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Models for Heteropoly Blues. Degrees of Valence Trapping in Vanadium(IV)- and Molybdenum(V)-Substituted Keggin Anions

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Optical and esr spectra and polarographic redox potentials are reported for the Keggin anions $PZW_{11}O_{40}^{n-}$ (Z = V^{IV}, Mo^V), $XV^{IV}W_{11}O_{40}^{n-}$ (X = P, Si, Ge, B, H_2, Zn), and $XV^{IV}Mo_{11}O_{40}^{n-}$ (X = P, Si), all of which are intensely colored "heteropoly blue"-like complexes. Single-crystal esr measurements prove that Mo(V) in $PMoW_{11}O_{40}^{4-}$ occupies one of the twelve equivalent metal sites in the Keggin structure. The esr parameters for V(IV) in the tungstate and molybdate anions are significantly different and show the valence electron to be more firmly trapped on vanadium in the tungstates than in the molybdates. Analysis of the intervalence charge-transfer spectra of these complexes according to the method of Hush leads to a similar conclusion. Variations and trends of the reversible redox potentials of Keggin anions are discussed in terms of a "localized" model for heteropoly blues and analogous complexes.

Introduction

Heteropoly anions that contain vanadium(IV) in place of a single molybdenum or tungsten atom in the well-known Keggin structure[1] are dark species[2-4] reminiscent of the mixed-valence "heteropoly blues."[5] We have suggested that such anions, *e.g.*, $PV^{IV}W_{11}O_{40}^{5-}$, differ from the corresponding heteropoly blues ($PW^VW_{11}O_{40}^{4-}$) only in the degree to which the valence electron is trapped on a single metal atom. Direct evidence for the presence of weakly trapped electrons in heteropoly blues has recently been reported.[6]

In this paper we report spectral and electrochemical data for a series of isostructural polyanions that contain vanadium(IV) or molybdenum(V). These complexes were chosen to provide differing degrees of electron trapping and to explore the effects of intervalence charge transfer upon optical and esr spectra and upon reduction potentials.

Experimental Section

Preparation of Complexes. Molybdotungstophosphates. Reasonably pure samples of $Na_3PMoW_{11}O_{40}\cdot{\sim}13H_2O$ could be obtained by two methods. (a) The first is a modification of Wu's procedure[7] for 12-tungstophosphoric acid using 0.30 mol of sodium tungstate and 0.025 mol of sodium molybdate. Following the ether extraction process the sodium salt was precipitated and recrystallized from 1 *M* sulfuric acid. *Anal.* Calcd for $Na_3PMoW_{11}O_{40}\cdot 13H_2O$: Na, 2.23; P, 1.00; Mo, 3.10; W, 65.40; H_2O, 7.57. Found: Na, 2.22; P, 1.01; Mo, 3.71; W, 65.23; H_2O, 7.48; P:Mo:W = 1:1.2:10.9. (b) The second method is dissolution of a stoichiometric (11:1) mixture of $Na_3PW_{12}O_{40}$ and $Na_3PMo_{12}O_{40}$ in water and subsequent concentration to *ca.* 0.1 *M* on a hot plate. The precipitated product was recrystallized from sulfuric acid. *Anal.* Found: Na, 2.09; P, 0.94; Mo, 3.56; W, 66.44; H_2O, 7.81; P:Mo:W = 1:1.2:11.9. Products of both methods gave essentially identical polarograms (see Results).

A solution containing the reduced anion $PMo^VW_{11}O_{40}^{4-}$ could be obtained either by controlled-potential electrolysis of solutions of the molybdenum(VI) complex or by direct reaction of $MoOCl_5^{2-}$ with $PW_{11}O_{39}^{7-}$. Ten grams of $Na_3PW_{12}O_{40}$(aq) was dissolved in 100 ml of a 1 *M* dichloroacetate buffer of pH 2.3 and the solution deaerated with nitrogen. At this pH the anion is mostly in the form of $PW_{11}O_{39}^{7-}$. A solution of 7.83 g $Na_2MoO_4\cdot 2H_2O$ in 100 ml 40% HCl was shaken with 20 ml of mercury for 15 min. The resulting dark red-brown solution was filtered and 10 ml of the filtrate added to the solution of $PW_{11}O_{39}^{7-}$. The red-violet color of $PMoW_{11}O_{40}^{4-}$ developed within 15 min. For the esr measurements, single crystals of $K_4SiW_{12}O_{40}\cdot 17H_2O$[2] were grown from an acidic aqueous solution containing a small amount of the red-violet solution. A polycrystalline sample was prepared by grinding several single crystals.

