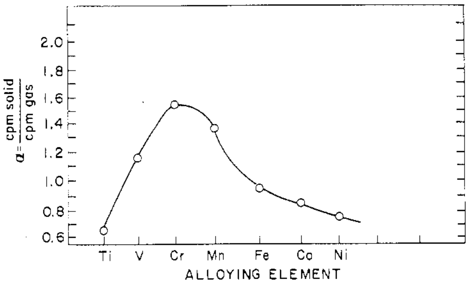


Figure 2. Tritium–protium separation factors for 1–1 titanium alloy hydrides.

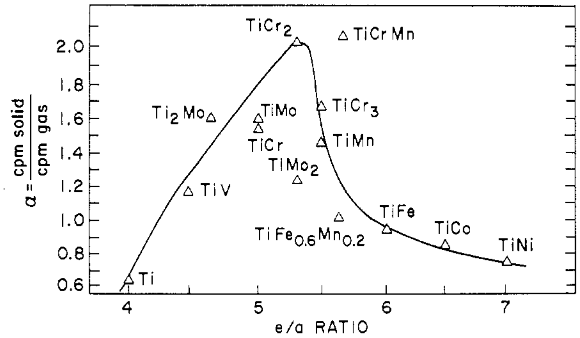


Figure 3. Tritium–protium separation factors for alloys of varying electron-to-atom ratio.

in order to get a measurable exchange rate. The other α values are for 40 °C. In order to place into comparison alloys other than 1:1 such as $TiMo_2$ and TiCrMn, the electron/atom (e/a) ratio was plotted vs. α as shown in Figure 3. The α values in this graph are for 40 °C except for several where the hydride stability dictated lower temperatures. $TiCr_2$ and TiCrMn were measured at 0 °C and $TiCr_3$ at 20 °C. The temperature coefficients for $TiCr_2$ and $TiCr_3$ seem to be relatively small so that the values plotted are probably close to the 40 °C values. Extrapolating the temperature coefficient determined on the basis of two points obtained for TiCrMn gives an extrapolated value of 1.4 for the α at 40 °C. This brings TiCrMn into line so that there seems to be a reasonable correlation between e/a and α. It is interesting to note that all the alloys which show significant inverse isotope ratios under our conditions fall in the approximate range of e/a 4.5 to 5.5. The approximate dependence of the α values on the electron/atom ratio is not surprising in that the heat of solution of hydrogen is dependent on the electronic structure of the metal.

Acknowledgment. The authors wish to thank Mr. A. Holtz for his expert help in preparing the alloys. This work was performed under the auspices of the Division of Basic Energy Sciences, U.S. Energy Research and Development Administration, Washington, D.C.

Registry No. TiH_2, 7704-98-5; TiV, 37219-66-2; TiCr, 64784-24-3; $TiCr_2$, 64784-25-4; $TiCr_3$, 64784-26-5; TiCrMn, 64784-27-6; Ti_2Mo, 64784-20-9; TiMo, 51401-84-4; $TiMo_2$, 64784-21-0; TiMn, 64784-22-1; FeTi, 12674-94-1; $Fe_{0.6}TiMo_{0.2}$, 64784-23-2; TiCo, 58221-15-1; TiNi, 11110-85-3.

References and Notes

(1) R. H. Wiswall, Jr., and J. J. Reilly, *Inorg. Chem.*, **11**, 1691 (1972).
(2) J. Novakova, P. Jiru and V. Zavadil, *Collect. Czech. Chem. Commun.*, **36**, 520 (1971).
(3) J. Novakova, P. Jiru, and V. Zavadil, *Collect. Czech. Chem. Commun.*, **36**, 520 (1971).
(4) P. Dantzer, O. J. Kleppa, and M. E. Melnichak, *J. Chem. Phys.*, **64**, 139 (1976).
(5) S. Steward, *J. Chem. Phys.*, **63**, 975 (1975).
(6) D. G. Westlake, Materials Science Division Physical Research Program Report, Sept 1973.
(7) B. Baronowski and M. Tkacz, *Rocz. Chem.*, **48**, 713 (1974).
(8) G. Sicking, *Z. Phys. Chem.* (*Frankfurt am Main*), **93**, 53 (1974).
(9) M. E. Martins, A. J. Calandra, and A. J. Arvia, *Electrochim. Acta*, **19**, 99 (1974).
(10) G. L. Powell, *J. Phys. Chem.*, **80**, 375 (1976).
(11) J. J. Reilly, A. Holtz, and R. H. Wiswall, Jr., *Rev. Sci. Instrum.*, **42**, 1485 (1971).
(12) W. Bernstein, and R. Ballentine, *Rev. Sci. Instrum.*, **21**, 158 (1950).

