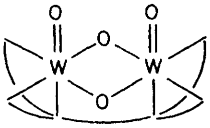
Studies on the μ-(*NN'*)-Ethylenediaminetetra-acetato-di-μ-oxo-bis-[oxotungstate(V)], $[W_2O_4(edta)]^{2-}$, Complex in Aqueous Solutions. Formation of an Aquo-ion and Redox Properties

By **Allan B. Soares, R. Craig Taylor,** and **A. Geoffrey Sykes,***,† Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The aquation of $[W_2O_4(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate) to $W_2O_4^{2+}$ (or a closely related species) proceeds to completion in HCl $\geqslant 2$ mol dm^{-3}. First-order kinetics have been observed, with the rate constant (1.16×10^{-4} s^{-1} at 25 °C) in 2 mol dm^{-3} HCl some 60 times less than for the corresponding reaction of $[Mo_2O_4(edta)]^{2-}$. With $HClO_4 \geqslant 2$ mol dm^{-3} aquation is accompanied by oxidation to W^{VI}. No aquation (or oxidation) has been observed with $HClO_4 < 0.5$ mol dm^{-3}, under which condition redox reactions of the edta complex could be investigated. At 25 °C, I = 0.50 mol dm^{-3} (H–LiClO$_4$) rate constants for the first stage of the 1 : 2 oxidations of $[W_2O_4(edta)]^{2-}$ with $[IrCl_6]^{2-}$ and $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) are 6.3×10^5 dm^3 mol^{-1} s^{-1} and $>10^7$ dm^3 mol^{-1} s^{-1} respectively. For the $[IrCl_6]^{2-}$ reaction activation parameters are $\Delta H^\ddagger$ = 5.4 kcal mol^{-1} and $\Delta S^\ddagger$ = −13.8 cal K^{-1} mol^{-1} respectively. Rate constants (dm^3 mol^{-1} s^{-1}) for other oxidants, I = 0.10 mol dm^{-3}, are $[Fe(CN)_6]^{3-}$ (0.058), $[Co(bipy)_3]^{3+}$ (2.0) (bipy = 2,2'-bipyridine), and I_3^- (*ca.* 20). The complex $[W_2O_4(edta)]^{2-}$ is a much stronger reducing agent than $[Mo_2O_4(edta)]^{2-}$.

WITH the exception of W^{VI} little information is currently available on the solution chemistry of different oxidation states of tungsten. One difficulty is that in comparison to molybdenum few complexes have been well characterized. An exception is the di-μ-oxo-complex of tungsten(V), $[W_2O_4(edta)]^{2-}$ (see below) (edta = ethylenediaminetetra-acetate),[1] the crystal structure of which



has recently been reported.[2] Studies relating to the aqueous solution chemistry of this complex have been carried out and are reported in this paper. Comparisons are made with the reactivity of the molybdenum(V) complex, $[Mo_2O_4(edta)]^{2-}$, which has been the subject of recent studies.[3,4]

EXPERIMENTAL

Preparation of Tungsten(V) *Oxalato-complex.*—The procedure described by Collenberg [5] has recently been used by Novak and Podlaha [1] to obtain $K_3[WO_2(C_2O_4)_2]\cdot 3H_2O$ and $[NH_4]_3[WO_2(C_2O_4)_2]\cdot 2H_2O$. A similar procedure was used in this study (Na^+ and NH_4^+ salts). Oxalic acid (10 g) and sodium oxalate (5 g) were dissolved in H_2O (150 cm^3). Sodium tungstate (7.8 g) was added and the solution brought to the boil. Granulated tin (7.8 g) was slowly added with stirring. Oxygen-free conditions were maintained throughout the preparation, use being made of glove-bag techniques. The solution was heated on a steam bath for 3—4 h during which time colour changes to a brown-red were observed. After reduction of the volume to 50—70 cm^3 and subsequent cooling to 0 °C, oxalic acid and sodium oxalate were removed by filtration. Tin sulphide was then precipitated by passing H_2S through the solution for 3—5 min at 0 °C. After filtration air-free methanol (20 cm^3) was added to precipitate any remaining oxalate. A further 150 cm^3 of ethanol were added, and the orange powder filtered off and washed with ethanol and ether. Analyses for tungsten were by addition of an excess of $[Fe(CN)_6]^{3-}$, and back titrating with iodide in an acid medium in the presence of a zinc salt. The non-interference of reagents such as oxalic acid was verified by the addition of a known excess of oxalic acid and repeating the determination. Sodium was determined by flame photometry. Analytical data for $Na_3[WO_2(C_2O_4)_2]\cdot 3H_2O$: Found: C, 9.3; H, 1.25; Na, 13.1; W, 36.0. Calc.: C, 9.3; H, 1.15; Na, 13.4; W, 35.8%. The use of ammonium for sodium salts yielded an ammonium product. The preparation did not always give satisfactory reproducibility, and analyses for W were in some cases as high as 46%. The presence of some $Na_2[W_2O_4(C_2O_4)_2]\cdot 2H_2O$, which gives a calculated W value of 53%, is not ruled out in such samples. All products gave satisfactory yields of the $[W_2O_4(edta)]^{2-}$ complex.

