$\rightarrow {}^1E(d_{xz}, d_{yz})$ transition. Since this band occurs at higher energy than in $[MoO(OH)(CN)_4]^{3-}$ (16,900 cm^{-1})[4a] and because the ν(Mo=O) frequency of ~950 cm^{-1} (Table I) is higher than for the oxohydroxotetracyanomolybdate(IV) complex (921 cm^{-1}),[4a] the degree of oxygen to metal π bonding appears to be slightly greater in the present compounds.

Studies of the chemical reactivity of the $[MoOX(CNR)_4]^+$ cations are in progress.

Acknowledgments. We thank Mr. Lawrence Stam for experimental assistance and the National Science Foundation for financial support under Grant GP-27239X.

Registry No. $[MoOCl(CNCH_3)_4](PF_6)$, 50432-35-4; $[MoOCl(CNCH_3)_4](I_3)$, 50432-36-5; $[MoOBr(CNCH_3)_4](BrI_2)$, 50432-37-6; $[MoOCl(CNC_2H_5)_4(I_3)$, 50432-38-7; $[MoOCl(CN\text{-}t\text{-}C_4H_9)_4](I_3)$, 50546-24-2; $[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, 41982-05-2; $MoCl_4$, 13320-71-3; $MoCl_5$, 10241-05-1; $Mo(CO)_6$, 13939-06-5.

Contribution from the Department of Chemistry,
Georgetown University, Washington, D. C. 20007

Tungstovanadate Heteropoly Complexes. V. The Ion $H_2W_{11}V^VO_{40}{}^{7-}$ and the Oxidation and Reduction of Tungstovanadates

C. M. FLYNN Jr., M. T. POPE,* and S. O'DONNELL

Received July 30, 1973

The yellow heteropoly anion $H_2W_{11}V^VO_{40}{}^{7-}$, isolated as potassium and tetramethylammonium salts, is obtained by chlorine oxidation of $H_2W_{11}V^{IV}O_{40}{}^{8-}$. The complex decomposes to metatungstate and cationic vanadium(V) at pH 0–2 and to $V_2W_4O_{19}{}^{4-}$ among other products at pH 5. Proton nmr demonstrates the presence of nonlabile (internal) protons in $H_2W_{11}VO_{40}{}^{7-}$ as in metatungstate. Reversible electron transfer for $H_2W_{11}VO_{40}{}^{7-} + e^- \rightarrow H_2W_{11}VO_{40}{}^{8-}$ ($E = +0.26$, pH 4) and for $VW_5O_{19}{}^{3-} + e^- \rightarrow VW_5O_{19}{}^4$ ($E = +0.20$ V, pH 2–4) is established by voltammetry at a wax-impregnated graphite electrode. Chemical reduction of tungstovanadates(V) and their interconversions are reported.

Introduction

In previous investigations[1] we have isolated and characterized eight tungstovanadates(IV) and -(V). This paper describes the preparation and characterization of 11-tungstovanadate(V) and cyclic voltammetry of complexes containing a single vanadium atom and summarizes the interconversion reactions of tungstovanadates(V).

Experimental Section

Reagents not obtained commercially were prepared as described.[1] Chlorine was conveniently handled as a solution in carbon tetrachloride, prepared by slowly passing the gas from a cylinder into the solvent under continuous agitation. Solutions up to 1 *M* in Cl_2 are easily prepared; they must be stored in a tightly stoppered container. The concentration was estimated by reaction of aliquots with excess aqueous KI followed by titration with sodium thiosulfate.

Chemical analyses and spectroscopic and electrochemical measurements were carried out as described previously.[1,2] A Bruker MFX-90 instrument was used for the ^1H and ^{51}V nmr measurements.