11-Metallovanado(IV) Anions. The preparations of $K_5PVW_{11}O_{40}\cdot 6H_2O$ and $K_8H_2VW_{11}O_{40}\cdot 13H_2O$ have been described elsewhere.[2,3] $K_8ZnVW_{11}O_{40}\cdot 5H_2O$ and $K_7BVW_{11}O_{40}\cdot 7H_2O$ were prepared by extensions of the method of Tourne *et al.*[4] The pH of a solution of 0.11 mol of Na_2WO_4 was adjusted to 6.3 with acetic acid and either 0.04 mol of boric acid or 0.01 mol of zinc chloride was added. The solution was heated to 80–90° and 0.01 mol of vanadyl(IV) sulfate was added whereupon the color changed to dark red-brown. Solid potassium chloride was added to the hot solution and the product crystallized upon cooling. The salts were recrystallized from an acetate buffer, pH 5. *Anal.* Calcd for $K_8ZnVW_{11}O_{40}\cdot 5H_2O$: V, 1.60; W, 63.57. Found: V, 1.60; W, 63.38; W:V = 10.96. Calcd for $K_7BVW_{11}O_{40}\cdot 7H_2O$: V, 1.64; W, 65.14. Found: V, 1.64; W, 65.02; W:V = 10.95.

The remaining vanadate complexes, $SiVW_{11}O_{40}^{6-}$, $GeVW_{11}O_{40}^{6-}$, $SiVMo_{11}O_{40}^{6-}$, and $PVMo_{11}O_{40}^{5-}$, were not isolated from solution. Solutions containing these anions were prepared by adding the stoichiometric quantity of vanadyl sulfate to solutions of the corresponding 12-metalates buffered at pH 5.

Physical Measurements. The electrochemical methods have been described in previous papers.[8,9] X-Band esr spectra were recorded, for the molybdate, on a Varian V-4500 spectrometer, and for the molybdo- and tungstovanadates, on a JEOL MES-3X spectrometer. Hyperfine and *g* parameters were corrected for second-order effects using Bleaney's equations.[10]

Results

Molybdo-11-tungstophosphate Anions. Direct synthesis of the pale yellow $PMo^{VI}W_{11}O_{40}^{3-}$ (I) and red-violet $PMo^VW_{11}O_{40}^{4-}$ (II) anions could be achieved as indicated in the Experimental Section. Owing to the hydrolytic instability of I (see below), it is difficult to avoid contamination[11] with $PMo_2W_{10}O_{40}^{3-}$ and $PW_{12}O_{40}^{3-}$.

Polarography, at the rotating platinum electrode, of both anions in 1.0 *M* sulfuric acid shows the molybdenum reduction–oxidation process at +0.52 and +0.56 V, respectively. The correct assignment of the polarographic wave was confirmed by controlled-potential electrolyses. The next observable reduction wave which appears at −0.04 V is a one-electron process, presumably

$$PMo^VW_{11}O_{40}^{4-} + e^- \rightarrow PMo^VW^VW_{10}O_{40}^{5-}$$

Solutions of anion I in 1.0 *M* sulfuric acid were unstable, and the height of the wave at +0.52 V diminished according to a first-order process with a half-life of 140 min at 25°. With very few exceptions, all other substituted Keggin anions, $XMW_{11}O_{40}^{n-}$, undergo similar hydrolyses in acid solution.[12]

The polarogram of anion II in 1.0 and 0.5 *M* H_2SO_4 was stable indefinitely, but at higher pH (2–5) the +0.56-V anodic wave slowly diminished in height and a new anodic wave grew at +0.2 V. The rate of this process increased with increasing pH and it probably indicates a hydrolytic disproportionation

$$2PMo^VW_{11}O_{40}^{4-} \xrightarrow{OH^-} PMo^V_2W_{10}O_{40}^{5-} + PW_{11}O_{39}^{7-}, \text{etc.}$$

An analogous reaction involving the oxidized anions $PVW_{11}O_{40}^{4-}$ and $PV_2W_{10}O_{40}^{5-}$ has been previously established.[9,13]

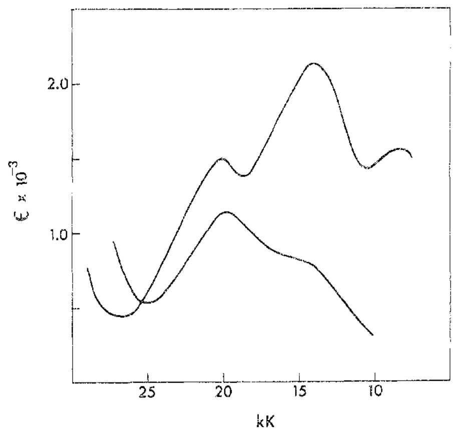

Figure 1. Optical spectra of $PW^VW_{11}O_{40}^{4-}$ (upper curve) and $PMo^VW_{11}O_{40}^{4-}$ (lower curve) in aqueous solution, pH 4.

