The results of this study can be compared with the Pd(II)–Cl^- equilibrium in aqueous solution.[2b] In water there is no evidence for dimer and above a chloride concentration of 0.1 *M* the Pd(II) exists almost entirely as $PdCl_4^{2-}$. It is not surprising that in a low dielectric constant solvent, such as acetic acid, Pd(II) exists as a chloride-bridged dimer at low [LiCl] and that the equilibrium constant for breaking the dimer bridge is only 0.1 M^{-1}. However, it does mean that the study of Pd(II)-catalyzed reactions in acetic acid will be more complex than in water, first, because there will be more Pd(II) species to consider and, second, because there are several ways for a dimeric Pd(II) species to interact with a substrate. Furthermore, when lithium chloride is involved in the reaction sequence, the association of LiCl must be taken into account.

Acknowledgment.—The authors gratefully acknowledge the following for excellent technical assistance: Mr. James Carey, who carried out the molecular weight measurements, and Mr. F. Kriss, who did the majority of the other laboratory work.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

A Kinetic Study of the Oxidation of the Tantalum Cluster Ion $Ta_6Br_{12}^{2+}$ by Chromium(VI)[1a]

BY JAMES H. ESPENSON*,[1b] AND ROBERT J. KINNEY[1c]

Received July 6, 1970

The oxidation of $Ta_6Br_{12}^{2+}$ to $Ta_6Br_{12}^{3+}$ by Cr(VI) occurs at a rate given by the expression $-d[Ta_6Br_{12}^{2+}]/dt = \{k_1 + k_2 \cdot [HCrO_4^-]\}[H^+][HCrO_4^-][Ta_6Br_{12}^{2+}]$, with $k_1 = (9.53 \pm 0.25) \times 10^3\ M^{-2}\ sec^{-1}$ and $k_2 = (3.72 \pm 0.09) \times 10^7\ M^{-3}\ sec^{-1}$ ($25.0°$, $\mu = 1.00\ M$). The kinetic data for k_1 are consistent with a mechanism in which three successive single-electron steps convert Cr(VI) to Cr(III), by way of intermediate Cr(V) and Cr(IV). The kinetic data are also consistent with a two-electron mechanism, and no distinction is possible at present. The second rate term can be interpreted as a parallel oxidation by $Cr_2O_7^{2-}$. The corresponding value of k_1 for $Ta_6Cl_{12}^{2+}$ is $2.8 \times 10^4\ M^{-2}\ sec^{-1}$.

Introduction

Tantalum cluster ions $Ta_6X_{12}^{n+}$, with X = Br or C and *n* = 2, 3, or 4, have been shown to undergo reversible electron transfer,[2-4] and the mechanisms of some of their redox reactions have been considered.[4-6] The oxidation of $Ta_6Br_{12}^{2+}$ by $HCrO_4^-$ occurs according to the net equation

$$3Ta_6Br_{12}^{2+} + HCrO_4^- + 7H^+ = 3Ta_6Br_{12}^{3+} + Cr(III) + 4H_2O \quad (1)$$

A consideration of the electrode potentials[3] indicates that further oxidation to the polynuclear 4+ ion should occur; that second step occurs more slowly, however, possibly accompanied by some decomposition of the cluster framework. The present work has been confined to a kinetic study of reaction 1 in acidic solution and to some related studies on $Ta_6Cl_{12}^{2+}$.

Experimental Section

The source of $Ta_6Br_{12}^{2+}$ is the hydrate salt $Ta_6Br_{14} \cdot 8H_2O$, prepared according to published procedures and purified by recrystallization from water.[2] Other reagents were prepared and purified as in earlier work.[7] The reaction kinetics were studied spectrophotometrically, using a Cary Model 14 instrument for most experiments,[7a] with a few experiments carried out using the stopped-flow method.[7b] In most of the rate runs the decrease in concentration of the $Ta_6Br_{12}^{2+}$ species was monitored using its intense absorption band at λ 637 nm (ε 7100 M^{-1} cm^{-1}), with a few runs performed at λ 870 nm, a maximum for the product $Ta_6Br_{12}^{3+}$ (ε ~6100 M^{-1} cm^{-1}). All the rate measurements were made at 25.0°, with lithium perchlorate added to maintain a constant ionic strength of 1.00 *M*.

Results and Interpretation

Stoichiometry.—The stoichiometry of the reaction was determined by spectrophotometric titrations of known amounts of $Ta_6Br_{12}^{2+}$ with $HCrO_4^-$. Breaks in the titration curves at $[Ta_6Br_{12}^{2+}]/[HCrO_4^-] = 3.0$ and 1.5 represent the two steps in the oxidation of $Ta_6Br_{12}^{2+}$ first to $Ta_6Br_{12}^{3+}$ and subsequently to $Ta_6Br_{12}^{4+}$.

The second reaction occurs much more slowly than the first, so that even with a considerable excess of $HCrO_4^-$, as was the case in the kinetic experiments described subsequently, no appreciable interference is caused by the reaction of the 3+ cluster ion and $HCrO_4^-$.

Kinetics.—In most kinetic experiments the concen-

---

* To whom correspondence should be addressed.

(1) (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 2780. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970. (c) Undergraduate research trainee in the Ames Laboratory, summer 1969.

(2) R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *Inorg. Chem.*, **4**, 1491 (1965).

(3) N. E. Cooke, T. Kuwana, and J. H. Espenson, submitted for publication.

(4) J. H. Espenson and R. E. McCarley, *J. Amer. Chem. Soc.*, **88**, 1063 (1966).

(5) J. H. Espenson, *Inorg. Chem.*, **7**, 631 (1968).