Preparation of $[W_2O_4(edta)]^{2-}$.—The oxalato-complex was converted into the edta complex which was isolated as the barium salt by the procedure of Novak and Podlaha.[1] The ammonium salt was obtained by addition of an equivalent of ammonium sulphate and filtering off the $Ba[SO_4]$. The volume of filtrate was reduced by rotary evaporation. Orange crystals were filtered off. Recrystallisation was from aqueous ethanol {Found: C, 15.7; H, 2.90; N, 7.25; W, 48.2. Calc. for $[NH_4]_2[W_2O_4(edta)]$: C, 15.9; H, 2.70; N, 7.4; W, 48.6}.

Electronic Spectrum and Stability of $[W_2O_4(edta)]^{2-}$.—Solutions of the complex are stable at pH 1—9. The spectrum in water gives absorption peaks λ(nm), ε(dm^3 mol^{-1} cm^{-1}) at 423, 401; 340, 1 115; and 275, 1.4×10^4, in satisfactory agreement with ref. 2. No reaction with O_2 is observed. The complex is stable in perchloric acid up to 0.5 mol dm^{-3} (<2% decrease in spectrum over 3 h at 25 °C), but no higher as discussed below.

Other Reactants.—Samples of perchlorate salts of tris-(1,10-phenanthroline)iron(III), $[Fe(phen)_3]^{3+}$, tris(2,2'-bipyridine)cobalt(III), $[Co(bipy)_3]^{3+}$, and sodium salts of hexachloroiridate-(III) and -(IV) were all used previously.[4,6] Potassium hexacyanoferrate(III), potassium iodide, iodine, fluoroboric acid, and perchloric acid were of AnalaR grade. Lithium perchlorate was prepared by reacting perchloric acid with lithium carbonate and recrystallising. A sample

---

† *Present address:* Department of Chemistry, The University, Newcastle-upon-Tyne NE1 7RU.

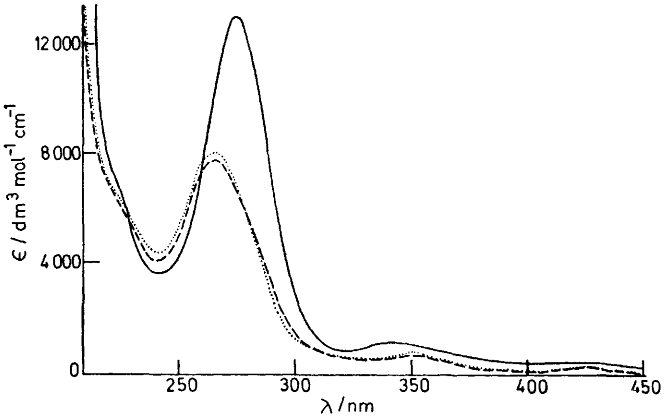
of the sodium salt of $[Mo_2O_4(edta)]^{2-}$ was prepared as described in ref. 3.

Stoicheiometries.—These were determined from spectrophotometric changes and corresponded to 2 : 1 (oxidant : dimer) reactions, consistent with the oxidation of W^V to W^{VI}. An edta complex of W^{VI} has been characterised,[7] but aquates under conditions of $[H^+]$ used in these experiments.