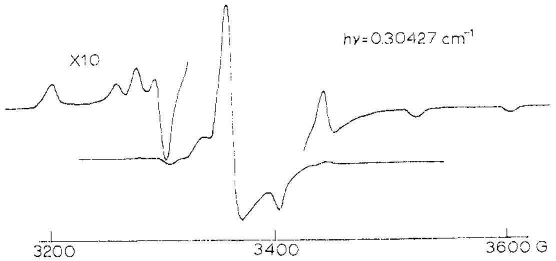

Figure 2. Polycrystalline esr spectrum of $PMo^VW_{11}O_{40}^{4-}$ doped into $K_4SiW_{12}O_{40}\cdot17H_2O$.

The optical spectrum of II in 1.0 *M* sulfuric acid is shown in Figure 1 together with that of the heteropoly blue $PW_{12}O_{40}^{4-}$. The features of the spectrum of II are a maximum at 20.0 kK (ε 1150 ± 20 M^{-1} cm^{-1}) and a shoulder at *ca.* 15 kK (ε 850).

Solutions of II exhibit a characteristic Mo(V) esr spectrum with hyperfine structure from ^{95}Mo (15.7%) and ^{97}Mo (9.6%), $I = {}^5/_2$. For the solution spectrum $g = 1.926$ and $a = 47.1 \times 10^{-4}$ cm^{-1}. A more complete esr analysis was carried out on a dilute crystalline sample using $K_4SiW_{12}O_{40}\cdot17H_2O$ as host. The polycrystalline spectrum of this sample is shown in Figure 2 and can be interpreted by the usual axial spin Hamiltonian for a d^1 system

$$\mathcal{H} = g_{\parallel}\beta HS_z + g_{\perp}\beta H(S_x + S_y) + AS_zI_z + B(S_xI_x + S_yI_y)$$

$g_{\parallel} = 1.9138 \pm 0.001$, $|A| = (73.1 \pm 0.5) \times 10^{-4}$ cm^{-1}, and $|B| = (34.3 \pm 1.0) \times 10^{-4}$ cm^{-1} were derived from the polycrystalline spectrum using Bleaney's perturbation expressions.[10] The maximum *g* value (1.9395) observed in the single-crystal spectra was taken as $g_{\perp}$. The single-crystal spectrum for $H \| c$ consists of two sets of lines with $g = 1.9265$ and $g = 1.9391$. The angles θ between the *g* directions and the *c* axis, derived from

$$g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$$

are 44.6 and 82.8°. We have shown elsewhere[2] that the site symmetry of the Keggin anion in the host crystal (space group $P6_222$) leads to only two independent orientations of terminal W═O groups with respect to *c*. These orientations correspond to angles of 48.1 and 80.8° (with undetermined errors) according a neutron diffraction study.[14] The similarity of these angles to those determined from the esr measurement provides further proof that the Mo^V═O group has replaced a W═O group in the Keggin structure.

Table I. Limiting Voltammetric Peak Potentials (WIGE, 0.5 V min^{-1}, 5 × 10^{-4} *M* Heteropoly Anion, 0.1 *M* Buffer^a)

Anion	pH	E_{p_a}, V	E_{p_c}, V
$PVW_{11}O_{40}^{5-}$	5	0.60	0.52
$SiVW_{11}O_{40}^{6-}$	5	0.44	0.35
$GeVW_{11}O_{40}^{6-}$	5	0.48	0.39
$BVW_{11}O_{40}^{7-}$	6	0.21	0.16
$H_2VW_{11}O_{40}^{8-}$	8	0.28	0.21
$ZnVW_{11}O_{40}^{8-}$	8	0.17	0.08
$PVMo_{11}O_{40}^{5-}$	5	0.49	0.39
$SiVMo_{11}O_{40}^{6-}$	5	0.31	0.23

^{a} Acetate (pH 5), phosphate (pH 6), ammonium (pH 8).

Table II. Optical Spectra of Vanadium(IV) Anions

Anion	Position, kK (ε, M^{-1} cm^{-1})	d-d shoulders,^{a} kK
$PVW_{11}O_{40}^{5-}$	20.0 (750), 25 sh^b (620)	12.0, 14.5
$SiVW_{11}O_{40}^{6-}$	20.2 (640)	11.6, 14.7
$GeVW_{11}O_{40}^{6-}$	20.2 (680)	11.5, 14.7
$BVW_{11}O_{40}^{7-}$	20.4 (620)	11.4, 14.7
$ZnVW_{11}O_{40}^{8-}$	20.5 (655)	11.4, 14.7
$H_2VW_{11}O_{40}^{8-}$	20.6 (635)	11.4, 14.7
$PVMo_{11}O_{40}^{5-}$	15.2 (1330)	*c*
$SiVMo_{11}O_{40}^{6-}$	15.7 (1270)	*c*

^{a} See text, uncertainty ±0.5 kK. ^{b} Shoulder. ^{c} Not observed.