Preparation of 11-Tungstovanadate(V). (a) Potassium Salt. Potassium 11-tungstovanadate(IV) (6.5 g, 2.0 mmol) was dissolved by heating in 50–60 ml of 0.02 *M* potassium acetate–0.04 *M* acetic acid. The solution was cooled quickly to 25–40° and treated immediately with a moderate excess of Cl_2–CCl_4 solution and shaken. This resulted in a rapid color change to lemon yellow. The solution was separated from the carbon tetrachloride. A solution prepared by dissolving 5 g (50 mmol) of potassium acetate in 5 ml of water and adding 6 ml (100 mmol) of glacial acetic acid and 40 ml of 95% ethanol was added slowly to the tungstovanadate(V) solution with stirring. The potassium salt precipitated as a yellow powder; after a few minutes it was isolated by filtration (washing with ethanol-water followed by 95% ethanol). A yield of 6.1 g (90–95%) of bright lemon-yellow powder was obtained (tiny rods or laths under the microscope). *Anal.* Calcd for $K_7H_2W_{11}V^VO_{40}\cdot 14H_2O$: V, 1.57; W, 62.40; K, 8.44; H_2O, 8.34. Found: V, 1.54 (1); W, 62.40; K, 8.61 (2); H_2O, 8.05 (8); matter sum 99.86. In another preparation, the product was recrystallized as follows. The solid was dissolved in 10 ml of 0.1 *M* potassium acetate–0.5 *M* acetic acid. Saturated aqueous KCl solution (10 ml) was added, whereupon some solid precipitated. Sufficient water was added to redissolve the precipitate, and the solution was allowed to stand. When it had evaporated to 10–15 ml, much product had separated as deep yellow tabular to prismatic crystals. The crystals were isolated by washing successively with aqueous 2 *M* potassium acetate–2 *M* acetic acid buffer to remove KCl, buffer–ethanol mixture, and 95% ethanol. The air-dried crystals appeared to be slightly efflorescent and were stored in a tightly closed container. *Anal.* Found: V, 1.53; W, 62.20; K, 8.54 (3); H_2O, 8.53 by difference.

(b) Tetramethylammonium Salt. A solution of potassium 11-tungstovanadate(IV) in 100 ml of 0.01 *M* potassium acetate–0.01 *M* acetic acid was chlorinated as described above. A solution of tetramethylammonium chloride (6.6 g, 60 mmol) in 10 ml of water was added slowly with stirring to precipitate the product. The mixture was cooled in ice with stirring (about 20 min); then the product was isolated by filtration and washed with aqueous 1 *M* tetramethylammonium chloride. For recrystallization the solid was redissolved in the minimum amount (about 400 ml) of 0.01 *M* potassium acetate–0.05 *M* acetic acid. A solution of 22 g (200 mmol) of tetramethylammonium chloride in 10 ml of water was added to precipitate the product. After the mixture was stirred for 20 min, the solid was isolated by filtration (washed successively with aqueous 1 *M* tetramethylammonium chloride, ethanol–water, and ethanol). The air-dried product consisted of 6.0 g (about 85%) of bright lemon-yellow powder (tiny six-sided laths under the microscope). *Anal.* Calcd for $((CH_3)_4N)_6H(H_2W_{11}V^VO_{40})\cdot 4H_2O$: V, 1.58; W, 62.55; C, 8.92; H, 2.59. Found: V, 1.54 (1); W, 62.56; C, 8.83; H, 2.25.

(c) Attempt to Obtain an Ammonium Salt. Substitution of ammonium 11-tungstovanadate(IV) and ammonium acetate for the potassium salts in the above procedure did not result in quantitative oxidation to the vanadate(V) complex because of reactions of ammonium ion with the chlorine. The reaction mixtures had an odor like that of hypochlorous acid, in contrast to the other preparations.

Results and Discussion

11-Tungstovanadate(V). The method of preparation of this anion indicates that it has a Keggin structure based on that of metatungstate, $H_2W_{12}O_{40}{}^{6-}$. The following evidence also supports this conclusion. (1) The tetramethylammonium salt formed solid solutions with the corresponding meta-

---

[1] (a) C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, 10, 2524 (1971); (b) *ibid.*, 10, 2745 (1971); (c) *ibid.*, 11, 1950 (1972); (d) C. M. Flynn, Jr., H. So, and M. T. Pope, *ibid.*, 12, 1626 (1973).