Kinetic Studies.—The aquation of $[W_2O_4(edta)]^{2-}$ was studied under rigorous air-free conditions. For redox studies solutions were at ionic strength $I = 0.50$ mol dm^{-3} (H–$LiClO_4$) or less as indicated. Reactions were monitored spectrophotometrically using a Durrum-Gibson stopped-flow, and Unicam SP500 and SP8000 spectrophotometers. First-order rate constants were obtained from slopes (× 2.303) of plots of absorbance changes, log ΔA, against time (linearity > two half-lives). Values of A_∞ were measured. Standard procedures were used to evaluate rate constants for runs carried out under second-order conditions.

RESULTS

Aquation of $[W_2O_4(edta)]^{2-}$ *in Dilute Acids.*—Addition of HCl >0.5 mol dm^{-3} to the complex (*ca.* 6 × 10^{-5} mol dm^{-3}) resulted in spectrophotometric changes corresponding to aquation of the edta ligand. The aquo-ion reacts with O_2 and air-free techniques were required. Isosbestics were obtained at 228 and 261 nm for solutions 2 and 3 mol dm^{-3} in HCl, and final spectra were very similar, see the Figure. The same process is also observed in 7 mol dm^{-3} HCl, suggesting that detachment of the edta ligand is complete. At 25 °C, [HCl] = 2.0 mol dm^{-3}, first-order plots at λ 275 nm (>75% linearity) gave rate constants 1.16 × 10^{-4} s^{-1} (error ±6%). With [HCl] = 3.0 mol dm^{-3} a value 3.3 × 10^{-4} s^{-1} was obtained. Rate constants were the same using the Guggenheim method.[8] With 2 mol dm^{-3} $HClO_4$ (instead of HCl) at least two stages were observed in kinetic plots, and the final spectrum indicated formation of W^{VI}. At least two stages were also apparent on aquating with 2 mol dm^{-3} HBF_4.



Spectra of $[W_2O_4(edta)]^{2-}$ (——) and the aquo-ion $W_2O_4^{2+}$ obtained on reacting with 2.0 mol dm^{-3} HCl (— — —) and 3.0 mol dm^{-3} HCl (· · · ·)

Oxidation with $[IrCl_6]^{2-}$.—Absorbance changes were monitored at the $[IrCl_6]^{2-}$ peak at 487 nm (ε 4 075 dm^3 mol^{-1} cm^{-1}) using the stopped-flow method. The kinetics conform to the rate law (1). Second-order plots were linear to ⩾87% completion. Rate constants are listed in Table 1. There was no dependence on $[H^+]$ = 0.01—0.10 mol dm^{-3}, and addition of a 30-fold excess of $[IrCl_6]^{3-}$ (over $[IrCl_6]^{2-}$) did not affect the kinetics. Using a non-linear least-squares programme,[9] weighting factor $1/k^2$, $k = 6.3 \times 10^5$ dm^3 mol^{-1} s^{-1} at 25 °C, $\Delta H^\ddagger = 5.4 \pm 0.2$ kcal mol^{-1},* and $\Delta S^\ddagger = -13.8 \pm 0.7$ cal K^{-1} mol^{-1}.

$$-\mathrm{d}\mathrm{Ir}^{IV}/\mathrm{d}t = 2k[\mathrm{W^V}_2][\mathrm{Ir^{IV}}] \qquad (1)$$

Oxidation with $[Fe(phen)_3]^{3+}$.—The reaction was too fast to monitor at the 510 nm peak for $[Fe(phen)_3]^{2+}$ (ε 1.11 × 10^4 dm^3 mol^{-1} cm^{-1}) with reactant concentrations $[W_2O_4(edta)^{2-}]$ = 1.0 × 10^{-5} mol dm^{-3}, $[Fe(phen)_3{}^{3+}]$ = 2.5 × 10^{-6} mol dm^{-3}, $[H^+]$ = 0.10 mol dm^{-3}, I = 0.50 mol dm^{-3} ($LiClO_4$). Assuming the reaction to be first order in each reactant it can be concluded that the rate constant is >10^7 dm^3 mol^{-1} s^{-1} at 25 °C.