Table III. Isotropic Esr Parameters for Vanadium(IV) Anions at 298°K

Anion	⟨*g*⟩	⟨*a*⟩, 10^{-4} cm^{-1}
$PVW_{11}O_{40}^{5-}$	1.952	90.7
$SiVW_{11}O_{40}^{6-}$	1.957	87.7
$GeVW_{11}O_{40}^{6-}$	1.953	92.1
$BVW_{11}O_{40}^{7-}$	1.953	92.3
$H_2VW_{11}O_{40}^{8-}$	1.957	94.1
$ZnVW_{11}O_{40}^{8-}$	1.953	90.2
$VO(aq)^{2+}$	1.963	97.2
$PVMo_{11}O_{40}^{5-}$	1.964	83.4
$SiVMo_{11}O_{40}^{6-}$	1.965	83.3

11-Metallovanado(IV) Anions. A number of these complexes have been briefly described previously by Tourne and Tourne,[4] and we have reported optical and esr data for $PVW_{11}O_{40}^{5-}$ [2] and $H_2VW_{11}O_{40}^{8-}$.[3] Recently, Otake, *et al.*,[15] have described the esr spectrum of supposed $PVMo_{11}O_{40}^{5-}$ (see Discussion).

The complexes are formed rapidly when the stoichiometric quantity of vanadyl(IV) sulfate is added to a solution of the 12-metallo anion which has been buffered (generally at pH ~5) to ensure that partial hydrolysis to the 11-anion $XZ_{11}O_{39}^{n-}$ has occurred. In those cases where crystalline products were not first isolated and analyzed, the compositions of the dark blue or purple-red solutions thus formed could be established by cyclic voltammetry and esr spectroscopy.

Cyclic voltammograms (wax-impregnated graphite electrode, WIGE) of each of the vanadium(IV) anions showed a one-electron oxidation–reduction feature which could be assigned to the process[16]

$$XV^{IV}Z_{11}O_{40}^{n-} \rightleftarrows XV^VZ_{11}O_{40}^{(n-1)-} + e^-$$

The potentials at which the oxidations occurred were pH dependent, indicating that a change in the extent of protonation of the anion occurred upon oxidation. All potentials tended to become pH independent above a pH that was characteristic for each charge type. Under these conditions the vanadium(V) anions were hydrolytically unstable and the oxidation was no longer reversible; *i.e.*, the difference between the anodic and cathodic peak potentials was greater than 59 mV. Details of the voltammograms are summarized in Table I; voltammetric data for $H_2VW_{11}O_{40}^{8-}$ have been reported elsewhere.[17]

The optical absorption spectra of the vanadium-containing anions have one or two intense bands in the visible region that are assigned as intervalence charge-transfer transitions (V^{IV} → W^{VI}, V^{IV} → Mo^{VI}). Weak shoulders observable on the

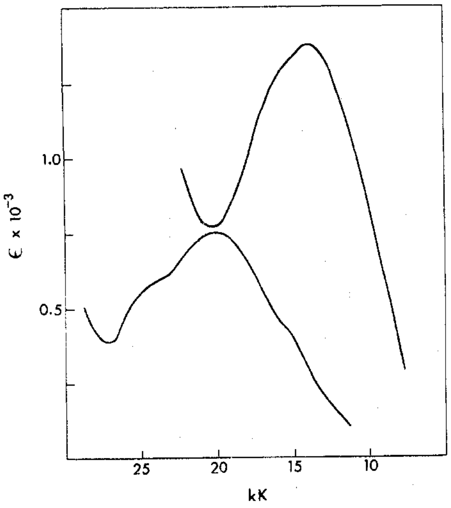

Figure 3. Optical spectra of $PV^{IV}W_{11}O_{40}{}^{5-}$ (lower curve) and $PV^{IV}Mo_{11}O_{40}{}^{5-}$ (upper curve) in aqueous solution, pH 5.