[2] D. P. Smith and M. T. Pope, *Inorg. Chem.*, 12, 331 (1973).

tungstate.[1b] (2) Infrared spectra (1300–400 cm^{-1}) consisted of the following bands: potassium salt, 925, 868, 765, 590 (br), *ca.* 400; tetramethylammonium salt, 942, 930, 867, 768, 580 (br), *ca.* 400. The range for 11-tungstovanadate(IV) salts[1d] is 945–929, 882–873, 787–778, 670–610 (w, br), and *ca.* 400. (3) An nmr signal (see below) corresponding to the "internal" protons was observed at 6.08 ppm downfield from Tiers' salt in aqueous (D_2O) solution. Under similar conditions the corresponding signal from metatungstate[3] was at 6.09 ppm. A solution containing metatungstate and $H_2W_{11}VO_{40}{}^{7-}$ gave both signals.

The solid salts underwent no color change in contact with the atmosphere during 4–5 months. The potassium salt is surprisingly soluble in water (*ca.* 0.2 *M* at 25°) in contrast with other 7- Keggin anions, *e.g.*, $K_7V_5W_8O_{40}\cdot12H_2O$[1c] which have solubilities an order of magnitude lower. The solutions are most stable at pH 4 and their absorption spectra conformed to Beer's law when fresh (0.02–2.0 m*M* in complex). Features were a weak inflection at ~390 nm (26 kK), ϵ 2.1 × 10^3, a shoulder at ~355 nm (28 kK), ϵ 2.7 × 10^3, and a shoulder at 250 nm (40 kK), ϵ 3.7 × 10^4. Solutions at pH 5 decomposed slowly during 40 days, developing a maximum at about 385 nm and a minimum at about 350 nm, indicative of partial conversion to $V_2W_4O_{19}{}^{4-}$. Absorbance data were inconsistent with the presence of only starting material, $V_2W_4O_{19}{}^{4-}$, and/or $VW_5O_{19}{}^{3-}$. Solutions at pH 4 decomposed slowly and incompletely during 40 days, showing no new spectral features. Solutions at pH 2 or lower decomposed (complete in several hours in 1.0 *M* HCl and 0.02 m*M* complex; incomplete in 40 days at pH 2 and 2.0 m*M*), giving colorless or very pale yellow solutions with spectra characteristic of metatungstate. Results of absorbance measurements were as follows (acidity, moles of metatungstate per mole of 11-tungstovanadate (V)): pH 2, 0.90 ± 0.01; 0.10 *M* HCl, 0.88 ± 0.01; 1.0 *M* HCl, 0.78–0.89 (increase with increasing concentration of complex). The metatungstate was observed to decompose slowly in 1.0 *M* HCl (up to 10% in 40 days at 23–25°). Solutions of $H_2W_{11}VO_{40}{}^{7-}$ showed nmr signals from the protons occupying the central cavity of the Keggin structure and, at 22.63 MHz, from the vanadium atom.[4] The vanadium resonance was 539 ± 1 ppm upfield from external $VOCl_3$ and was about 60 Hz wide. When 0.03 ml of 2 *M* DCl was added to 0.5 ml of 0.095 *M* $K_7H_2W_{11}VO_{40}$ in D_2O, the proton nmr signal disappeared within 5 min. This indicates a rapid opening up of the central tetrahedral cavity of the Keggin structure to permit exchange with solvent. Such an exchange does not occur in acidified solutions of metatungstate. The ^{51}V nmr spectrum of acidified solutions of $H_2W_{11}VO_{40}{}^{7-}$ still showed the original signal at 539 ppm after 4.5 hr, together with a new signal at 548–550 ppm. Both signals appeared in freshly acidified solutions (*i.e.*, after 5 min) with relative intensities (539:548) of about 2:1. Only after addition of more acid (a total of 0.28 ml of 2 *M* HCl to 1.5 ml of 0.095 *M* $H_2W_{11}VO_{40}{}^{7-}$) and prolonged standing did the intensity of the 548-ppm peak increase relative to that of the peak at 539 ppm. The resonance at 539 ppm in the acidified solutions was about 100 Hz wide, a broadening that can be attributed to protonation of the anion.[5] It seems likely that protonation occurs at the oxygen atoms that connect the vanadium atom to the rest of the Keggin structure and that subsequently one or more of the V–O–W bonds are broken, opening up the center of the structure to proton exchange.[5]