TABLE 1

Rate constants for the $[IrCl_6]^{2-}$ oxidation of $[W_2O_4(edta)]^{2-}$, λ = 487 nm, I = 0.50 mol dm^{-3} ($LiClO_4$)

Temperature (°C)	$[H^+]$ mol dm^{-3}	$10^5[(W^V)_2]$ mol dm^{-3}	$10^5[Ir^{IV}]$ mol dm^{-3}	10^6k (dm^3 mol^{-1} s^{-1})
25.0	0.10	2.5	10	0.60
	0.10	5.0	2.5	0.64 [a]
	0.10	5.0	2.5	0.65
	0.10	5.0	10.0	0.62
	0.10	7.5	2.5	0.63
	0.10	10.0	2.5	0.64
	0.05	10.0	2.5	0.64
	0.01	10.0	2.5	0.64
	0.10	10.0	5.0	0.65
	0.01	10.0	10.0	0.63
	0.10	10.0	10.0	0.64 [b]
	0.10	10.0	10.0	0.64
	0.10	12.5	2.5	0.62
20.0	0.10	10.0	10.0	0.53
	0.01	10.0	10.0	0.52
	0.10	10.0	2.5	0.54
15.0	0.10	10.0	10.0	0.45
	0.01	10.0	10.0	0.43
	0.10	20.0	2.5	0.42
10.0	0.01	2.5	2.5	0.38
	0.01	10.0	2.5	0.35
	0.01	10.0	10.0	0.37
	0.05	10.0	10.0	0.37
	0.10	10.0	10.0	0.37
	0.10	20.0	2.5	0.37
0.5	0.10	1.10	0.35	0.20
	0.10	4.30	0.40	0.30
	0.01	5.30	0.50	0.26
	0.01	7.50	0.70	0.29
	0.10	8.65	0.80	0.29
	0.10	10.10	1.23	0.27

[a] 15-fold excess of $[IrCl_6]^{3-}$ over $[IrCl_6]^{2-}$. [b] 30-fold excess of $[IrCl_6]^{3-}$ over $[IrCl_6]^{2-}$.

Other Oxidants.—With $[Fe(CN)_6]^{3-}$ the reaction was monitored by conventional techniques at the 420 nm peak for $[Fe(CN)_6]^{3-}$ (ε 1.01 × 10^3 dm^3 mol^{-1} cm^{-1}). Reactant concentrations were typically $[W_2O_4(edta)^{2-}]$ = 5 × 10^{-5} mol dm^{-3}, $[Fe(CN)_6{}^{3-}]$ = 10^{-4} mol dm^{-3}, I = 0.50 mol dm^{-3} ($LiClO_4$). At 25 °C second-order rate constants (dm^3 mol^{-1} s^{-1}) gave small trends with $[H^+]$, 0.40 ($[H^+]$ = 0.10 mol dm^{-3}) and 0.30 ($[H^+]$ = 0.01 mol dm^{-3}); and ionic strength 0.15 (I = 0.05 mol dm^{-3}) and 0.058 (I = 0.01 mol dm^{-3}), both the latter with $[H^+]$ = 0.02 mol dm^{-3}.

The reaction with $[Co(bipy)_3]^{3+}$ was monitored at 318 nm where $[W_2O_4(edta)]^{2-}$ is the strongest absorbant. Reactant concentrations were $[W_2O_4(edta)^{2-}]$ = *ca.* 2.5 × 10^{-5} mol

---

* Throughout this paper: 1 cal = 4.184 J.

dm^{-3} and [Co(bipy)$_3$$^{3+}$] = 2.5 × 10^{-6} mol dm^{-3}. At 25° C with I = 0.50 mol dm^{-3} (LiClO$_4$) and [H$^+$] = 0.01 mol dm^{-3}, the reaction is extremely slow with <5% conversion in 8 h. Rate constants increase as the ionic strength is decreased (Table 2), as expected for a reaction between oppositely charged species. Addition of Co^{2+} (2.5 × 10^{-6} mol dm^{-3}) and bipyridine (3 × 10^{-5} mol dm^{-3}) initially had no effect on rates.

TABLE 2

Rate constants (k) for the [Co(bipy)$_3$]$^{3+}$ oxidation of [W$_2$O$_4$(edta)]$^{2-}$ at 25 °C, λ = 318 nm, [W$_2$O$_4$(edta)$^{2-}$] = 2.5 × 10^{-5} mol dm^{-3}, [Co(bipy)$_3$$^{3+}$] = 2.5 × 10^{-6} mol dm^{-3}

I	10^4[H$^+$]	k *
mol dm^{-3}		(dm^3 mol^{-1} s^{-1})
0.010	1.0	1.8
0.010	10.0	2.0
0.010	1.00	1.7
0.010	100	1.5
0.025	100	1.2
0.050	100	0.57

* Plots linear to >80%.