Table IV. Esr Parameters[a] for Vanadium(IV) Anions at 77°K

Anion	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
$PVW_{11}O_{40}{}^{5-}$	1.915	1.970	167.2	59.7
$SiVW_{11}O_{40}{}^{6-}$	1.918	1.969	164.8	57.6
$GeVW_{11}O_{40}{}^{6-}$	1.918	1.967	166.9	59.7
$BVW_{11}O_{40}{}^{7-}$	1.918	1.967	167.3	59.4
$H_2VW_{11}O_{40}{}^{8-}$	1.922	1.966	164.9	57.6
$ZnVW_{11}O_{40}{}^{8-}$	1.921	1.967	164.8	58.5
$VO(aq)^{2+}$	1.938	1.978	172.5	63.6
$PVMo_{11}O_{40}{}^{5-}$	1.939	1.974	151.2	53.4
$SiVMo_{11}O_{40}{}^{6-}$	1.936	1.975	149.5	54.2

[a] Hyperfine parameters are in units of 10^{-4} cm^{-1}. Estimated errors are ±0.001 for g values and $\pm 0.5 \times 10^{-4}$ cm^{-1} for hyperfine parameters. All data from frozen solutions except for $PVW_{11}O_{40}{}^{5-}$ and $PVMo_{11}O_{40}{}^{5-}$ which were also measured as dilute polycrystalline samples in $K_5BW_{12}O_{40} \cdot nH_2O$ with identical results.

low-energy side of the intervalence absorption of the tungstates are probably d–d transitions of V(IV).[2] Typical spectra are shown in Figure 3 and all spectral data are given in Table II.

Esr parameters derived from aqueous and rigid (frozen solution or dilute polycrystalline) samples are listed in Tables III and IV together with those for a solution of vanadyl(IV) sulfate at the same pH (*ca.* 5). In view of the significant differences in hyperfine parameters it was easy to verify from the spectra that solutions of the heteropoly anions contained no free vanadyl ion.[3]

Discussion

We have pointed out elsewhere[18] that the charge-transfer spectra of heteropoly blues and analogous complexes such as those described in this paper may be discussed in terms of the optical electronegativities of the "donor" and "acceptor" metal atoms, *i.e.*, V(IV) and W(VI), respectively, in $PVW_{11}O_{40}{}^{5-}$. For the present discussion it is convenient to view such anions as coordination complexes of VO^{2+} (or MoO^{3+}) with pentadentate oxo ligands,[19] *e.g.*, $[(PW_{11}O_{39})VO]^{5-}$. From this viewpoint the optical transitions can be labeled "metal-to-ligand charge transfer" since the polymetalate network of the Keggin anion acts as an acceptor ligand by virtue of the reducibility of the individual tungsten or molybdenum atoms. Other examples of such transitions include Cu(I) → W(VI)[20] (20.6 kK, ε 2400 in $CuW_{12}O_{40}{}^{7-}$) and Ce(III) → W(VI)[21] (23.8 kK, ε 300 in $[Ce(SiW_{11}O_{39})_2]^{13-}$; 28.8 kK, ε 480 in $CeW_{10}O_{35}{}^{7-}$). All of these complexes have type I,[22] and therefore reducible, polytungstate structures. In contrast, the presumed Ce(III) → Mo(VI)[23] transition in nonreducible[24] $CeMo_{12}O_{42}{}^{9-}$ (a type II structure) appears to be somewhat less allowed (22.2 kK, $\epsilon < 100$).

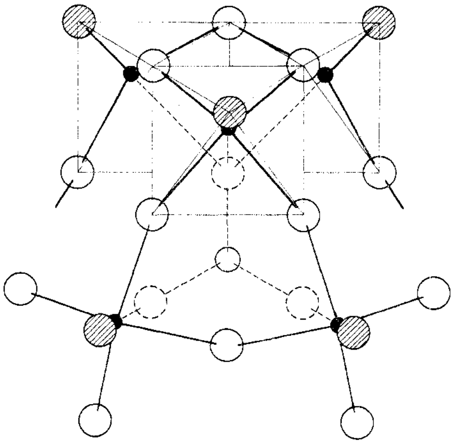

Figure 4. Portion of the Keggin structure, $XM_{12}O_{40}{}^{n-}$, showing five of the twelve equivalent MO_6 octahedra. This view shows the disposition of the four nearest "acceptor" metal atoms around a given "donor" (central black circle). The central atom, X, (small open circle) is attached to a quadruply-bridging oxygen atom (broken circle) that is trans to the metals' terminal oxo oxygens (shaded circles).

The *energies* of charge-transfer bands of this type (*i.e.*, transitions between two reasonably localized states) are determined both by differences in donor and acceptor orbital energies ("optical electronegativity" differences) and by a Madelung term which is dependent, among other factors, upon the distance between the donor and acceptor atoms.[25,26] The *intensities* of such bands are determined by the extent of orbital overlap (through bridging atoms if necessary) between the donor and acceptor atoms. Such overlap results in partial delocalization of the optical electron onto the acceptor atom. We refer to this delocalization as ground-state delocalization in order to distinguish it from delocalization that occurs in true mixed-valence complexes of the "weak interaction" type or Robin–Day[25] class II as a result of optical or thermal activation.