Table I. Voltammetric Data for $H_2W_{11}VO_{40}{}^{7-}$ and $H_2W_{11}VO_{40}{}^{8-}$ in 0.2 *M* Sulfate or Acetate at 25° (WIGE, Voltage Scan Rate 0.5 V min^{-1})

pH	E_{p_c}	E_{p_a}
	$H_2W_{11}VO_{40}{}^{7-}$, 0.41 m*M*	
2.0	+0.37	not observed
2.6	0.33	+0.44
4.0	0.23	0.30
5.0	0.14	0.29
	$H_2W_{11}VO_{40}{}^{8-}$, 0.20 m*M*	
4.80	+0.13	+0.30

Cyclic voltammetry of solutions of both 11-tungstovanadate(V) and -(IV) complexes using a wax-impregnated graphite electrode (WIGE) is consistent with a simple one-electron transfer process. The results are given in Table I. The variation of peak potential with pH shows that protonation accompanies reduction in this pH range; spectrophotometric evidence for protonation of $H_2W_{11}VO_{40}{}^{8-}$ was presented in a previous paper.[1d] According to the separation of anodic and cathodic peaks, the electron transfer process is reversible only at pH 4 where decomposition of the oxidized and reduced species is minimal. A solution of 11-tungstovanadate(V) (0.95 m*M*) in a pH 4 acetate buffer was stirred with granulated zinc for 3 hr. A visible spectrum of the resulting wine-red solution was characteristic of 11-tungstovanadate(IV) (shoulder at 660 nm; maximum at 490 nm). Absorbance data indicated 97–99 mol % reduction.

Reduction of Other Tungstovanadates(V). We have previously reported[1a,d] independent direct syntheses of 5-tungstovanadates(IV) and -(V), $VW_5O_{19}{}^{4-}$ and $VW_5O_{19}{}^{3-}$. At pH 4 $VW_5O_{19}{}^{3-}$ reacts with excess hydrazine in hot solution with a color change to purple-pink indicative of $VW_5O_{19}{}^{4-}$. Voltammograms (WIGE) of 5-tungstovanadate(V) show the reduction occurring at *ca.* +0.2 V (at pH 2, E_{p_c} = +0.18, E_{p_a} = +0.26; pH 4, E_{p_c} = +0.15, E_{p_a} = +0.24 V). A voltammogram of 5-tungstovanadate(IV) at pH 4 has E_{p_a} = +0.16 and E_{p_c} = +0.24.

Tungstovanadate complexes containing more than one vanadium atom per molecule, *e.g.*, $V_2W_4O_{19}{}^{4-}$, $V_3W_{10}O_{40}{}^{5-}$, and $V_4W_9O_{40}{}^{6-}$, are all reduced by hydrazine, but no stoichiometric products could be isolated. The 4-tungsto-2-vanadate(V) complex is reduced by hydrazine at pH 8 (operations were performed under nitrogen), but much decomposition occurs. In the presence of guanidinium ion, much dark precipitate and a low yield of dark square block crystals were formed. The precipitate contained little tungsten. The crystals were isolated (the solution was brownish yellow). *Anal.* Calcd for $(CN_3H_6)_5HV^{IV}{}_2W_4O_{19}$:[1d] V, 6.97. Found: V, 6.00. The product could be solid solution containing some $V^V{}_2W_4O_{19}{}^{4-}$ and $V^{IV}W_5O_{19}{}^{4-}$. No evidence was found for the existence of $V^{IV}V^VW_4O_{19}{}^{5-}$, which would be expected to have a very intense color, possibly blue or green in analogy with isopolyvanadates(IV) and -(V). A voltammogram of $V_2W_4O_{19}{}^{4-}$ at pH 5 showed a very irreversible wave, E_{p_c} = −0.3, E_{p_a} = +0.1 V.