Finally, to study the reaction with I$_3$$^-$ (1.0 × 10^{-5} mol dm^{-3}) as oxidant, solutions of I$_2$ (1.0 × 10^{-5} mol dm^{-3}) were made up with an excess of iodide (5 × 10^{-3} mol dm^{-3}). Absorbance changes were monitored at λ 353 nm with [W$_2$O$_4$(edta)$^{2-}$] = 5.0 × 10^{-5} mol dm^{-3} and [H$^+$] = 5.0 × 10^{-3} mol dm^{-3}. At 25 °C rate constants were *ca.* 20 dm^3 mol^{-1} s^{-1}.

Reactions of [Mo$_2$O$_4$(edta)]$^{2-}$.—Full studies have already been reported for the reactions with [IrCl$_6$]$^{2-}$ and [Fe(phen)$_3$]$^{3+}$ as oxidants.[4] No reaction was observed within 4 h at 25 °C with [Fe(CN)$_6$]$^{3-}$ (I = 0.5 mol dm^{-3}) and [Co(bipy)$_3$]$^{3+}$ (I = 0.05 mol dm^{-3}) as oxidants. With I$_3$$^-$ the rate constant (25 °C) is *ca.* 1 dm^3 mol^{-1} s^{-1}. Reactant concentrations were as in the corresponding [W$_2$O$_4$(edta)]$^{2-}$ reactions.

DISCUSSION

Aquation of the multidentate edta ligand from [W$_2$O$_4$(edta)]$^{2-}$ proceeds to completion in HCl ⩾2.0 mol dm^{-3} with retention of two isosbestic points. The final spectrum is essentially the same in 2.0 and 3.0 mol dm^{-3} HCl (Figure) and complexing with Cl$^-$ is probably not extensive. Ardon and Pernick[10] have reported that identical spectra are obtained for Mo$_2$O$_4$$^{2+}$ in 1 mol dm^{-3} HCl and HClO$_4$, and in keeping with this observation other early transition-metal ions (*e.g.* Ti^{3+})[6] exhibit only weak complexing with chloride. Spectra of [W$_2$O$_4$(edta)]$^{2-}$ and the aquo-ion have similar features and there seems little doubt that the W$_2$O$_4$ structural unit is retained on aquation of the edta. Attempts to separate the aquo-ion from edta using a variety of ion-exchange–Sephadex procedures were in this case unsuccessful, the main problem being that recomplexing took place on decreasing the concentration of hydrogen ions in order to load such columns.

The retention of isosbestics and first-order kinetics observed for the aquation process in 2—3 mol dm^{-3} HCl indicate a single rate-determining process. The rate constants of 1.16 × 10^{-4} s^{-1} (2.0 mol dm^{-3} HCl) and 3.3 × 10^{-4} s^{-1} (3.0 mol dm^{-3} HCl) suggest a complex [H$^+$]-dependence similar to that observed in the aquation of [Mo$_2$O$_4$(edta)]$^{2-}$. In other words observed rate constants incorporate and are dependent on protonation constants for steps involving partial dissociation of the edta prior to the rate-determining process. The rate constant for the aquation of [W$_2$O$_4$(edta)]$^{2-}$ (1.16 × 10^{-4} s^{-1}) is 60 times slower than the corresponding value for [Mo$_2$O$_4$(edta)]$^{2-}$ (6.9 × 10^{-3} s^{-1}) in 2.0 mol dm^{-3} HCl. While these values suggest that W$^{\text{V}}$ is more inert than Mo$^{\text{V}}$, some caution is required because of the need to take account of the protonation constants. Miller and Wentworth[11] in a recent n.m.r. study on aminocarboxylate complexes of W$^{\text{VI}}$ and Mo$^{\text{VI}}$ have found the tungsten complexes to be more inert. However, von Felten *et al.*[12] in studies on the exchange of the oxy-anions with H$_2$^{18}O have observed that rate constants for WO$_4$$^{2-}$ + H$_2$O (0.44 s^{-1}) and MoO$_4$$^{2-}$ + H$_2$O (0.33 s^{-1}) are about the same, and that with OH$^-$ the reaction of WO$_4$$^{2-}$ (273 dm^3 mol^{-1} s^{-1}) is faster than with MoO$_4$$^{2-}$ (2.2 dm^3 mol^{-1} s^{-1}).