Contribution from the Department of Chemistry,
Georgetown University, Washington, D.C. 20057

Reduction of the Decatungstate Anion in Nonaqueous Solution and Its Confirmation as "Polytungstate-Y"

Silvia C. Termes and Michael T. Pope*

Received August 12, 1977

The pale yellow isopoly anion known as "polytungstate-Y" (W_y) has been formulated by different research groups as a dodecatungstate,[1] $[HW_{12}O_{39}]^{5-}$, and as a decatungstate,[2] $[W_{10}O_{32}]^{4-}$. The latter species (see Figure 1) was found in the crystal structure[3] of the salt $(Bu_3NH)_4W_{10}O_{32}$, which can be precipitated from a freshly prepared aqueous solution containing W_y. Both the original aqueous solution and a solution of the tributylammonium salt in acetonitrile gave an absorption spectrum with a maximum at ~325 nm.[2] Since aqueous solutions of W_y are unstable and are slowly converted into equilibrium mixtures of other isopolytungstates,[4] there still remains an element of uncertainty[5,6] about a positive identification of W_y as $[W_{10}O_{32}]^{4-}$. It is possible, for example, that both W_{10} and W_{12} species could have similar UV spectra.

In the course of an investigation of the redox chemistry of heteropoly(tungstouranates), we had occasion to study the reduction of the decatungstate anion in a nonhydrolytic solvent. The results of this study are reported here and are compared with those obtained by Boyer[7] for the reduction of W_y in aqueous solution.

Experimental Section

The potassium salt of W_y was prepared by the method of Chauveau et al.[1] and the product was identified by its infrared and ultraviolet spectra.[1] Tributylammonium decatungstate was prepared by the method of Birkholtz et al.[2] and recrystallized from acetone. Anal. Calcd for $[(C_4H_9)_3NH]_4W_{10}O_{32}$: C, 18.62; H, 3.64; N, 1.81. Found: C, 18.41; H, 3.68; N, 1.71. Electrochemical and spectroscopic measurements were made as described elsewhere.[8] Propanediol 1,2-carbonate (PDC) was distilled before use. Voltammetry in this solvent was carried out using a thread of graphite cloth (type X2014, Union Carbide Corp.) as the working electrode.

Results and Discussion

Boyer's results for the reduction behavior of aqueous solutions of W_y were confirmed in all respects. By using a wax-impregnated electrode for cyclic voltammetry and a graphite cloth cathode for controlled potential electrolysis, the problems of adsorption on mercury, encountered by Boyer, could be avoided. At 1 °C and pH 2.0 (sulfate/bisulfate) the cyclic voltammogram showed two reversible "one-electron" reductions with cathodic peak potentials of −0.19 and −0.34 V. Solutions of the one- and two-electron reduced products (W_{yI} and W_{yII}) were prepared by controlled potential electrolysis at −0.21 and −0.50 V, respectively, and the visible absorption spectra of these products were in agreement with those reported by Boyer. The corresponding UV spectra, which have not been previously reported, show that the 325-nm band is progressively lost upon reduction and is restored upon reoxidation. The restoration of intensity is never complete, however, because of the slow hydrolysis of aqueous solutions of W_y.

0020-1669/78/1317-0500$01.00/0

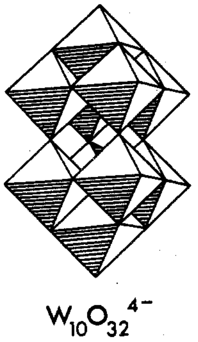


Figure 1. Polyhedral representation of the structure of $W_{10}O_{32}^{4-}$.