The optical spectra depicted in Figures 1 and 3 can be qualitatively interpreted using the above model and they show the expected effects upon both the energy and intensity of the charge-transfer transition when (a) the donor atom is changed from W(V) to Mo(V) (Figure 1) and (b) the acceptor atom is changed from Mo(VI) to W(VI) (Figure 3). A semiquantitative estimate of the difference in ground-state delocalization between $PVW_{11}O_{40}{}^{5-}$ and $PVMo_{11}O_{40}{}^{5-}$ can be obtained using the method described by Hush.[26] For this approach we estimate the half-width of the intervalence bands in both complexes to be 10 kK. Recalling that in the Keggin structure there are *four* acceptor atoms at a distance of *ca* 3.3 Å from a given donor, see Figure 4, the data of Table II can be interpreted to show that the optical electron is 98.5% localized on vanadium in $PVW_{11}O_{40}{}^{5-}$ and 96.6% localized in $PVMo_{11}O_{40}{}^{5-}$.

A more direct measure of the differences in ground-state delocalization in vanadotungstates and vanadomolybdates can be provided by the esr parameters. Before discussing the esr results it is first necessary to consider a recent paper by Otake, *et al.*[15] These workers reduced a number of isopoly anions and heteropoly molybdic acids, including $H_5PVMo_{11}O_{40}(aq)$ (no analysis reported), with molecular hydrogen at 280°. The resulting powders gave esr spectra typical of axial V(IV) or Mo(V) and the spectra were assumed to be those of the reduced Keggin anions. The esr parameters reported for reduced $H_5PVMo_{11}O_{40}$ do not agree with ours and indeed are very close to those for free VO^{2+} into which such heteropoly anions decompose at low pH.[27] Also, the esr spectrum of "reduced $H_3PMo_{12}O_{40}$" is quite unlike those reported for reduced

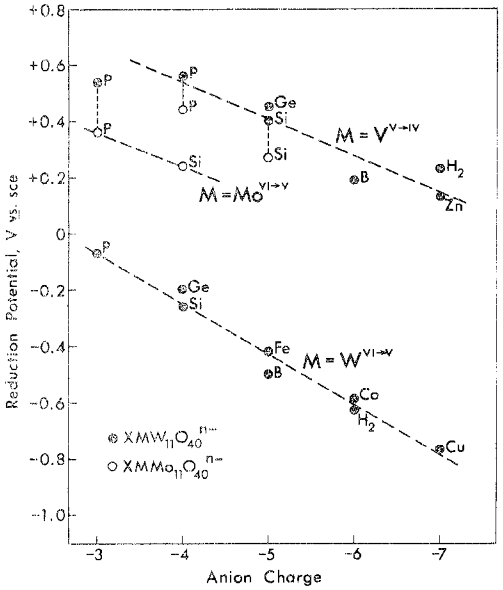

Figure 5. Limiting, pH-independent reduction potentials for Keggin anions as a function of anion charge.

12-molybdates that have been prepared under carefully controlled conditions.[6,28] It seems clear therefore that under the acid conditions used by Otake, *et al.*, all of the poly anions had at least partly decomposed upon reduction.

The esr parameters listed in Tables III and IV show significant differences between the tungstate and molybdate anions, but only very small effects of the central atom and anion charge. The mean values and standard deviations for the six tungstovanadates may be compared with the mean values (in parentheses) for the two molybdovanadates: $g_{\parallel}$, 1.919 ± 0.003 (1.937); $g_{\perp}$, 1.968 ± 0.002 (1.975); $10^4 A_{\parallel}$, 166.0 ± 1.3 (150) cm^{-1}; $10^4 A_{\perp}$, 58.7 ± 1.0 (54) cm^{-1}. In view of the identical structures and nearly identical bond lengths of these eight complexes we believe such differences indicate differences in ground-state delocalization. We can, for the purposes of comparison, further analyze the esr parameters in the following conventional manner. The appropriate expressions[29] for a d^1 axial complex with the unpaired electron in a d_{xy} orbital are

$$A_{\parallel} = P[-{}^4/_7\alpha^2 - \kappa + g_{\parallel} - 2.0023 + {}^3/_7(g_{\perp} - 2.0023)]$$

$$A_{\perp} = P[{}^2/_7\alpha^2 - \kappa + {}^{11}/_{14}(g_{\perp} - 2.0023)]$$

where P is $2.0023\beta_e g_N \beta_N \langle r^{-3} \rangle$, α^2 is the fractional contribution of the d_{xy} orbital to the in-plane π bonding, and κ is the isotropic Fermi contact term. These equations can be rearranged to give values for α^2 and κ, provided a suitable value of P is available. The value chosen for P depends upon the charge that is assumed to be on the vanadium atom, and a value (0.0128 cm^{-1}) appropriate for V^{2+} is often used for vanadyl complexes.[30] Using this value we calculate $\alpha^2 = 0.895$ and $\kappa = 0.687$ for the tungstates and $\alpha^2 = 0.810$ and $\kappa = 0.632$ for the molybdates. Although the absolute values of α^2 and κ may not be correct, the two sets of values are consistent with the relation proposed by Kivelson and Neiman,[31] $\kappa = \alpha^2\kappa_0$, with $\kappa_0 = 0.78$. The smaller values of α^2 and κ for the molybdovanadates are consistent with a greater degree of electron delocalization in these complexes than in the tungstovanadates.[32]