At least two stages are observed in the aquation of [W$_2$O$_4$(edta)]$^{2-}$ with 2.0 mol dm^{-3} HClO$_4$, and some W$^{\text{VI}}$ is formed. Since no reaction is observed with [H$^+$] <0.5 mol dm^{-3} and [ClO$_4$$^-$] = 3.0 mol dm^{-3}, it is concluded that ClO$_4$$^-$ oxidation of the aquo-ion (and not the edta complex) occurs. No similar redox reaction is observed with [Mo$_2$O$_4$(edta)]$^{2-}$. The aquations of [W$_2$O$_4$(edta)]$^{2-}$ and [Mo$_2$O$_4$(edta)]$^{2-}$ in 2.0 mol dm^{-3} HBF$_4$ give complications which may be due to coordination of BF$_4$$^-$ to the aquo-ions, but which are not readily understood.

A detailed kinetic study has been made of the [IrCl$_6$]$^{2-}$ oxidation of [W$_2$O$_4$(edta)]$^{2-}$. The rate law is consistent with a reaction sequence (2)—(3), where k is as defined in

$$\text{W}^{\text{V}}{}_2 + \text{Ir}^{\text{IV}} \xrightarrow{k} \text{W}^{\text{V,VI}} + \text{Ir}^{\text{III}} \qquad (2)$$

$$\text{W}^{\text{V,VI}} + \text{Ir}^{\text{IV}} \xrightarrow{\text{fast}} 2\,\text{W}^{\text{VI}} + \text{Ir}^{\text{III}} \qquad (3)$$

(1). No information was obtained as to whether W$^{\text{V,VI}}$ dissociation to mononuclear species occurs before or after oxidation by the second Ir$^{\text{IV}}$. Unlike the corresponding [Mo$_2$O$_4$(edta)]$^{2-}$ study,[4] addition of Ir$^{\text{III}}$ initially does not retard the reverse of (2). It is concluded that Ir$^{\text{III}}$ is not a sufficiently strong reductant to reduce W$^{\text{V,VI}}$ back to W$^{\text{V}}{}_2$ within the lifetime of the W$^{\text{V,VI}}$ intermediate. The entropy of activation $\Delta S^\ddagger$ = −13.8 cal K^{-1} mol^{-1} for oxidation of [W$_2$O$_4$(edta)]$^{2-}$ is very similar to that of [Mo$_2$O$_4$(edta)]$^{2-}$ (−10.0 cal K^{-1} mol^{-1}), consistent with similar charge interactions. The enthalpy term $\Delta H^\ddagger$ = 5.4 kcal mol^{-1} is considerably less than for [Mo$_2$O$_4$(edta)]$^{2-}$ (13.3 kcal mol^{-1}) and is largely responsible for the *ca.* 10^5 times difference in rate constants.

The rate constant for the [Fe(phen)$_3$]$^{3+}$ oxidation of [W$_2$O$_4$(edta)]$^{2-}$ (>10^7 dm^3 mol^{-1} s^{-1}) is also very much faster than with [Mo$_2$O$_4$(edta)]$^{2-}$ as reductant (1.9 × 10^3 dm^3 mol^{-1} s^{-1}). Rate constants for other oxidations of [W$_2$O$_4$(edta)]$^{2-}$ (I = 0.01 mol dm^{-3}, 25 °C) have furthermore been determined with $[Fe(CN)_6]^{3-}$ (0.058 dm^3 mol^{-1} s^{-1}), $[Co(bipy)_3]^{3+}$ (2.0 dm^3 mol^{-1} s^{-1}), and I_3^- (*ca.* 20 dm^3 mol^{-1} s^{-1}). The rate constant for the oxidation of $[Mo_2O_4(edta)]^{2-}$ with I_3^- (*ca.* 1 dm^3 mol^{-1} s^{-1}) has also been determined. However no reaction of $[Mo_2O_4(edta)]^{2-}$ with $[Fe(CN)_6]^{3-}$ and $[Co(bipy)_3]^{3+}$ is observed. Reduction potentials for the oxidants employed are $[Fe(phen)_3]^{3+}$ (1.06 V),[13] $[IrCl_6]^{2-}$ (0.89 V),[14] I_3^- (2e$^-$, 0.54 V),[15] $[Fe(CN)_6]^{3-}$ (0.40 V),[16] and $[Co(bipy)_3]^{3+}$ (0.37 V).[17] What seems clear from these studies is that $[W_2O_4(edta)]^{2-}$ is a substantially better reducing agent than $[Mo_2O_4(edta)]^{2-}$. This is of interest in view of the virtually identical size and bond dimensions of the W_2O_4 and Mo_2O_4 structures and hence similar energy requirements for reorganization.[2]