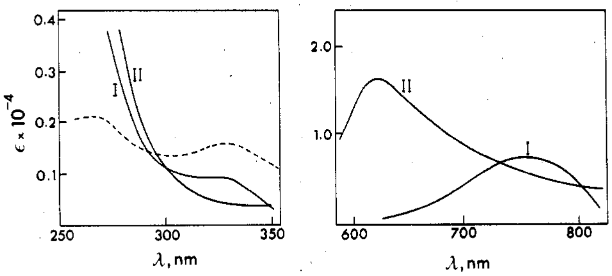


Figure 2. Absorption spectra of $W_{10}O_{32}^{4-}$ (broken line), $W_{10}O_{32}^{5-}$ (I), and $W_{10}O_{32}^{6-}$ (II) in PDC. The spectra of W_y, W_{yI}, and W_{yII} in aqueous solution correspond almost exactly with those shown here.

Solutions of tributylammonium decatungstate in acetonitrile or PDC are stable indefinitely according to their UV spectra. Cyclic voltammograms of the decatungstate in PDC (0.50 mM polyanion, 0.1 M $[(C_4H_9)_3NH]ClO_4$, sweep rate 1 V min^{-1}) showed two quasi-reversible reductions at −0.66 and −0.93 V (cathodic peak potentials) and with cathodic–anodic peak potential separations of 140 and 160 mV, respectively.[9] Controlled potential reductions at −0.8 and −1.0 V led respectively to the addition of one and two electrons per W_{10} species. The absorption spectra of the reduced products, presumably $[W_{10}O_{32}]^{5-}$ and $[W_{10}O_{32}]^{6-}$, are shown in Figure 2 and are virtually identical with those found for W_{yI} and W_{yII}. Complete restoration of the UV spectrum of $[W_{10}O_{32}]^{4-}$ was observed upon reoxidation. Since these measurements were made under nonhydrolytic conditions, they provide confirmatory evidence for the identification of $[W_{10}O_{32}]^{4-}$ with W_y.[10]

That the decatungstate structure is reducible in reversible one-electron steps to "heteropoly blue" species is consistent with the observation that only polyanions with one terminal oxo-oxygen per metal are reducible in this way.[11] There are, however, two unusual features of decatungstate: the 325-nm band and the high intensities of the intervalence bands in the spectra of the reduced anions. We suggest that both features are related to the presence of the near-linear (175°) W–O–W bridges that link both halves of the anion. The only other polytungstates with charge-transfer bands[12] as low as 325 nm are α- and β-$[P_2W_{18}O_{62}]^{6-}$ which also have dimeric structures[13] linked by almost linear (162°) W–O–W bridges. Furthermore the intervalence charge-transfer bands in reduced $P_2W_{18}O_{62}$ anions have relatively high extinction coefficients for a heteropoly blue (3600–6000 $M^{-1}\,cm^{-1}$ per W(V)).[14] Launay[15] has pointed out that the intensities of intervalence transitions $W^{V}\text{–O–}W^{VI} \leftrightarrow W^{VI}\text{–O–}W^{V}$ increase as the bond angle increases toward 180°. This principle is most dramatically illustrated with the spectra of $[W_6O_{19}]^{3-}$, $\epsilon_{max} = 280$,[15] and $[W_{10}O_{32}]^{5-}$, $\epsilon_{max} = 7500$, which correspond to intervalence transitions involving ~90 and ~180° bridges, respectively.

Acknowledgment. This work has been supported in part by National Science Foundation Grant No. CHE73-04793.

Registry No. W_y, 52261-16-2; W_{yI}, 64825-40-7; W_{yII}, 64825-39-4.

