air for fifteen minutes to insure reoxidation to the +4 state of the small amount of +3 vanadium present. Finally 2 cc. of saturated manganous sulfate solution was added, and the solutions were heated to about 80° and titrated with permanganate to a visual end-point.

In five other determinations with the silver reductor, 25-cc. portions of the same ammonium vanadate solution used in the experiments of Table II were reduced without removing air from the solutions. The results averaged 1.3% higher than those in Table II (corresponding to an average excess consumption of 0.24 cc. of 0.1 *N* permanganate), thus confirming the conclusions of Fryling and Tooley[7] that considerable amounts of hydrogen peroxide are formed in the silver reductor and that air must be excluded in accurate work. The excess consumption of permanganate in these experiments is several times larger than that found by Fryling and Tooley[7] in the determination of iron, which indicates that the reaction $O_2 + 2Ag + 2H^+ + 2Cl^- = H_2O_2 + 2AgCl$ is catalyzed by the simultaneous reduction of +5 vanadium. It is interesting to note that these results are in harmony with the polarographic characteristics of oxygen.[8]

Summary

In spite of the fact that the equilibrium constant of the reaction $VO^{++} + Ag + 2H^+ + Cl^- = V^{+++} + AgCl + H_2O$ is 87.9, this reaction takes place so slowly at room temperature that only very slight amounts of +3 vanadium are formed when solutions of +5 vanadium in 0.2 to 2 *M* hydrochloric acid are passed through the silver reductor at a temperature of 25° or lower. Within wide limits, the rate of flow of the solution and the dimensions of the silver column are without effect, but large amounts of +3 vanadium are formed when the hydrochloric acid concentration is increased above 2 *M* and/or when the temperature is increased above 25°.

Experiments in which air-free solutions of +5 and +4 vanadium were shaken with powdered silver demonstrated that many hours are required for the attainment of equilibrium in the foregoing reaction; the equilibrium concentration of +3 vanadium agrees with the value predicted from the standard potentials of the vanadyl–vanadic and silver–silver chloride half-reactions.

The conditions required for an accurate determination of vanadium with the silver reductor *via* reduction to the +4 state and titration with permanganate have been defined.

---

(6) E. D. Campbell and E. L. Woodhams, THIS JOURNAL, **30**, 1233 (1908).

(7) C. F. Fryling and F. V. Tooley, *ibid.*, **58**, 826 (1936).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 307.

CAMBRIDGE, MASSACHUSETTS RECEIVED OCTOBER 9, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Contrast in the Dimerization of Polychloro- and Polyfluoro-ethylene

BY ALBERT L. HENNE AND ROBERT P. RUH

Halogenated derivatives of ethylene are easily polymerized, and several of them give commercial products, for example, $CH_2{=}CHCl$, $CH_2{=}CCl_2$, $CF_2{=}CF_2$. The mechanism of polymerization is mostly postulated, and on insufficient experimental data. We have prepared and examined the dimers of $CHCl{=}CCl_2$, $CClF{=}CF_2$ and $CCl_2{=}CF_2$. None of these dimerizations occurs at random. The first one is a "head to tail" type of polymerization leading to an open chain olefinic dimer; "head to head" type of polymerization does not occur; "head to tail" leads to $CHCl_2CCl_2CH{=}CCl_2$, and "tail to head" leads to $CHCl{=}CClCHClCCl_3$; both formulas are allylic halides, capable of a second form $CHCl_2CCl{=}CHCCl_3$, identical in both cases; the dimer is therefore represented as an allylic equilibrium of chlorinated butenes: $CHCl_2CCl_2CH{=}CCl_2 \rightleftarrows CHCl_2CCl{=}CHCCl_3 \rightleftarrows CHCl{=}CClCHClCCl_3$. In contrast, the fluorinated olefins undergo a *cyclic* dimerization leading to *only one* of the isomers which would result from random polymerization; specifically, $CClF{=}CF_2$ gives $\overline{CClFCClFCF_2CF_2}$; and $CCl_2{=}CF_2$ gives $\underline{CCl_2CCl_2CF_2CF_2}$; in contrast with the general