Next we turn to the electrochemical data, and in Figure 5 show the initial one-electron reduction potentials for a number of Keggin anions plotted against the anion charge. The potentials shown were determined under pH conditions where no protonation of the anions occurred; *i.e.*, they are limiting, pH-independent values. The data for Figure 5 are taken from Table I, from earlier papers,[20,33] and from Fruchart and Souchay.[34]

All the potentials lie close to one of three lines depending upon the nature of the atom that is reduced (vanadium, molybdenum, or tungsten). The negative slope (*ca.* -0.18 V e^{-1}) of these lines can be qualitatively and even semiquantitatively rationalized in terms of a simple electrostatic model.[33]

Reduction potentials of anions with the same charge show small influences of the central atom, *e.g.*, $SiW_{12}O_{40}^{4-}$ *vs.* $GeW_{12}O_{40}^{4-}$, etc. We shall label such differences a "trans effect"[35] since the central atom (X) of the Keggin structure functions as a ligand that is trans to the terminal oxo oxygen of the reducible metal atom (M), see Figure 4. The effect is expected to be small, especially for closed-shell central atoms, in view of the "saturated" μ_4-type oxygen bridge between X and M. The trans effect is also manifested in shifts of the first uv charge-transfer band which occurs at *ca.* 250 nm in the tungstates. If this transition is regarded simply as oxygen-to-tungsten charge transfer, there should be a one-to-one correspondence between absorption band shifts and reduction potential shifts for pairs of anions with the same charge. Evidence for such a correspondence has been presented elsewhere,[36] although the shifts are small.

Finally, we can observe a surprisingly large "cis effect" which is illustrated by the vertical broken lines in Figure 5. For anions with the same central atom it is easier to reduce vanadium (or molybdenum) in a tungstate than in a molybdate anion. For example, the reaction

$$PV^{V}W_{11}O_{40}^{4-} + PV^{IV}Mo_{11}O_{40}^{5-} \rightarrow PV^{IV}W_{11}O_{40}^{5-} + PV^{V}Mo_{11}O_{40}^{4-}$$

has a potential of 0.12 V corresponding to an equilibrium constant of *ca.* 100. In every case the equilibrium favors that reduced anion in which the electron is the more firmly localized. A naive argument based upon modification of the energy of the vanadium's d_{xy} orbital caused by partial delocalization predicts an opposite effect, *i.e.*, that the more delocalized anion should be the most stable. The reason for the observed behavior may therefore be preferential solvation at a localized vanadium(IV) or molybdenum(V) center.[37]

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Registry No. $PVW_{11}O_{40}^{5-}$, 12412-86-1; $SiVW_{11}O_{40}^{6-}$, 12412-87-2; $GeVW_{11}O_{40}^{6-}$, 53260-20-1; $BVW_{11}O_{40}^{7-}$, 53260-17-6; $H_2VW_{11}O_{40}^{8-}$, 50639-87-7; $ZnVW_{11}O_{40}^{8-}$, 37267-67-7; VO^{2+}, 20644-97-7; $PVMo_{11}O_{40}^{5-}$, 12777-00-3; $SiVMo_{11}O_{40}^{6-}$, 53260-22-3; $PW^{V}W_{11}O_{40}^{4-}$, 12534-78-0; $PMo^{V}W_{11}O_{40}^{4-}$, 12776-99-7.

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Kinetics of the Alkaline Hydrolysis of Hydroxylamine-*O*-sulfonic Acid and Its Reactions with Hydrazine and Hydroxylamine