References and Notes

(1) F. Chauveau, M. Boyer, and B. LeMeur, *C.R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 479 (1969).
(2) E. Birkholtz, J. Fuchs, W. Schiller, and H.-P. Stock, *Z. Naturforsch. B*, **26**, 365 (1971).
(3) J. Fuchs, H. Hartl, and W. Schiller, *Angew. Chem., Int. Ed. Engl.*, **12**, 420 (1973); J. Fuchs, H. Hartl, W. Schiller, and U. Gerlach, *Acta Crystallogr. Sect. B*, **32**, 740 (1976).
(4) P. Souchay, M. Boyer, and F. Chauveau, *Trans. R. Inst. Technol., Stockholm*, **259**, 161 (1972).
(5) P. Courtin and J. Lefebvre, *Bull. Soc. Chim. Fr.*, 1983 (1975).
(6) J.-P. Launay, M. Boyer, and F. Chauveau, *J. Inorg. Nucl. Chem.*, **38**, 243 (1976).
(7) M. Boyer, *J. Electroanal. Chem.*, **31**, 441 (1971).
(8) R. A. Prados and M. T. Pope, *Inorg. Chem.*, **15**, 2547 (1976).
(9) The voltammetric peak potentials were affected by the voltage sweep rate: at 2 V min^{-1}, −0.69, −0.97 V; at 3 V min^{-1}, 0.72, −1.01 V. The mean of the cathodic and anodic peak potentials remained constant at −0.59 and −0.85 V.
(10) Courtin and Lefebvre[5] have reported a molybdotungstate with UV and IR spectra very similar to those of W_y (but also to those reported for $W_{10}O_{32}^{4-}$). According to chemical analysis (C, H, N, Mo, W) of a tetramethylammonium salt, the formula of the molybdotungstate is $HMo_2W_{10}O_{39}^{5-}$, i.e., analogous to that given to W_y by Boyer. The analytical data are also in satisfactory agreement with the formula $(N(CH_3)_4)_4Mo_2W_8O_{32}$, except for Mo (found 6.22; calcd 7.76). Since Mo was determined polarographically and by difference, it is possible that a distinction between the 2:10 and 2:8 formulas cannot be made based on these analytical data.
(11) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).
(12) This statement excludes reduced anions and charge transfer involving the heteroatom. Oxygen-to-tungsten(VI) charge-transfer bands generally fall within the range 240–270 nm.
(13) H. D'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976); K. Y. Matsumoto and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 691 (1975).
(14) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9**, 667 (1970).
(15) J. P. Launay, private communication, 1977; J. M. Fruchart, G. Hervé, J. P. Launay, and R. Massart, *J. Inorg. Nucl. Chem.*, **38**, 1627 (1976); M. Dabbabi, M. Boyer, J. P. Launay, and Y. Jeannin, *J. Electroanal. Chem.*, **76**, 153 (1977). See also C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **12**, 1626 (1973), for discussion of $V^{IV} \rightarrow W^{VI}$ band intensities.
(16) M. Boyer and B. LeMeur, *C.R. Hebd. Seances Acad. Sci., Ser. C*, **281**, 59 (1975).

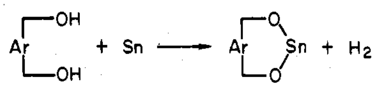
Contribution from the Department of Chemistry,
University of Oklahoma, Norman, Oklahoma 73019

Organotin(II)–Oxygen and –Sulfur Heterocycles through Protolysis of Tin(II) Dimethoxide

W. D. Honnick and J. J. Zuckerman*

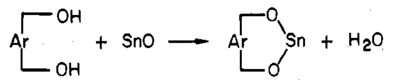
Received June 20, 1977

Protolysis by various tin substrates has been used to yield organotin(II)–oxygen derivatives, beginning with the action of tin metal with dihydric phenols at elevated temperatures to liberate hydrogen gas:[1]



(1)

Protolysis by blue-black tin(II) oxide releases water[2]



(2)

but long reaction times are required and the hydrous form of tin(II) oxide is a superior reagent since milder conditions can be used and the reaction is more general.[3] More recently, the high reactivity of the η^5-cyclopentadienyltin(II) linkage in stannocene has allowed the preparation of tin(II) oximes, hydroxylamines,[4] di- and triazoles,[4] thiolates,[5] β-keto–enolates,[6] alkyl- and arylcarboxylates,[7] and phenoxides[8] by protolysis

$$(\eta^5\text{-}C_5H_5)_2Sn + 2HOR \rightarrow Sn(OR)_2 + 2C_5H_6 \qquad (3)$$

but the method requires preliminary preparation of

0020-1669/78/1317-0501$01.00/0