A solution of $K_5V_3W_{10}O_{40}$ in pH 3 formate buffer was treated immediately with excess N_2H_5Cl (5 mol/mol complex). The solution was warmed briefly, allowed to stand one day, neutralized to pH near 4 with $KHCO_3$, and evapo-

---

[3] M. T. Pope and G. M. Varga, Jr., *Chem. Commun.*, 653 (1966).

[4] M. T. Pope, C. M. Flynn, Jr., H. So, and S. O'Donnell, Abstracts, Seventh Hudson Symposium, Plattsburgh, N. Y., 1972; S. O'Donnell and M. T. Pope, in preparation.

[5] Although the ^{51}V nmr signal at 548 ppm occurs at the same position as that of $VO_2{}^+$(aq), a likely final product of the reaction, its width is only 80 Hz compared with 800–1000 Hz for $VO_2{}^+$(aq). Further details of the V nmr studies are given elsewhere.[4]

rated on the hotplate until black crystalline solid began to form. Crops of small black square block crystals were obtained. The crops had variable vanadium content. *Anal.* Calcd for $K_7V^VW_{10}V^{IV}{}_2O_{40}\cdot12H_2O$: V, 4.90; K, 8.77. Found (first crop): V, 5.04; K, 8.67. Found (second crop): V, 5.23.

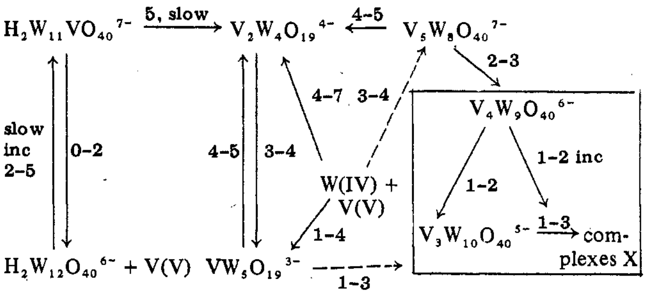
The complex $V_4W_9O_{40}{}^{6-}$ reacts similarly with hydrazine, with color change to brown or purple-brown. Reduction of the potassium salt was carried out as with the 3:10 complex but in pH 4 formate buffer. Solid crystallized during standing; the solution was subsequently evaporated (no neutralization) to obtain more product. The crops of small black square block crystals varied in vanadium content. *Anal.* Calcd for $K_7V^VW_9V^V{}_2V^{IV}O_{40}\cdot12H_2O$: V, 6.82; K, 9.16. Found (first crop): V, 6.60; K, 8.68. Found (second crop): V, 5.78.

When the filtrate from a preparation of $K_7V_5W_8O_{40}$[1c] was allowed to stand for 5 months in a closed container, black square block crystals formed. Analyses indicated that this phase was mainly $K_7V_5W_8O_{40}\cdot12H_2O$ with only a small proportion of reduced species in solid solution.

Interconversion of Tungstovanadates. Scheme I summarizes the main reactions that occur in aqueous tungstate(VI)-vanadate(V) solutions. The product of each reaction in the scheme has been identified by crystallization of sparingly soluble salts. Many of the reactions are slow or incomplete and no attempts were made to determine reaction stoichiometries. At pH >8 all tungstovanadates decompose to $HVO_4{}^{3-}$ and $WO_4{}^{2-}$ at varying rates.