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The kinetics of the hydrolysis of hydroxylamine-*O*-sulfonic acid, H_3NOSO_3, in alkaline aqueous solution have been studied in the range $[OH^-] = 0.1\text{–}1.5\ M$ at 26.6° and an ionic strength of 1.5. The observed rate law is $-d[H_2NOSO_3^-]/dt = (k_A + k_B[OH^-])[H_2NOSO_3^-]$ where $k_A = (0.43 \pm 0.09) \times 10^{-4}\ \text{sec}^{-1}$ and $k_B = (1.84 \pm 0.10) \times 10^{-4}\ \text{sec}^{-1}\ M^{-1}$. The k_A term is shown to be due to reaction with $EDTA^{4-}$ added to complex trace metal ions. The same rate law is found when the hydrolysis occurs in the presence of a large excess of the diazene scavenger fumarate ion with $k_B = (1.72 \pm 0.07) \times 10^{-4}\ \text{sec}^{-1}\ M^{-1}$. The kinetics of the reaction of H_3NOSO_3 with N_2H_4 and H_2NOH in alkaline solution were also studied and found to obey a second-order rate law, rate $= k_{obsd}[H_2NOSO_3^-][M]$. For $M = N_2H_4$, $k_{obsd} = 0.010 \pm 0.002\ \text{sec}^{-1}\ M^{-1}$ and is hydroxide independent. For $M = H_2NOH$, k_{obsd} is dependent on $[OH^-]$. The reaction is interpreted as involving the conjugate base of H_2NOH. Taking $pK_A = 13.7$ for H_2NOH a value of $0.16 \pm 0.06\ M^{-1}\ \text{sec}^{-1}$ is found for the reaction of H_2NO^- with $H_2NOSO_3^-$. The above data are incorporated into a mechanism for $H_2NOSO_3^-$ hydrolysis and shown to fit satisfactorily the overall rate of $H_2NOSO_3^-$ by computer simulation. It is concluded that nucleophilic attack at the $H_2NOSO_3^-$ sp^3 nitrogen proceeds in the order $H_2NO^- > N_2H_4 >> OH^-$. This observation supports earlier work which proposed that polarizability and ease of oxidation of the nucleophile are more important than proton basicity for attack at this nitrogen center.

Introduction

Since it was first reported in 1914,[1] hydroxylamine-*O*-sulfonic acid, $H_3N^+OSO_3^-$, has proved to be an interesting and useful chemical.[2] Among the more intriguing of its reactions is the ability to hydrogenate multiple bonds stereospecifically during decomposition in alkaline solution through the formation of the diazene molecule, HN=NH.[2-5] The postulated intermediacy of diazene stimulated our interest in the mode of decomposition of $H_2NOSO_3^-$ in alkaline solution and ultimately led to a synthetic route to monosubstituted alkyldiazenes, RN=NH, from the reaction of $H_2NOSO_3^-$ with *N*-alkylhydroxylamines, RNHOH.[6] On the basis of reaction chemistry and the use of isotopically labeled nitrogen compounds Schmitz, *et al.*,[7] have proposed that the alkaline decomposition of $H_2NOSO_3^-$ occurs according to eq 1–4.

$$H_2NOSO_3^- + OH^- \rightarrow H_2NOH + SO_4^{2-} \qquad (1)$$

$$\begin{aligned}H_2NOSO_3^- + H_2NOH + OH^- &\rightarrow [HONHNH_2] + SO_4^{2-} + H_2O\\ &\qquad\hookrightarrow HN{=}NH + H_2O \qquad (2)\end{aligned}$$

$$2HN{=}NH \rightarrow N_2H_4 + N_2 \qquad (3)$$

$$\begin{aligned}H_2NOSO_3^- + N_2H_4 + OH^- &\rightarrow [H_2NNHNH_2] + SO_4^{2-} + H_2O\\ &\qquad\hookrightarrow NH_3 + HN{=}NH \qquad (4)\end{aligned}$$

Except for a demonstration by Schmitz that the rate of alkaline hydrolysis of $H_2NOSO_3^-$ is accelerated by addition of hydroxylamine and an earlier general study of the stability of $H_2NOSO_3^-$ solutions,[8] the kinetics of the alkaline decomposition have not been studied.

The present kinetic study has shown the Schmitz mechanism, with minor modification, can satisfactorily explain the rate data. Among the reactions we have investigated are the alkaline decomposition of $H_2NOSO_3^-$ in both the presence and absence of fumarate ion (a diazene scavenger) and the reaction of $H_2NOSO_3^-$ with hydroxylamine and hydrazine.

Our results are also of interest in relationship to the recent use of $H_2NOSO_3^-$ as a model to study nucleophilic attack at an sp^3 nitrogen center.[9,10]

Experimental Section

Materials. Hydroxylamine-*O*-sulfonic acid, H_3NOSO_3, was prepared by treating hydroxylammonium sulfate with freshly distilled chlorosulfonic acid[11] and stored *in vacuo* over phosphorus pentoxide. It assayed at 98+% purity by iodometry,[12] the low assay being due to the presence of some unconverted hydroxylammonium sulfate. Slight hydrolysis (<4%) of the H_3NOSO_3 to hydroxylamine from exposure to moisture during handling was monitored by periodic reassay. The sodium salt of fumaric acid was prepared by neu-