It has not been possible as a part of this study to obtain reduction potentials for the $W^V{}_2$–$W^{VI}{}_2$ and $Mo^V{}_2$–$Mo^{VI}{}_2$ couples involved. Previously, however, it has been concluded from one-electron reduction potentials of Keggin heteropoly-anions incorporating W and Mo that the W^{VI}–W^V couple is $>$0.4 V more strongly reducing than the Mo^{VI}–Mo^V couple.[18] Latimer[15] also lists potentials for $WO_3(s)$–W_2O_5 (0.03 V) and $MoO_3(aq)$–MoO_2^+ (0.40 V) couples. Observations in this paper are consistent with differences in reduction potentials of this magnitude. From a biological standpoint the fact that molybdenum rather than tungsten has been incorporated and is utilized in certain metalloenzymes may be due to the more favourable reduction potentials as suggested previously.[19,20] The picture regarding relative labilities of similar Mo and W complexes is at this stage less clearcut. A trend to decreasing lability with the heavier transition elements found in any one group has been observed,[21,22] and present data are consistent with this trend.

We are grateful to U.K. Science Research Council, London for a post-graduate studentship (to A. B. S.). We also acknowledge a period of study leave and partial financial support (to R. C. T.) (Faculty Research Fellowship) from Oakland University, Michigan.

[9/695 *Received, 4th May,* 1979]

REFERENCES

[1] J. Novak and J. Podlaha, *J. Inorg. Nuclear Chem.*, 1975, **36**, 1061.

[2] S. Khalil, B. Sheldrick, A. B. Soares, and A. G. Sykes, *Inorg. Chim. Acta*, 1977, **25**, L83.

[3] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1974, 1468.

[4] R. K. Wharton, J. F. Ojo, and A. G. Sykes, *J.C.S. Dalton*, 1975, 1526.

[5] O. Collenberg, *Z. anorg. Chem.*, 1918, **102**, 247 and detailed in G. W. A. Fowles, ' Preparative Inorganic Reactions,' Interscience, New York, 1964, vol. 1, p. 137.

[6] G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 638.

[7] P. B. Thich and J. Podlahova, *Coll. Czech. Chem. Comm.*, 1975, **40**, 347.

[8] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1962, p. 49.

[9] R. H. Moore and R. K. Zeigler, Los Alamos Report LA 2367 and Addenda, 1959.

[10] M. Ardon and A. Pernick, *Inorg. Chem.*, 1973, **12**, 2484.

[11] K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, 1978, **17**, 2769.

[12] H. von Felten, B. Wernli, H. Gamsjäger, and P. Baertschi, *J.C.S. Dalton*, 1978, 496.

[13] G. F. Smith and F. P. Richter, *Ind. and Eng. Chem. Anal.*, 1944, **16**, 580.

[14] D. W. Margerum, K. L. Chellappa, F. P. Bossu, and G. L. Bruce, *J. Amer. Chem. Soc.*, 1975, **97**, 6894.

[15] W. M. Latimer, ' Oxidation States of the Elements and their Potentials in Aqueous Solutions,' 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey, 1952.

[16] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, 1935, **39**, 945.

[17] E. Paglia and C. Sironi, *Gazzetta*, 1957, **81**, 1125.

[18] J. J. Altenau, M. T. Pope, R. A. Prados, and H. So, *Inorg. Chem.*, 1975, **14**, 417.

[19] E. I. Stiefel, W. E. Newton, G. D. Watt, and K. C. Hatfield, *Adv. Chem. Ser.*, 1977, **162**, 353.

[20] G. E. Callis and R. A. D. Wentworth, *Bioinorg. Chem.*, 1976, **7**, 57.

[21] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1968.

[22] L. H. Pignolet, *Topics Current Chem.*, 1975, **56**, 91.