The complexes X identified in the scheme were phases consisting of lustrous orange leaflets or red parallelopipeds that were obtained as by-products in the preparations[1b] of $K_6V_4W_9O_{40}$ and $K_5V_3W_{10}O_{40}$. These phases did not possess constant composition, despite optical homogeneity. The two phases were interconvertible by recrystallization (leaflets at pH 2-3, parallelopipeds at pH 0-1, mixtures of these at pH 1-2) but were not observed to convert to the 4:9 or 3:10 complexes. They were also produced in attempts to recrystalize the 4:9 complex at pH below 2 and in attempts to recrystallize the 3:10 complex (pH below 3). If tetramethylammonium metatungstate was recrystallized from solutions containing small proportions of the 3:10 or 4:9 complex, the crystals were orange, indicating extensive solid solution formation. If such recrystallizations were carried out in the presence of small proportions of the leaflet or parallelopiped potassium salts, the metatungstate crystals were colorless, indicating no significant solid solution formation. When aqueous solutions of the potassium compounds were made about 5 *M* in sulfuric acid and shaken with diethyl ether, dense orange-red oils were formed. All of these data, combined with complete metal analyses for two samples each of leaflets and parallelopipeds, suggested that these materials were solid solutions containing anions based on the structure of $P_2W_{18}O_{62}{}^{6-}$, *i.e.*, $K_{6+x}V_2W_{18-x}V_xO_{62}\cdot nH_2O$, with $x \cong 3$–4 for leaflets and $x \cong 2$-3 for parallelopipeds.

Scheme I. Interconversions of Tungstovanadates(V)[a]



[a] Numbers indicate the range of pH for each reaction. Broken arrows denote slow reactions occurring in concentrated solutions. Complexes enclosed in the box are extractable by ether from strongly acid solutions; the resulting free acids slowly decompose to oxide precipitates.

When K_2WO_4 was refluxed with vanadate(V) (W/V = 5 to 11) in acetic acid, as in the new preparation of metatungstate,[1d] one of the products obtained consisted of yellow leaflets. These were similar in habit and solubility to the leaflet potassium salts described above and also had variable composition. Complete analyses for one preparation suggested a composition close to $K_{10}V_2W_{17}O_{61}\cdot18H_2O$. An aqueous solution of the product treated with acid and ether as above gave a dense brown-yellow oil. This and the leaflet and parallelopiped phases described above all appear to be closely related.

The potassium salts of complexes X were soluble in aqueous HCl; the solutions of the red phases lightened to orange on heating. Decomposition to oxide precipitates was slow and required HCl concentrations ⩾6 *M*. It was thought that $V_2W_{18}O_{62}{}^{6-}$ might exist in these solutions. Tetramethylammonium and guanidinium ions each gave slightly soluble products which were shown by microscopy to be mixtures of fine crystals. Near-ultraviolet spectra of these solutions showed featureless increasing absorbance as wavelength decreased from 550 to 330 nm.

Acknowledgments. This work has been supported by AFOSR, Grant No. AF70-1833, and, in part, by NSF, Grant No. GP 10538.

Registry No. $K_7H_2W_{11}V^VO_{40}$, 50639-93-5; $((CH_3)_4N)_6H(H_2W_{11}V^VO_{40})$, 50639-85-5; $H_2W_{11}VO_{40}{}^{7-}$; 50639-86-6; $H_2W_{11}VO_{40}{}^{8-}$; 50639-87-7; $VW_5O_{19}{}^{3-}$. 50639-95-7; $VW_5O_{19}{}^{4-}$, 50639-96-8; $V_2W_4O_{19}{}^{4-}$, 11074-97-8; $(CN_3H_6)_5HV^{IV}{}_2W_4O_{19})$, 50639-89-9; $K_7VW_{10}V^{IV}{}_2O_{40}$, 50639-91-3; $K_7V^VW_9V^V{}_2V^{IV}$, 50639-92-4; $K_8H_2W_{11}V^{IV}O_{40}$, 50639-94-6; $K_5V_3W_{10}O_{40}$, 50639-88-8; $K_6V_4W_9O_{40}$, 50639-90-2.