(6) J. H. Espenson and D. J. Boone, *ibid.*, **7**, 638 (1968).

(7) (a) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964); (b) K. M. Davies and J. H. Espenson, *ibid.*, **92**, 1884 (1970).

trations of H^+ and $HCrO_4^-$ were both considerably higher than that of $Ta_6Br_{12}^{2+}$, so that the latter was the only significant concentration variable. Pseudo-first-order plots constructed from the absorbance data were found to be linear to at least 80% completion. The slopes of such plots are designated k_{exptl}, which is seen to be $-\text{d} \ln [Ta_6Br_{12}^{2+}]/\text{d}t$. The values of k_{exptl} proved to be independent of the initial concentration of $Ta_6Br_{12}^{2+}$ over the range of values $(0.5\text{–}2.0) \times 10^{-5}$ *M* and were reproducible to a mean deviation of 2.1% (maximum 5.1%).

These results indicate that the rate does not depend on the concentration of a reaction product, $Ta_6Br_{12}^{3+}$, as is sometimes the case in multistep Cr(VI) oxidations.[7,8] The absence of any dependence on product concentration was confirmed by independent experiments in which the 3+ cluster ion was added at concentrations 2–10-fold higher than the levels at which it was produced in the earlier runs; the rate constant did not change.

Further variables were Cr(VI) and H^+ concentrations. The formal concentration of Cr(VI) was varied between 0.40 and 6.00×10^{-4} *F*. After accounting for the very rapid equilibrium shown in reaction 2, for

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \quad (K_d) \qquad (2)$$

which K_d is 98 M^{-1} at 25.0° and 1.00 *M* ionic strength,[9] the variation in $[HCrO_4^-]$ is $(0.38\text{–}5.41) \times 10^{-4}$ *M*. The range of hydrogen ion concentrations studied was 5.00×10^{-3} to 0.100 *M*. Table I summarizes the values of k_{exptl} at all the concentrations studied. The data conform to the equation

$$k_{\text{exptl}} = k_1[H^+][HCrO_4^-] + k_2[HCrO_4^-]^2[H^+] \qquad (3)$$

A plot of $k_{\text{exptl}}/[H^+][HCrO_4^-]$ *vs.* $[HCrO_4^-]$ is linear as shown in Figure 1. The least-squares parameters are $k_1 = (9.53 \pm 0.25) \times 10^3\ M^{-2}\ \text{sec}^{-1}$ and $k_2 = (3.72 \pm 0.09) \times 10^7\ M^{-3}\ \text{sec}^{-1}$, where the uncertainties are the standard deviations. These parameters reproduce the experimental results with an average deviation of 3.3% (maximum 8.3%).

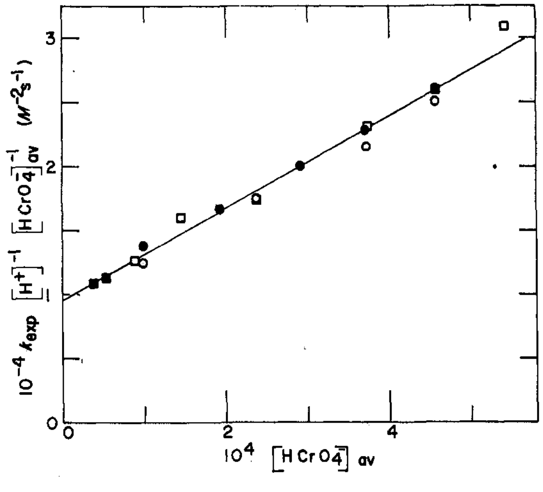


Figure 1.—A plot of the kinetic data in accord with eq 3. The legend refers to different $[H^+]$: 5×10^{-3} (open circles), 7.5×10^{-3} (filled circles), 10^{-2} (open squares), and 0.10 *M* (filled squares). The line is the least-squares fit of the data to eq 3.

TABLE I

KINETIC DATA FOR THE OXIDATION OF $Ta_6Br_{12}^{2+}$ BY CHROMIUM(VI)[a]

$[H^+]$, *M*	$10^4 \times [HCrO_4^-]_{av}$, *M*	$10^2 k_{\text{exptl}}$, sec^{-1}	$10^{-4} k_{\text{exptl}}/[H^+][HCrO_4^-]$, $M^{-2}\ \text{sec}^{-1}$ Calcd[c]	Obsd[b]
0.00500	0.981	0.609	1.32	1.24 ± 0.01
	2.38	2.10	1.84	1.77 ± 0.03
	3.72	4.15	2.34	2.16 ± 0.06 (4)
	4.56	5.64	2.65	2.49 ± 0.09
0.00750	0.981	1.02	1.32	1.38 ± 0.07
	1.92	2.36	1.67	1.67 ± 0.07 (4)
	2.91	4.74	2.04	2.00 ± 0.02
	3.72	7.07	2.34	2.53 ± 0.02
	4.56	9.27	2.65	2.61 ± 0.07
0.0100	0.870	1.13	1.28	1.27 ± 0
	0.981	1.31	1.32	1.33
	1.45	2.31	1.49	1.59 ± 0.01
	2.38	4.16	1.84	1.75 ± 0.09
	3.72	8.61	2.34	2.31 ± 0.01
	4.56	12.1	2.65	2.65 ± 0.01
	5.41	16.7	2.97	3.08 ± 0.10 (4)
0.100	0.384	4.34	1.10	1.10
	0.534	6.11	1.15	1.13 ± 0.01 (3)

[a] At 25.0°, $\mu = 1.00$ *M*; $[Ta_6Br_{12}^{2+}]_0 = 10^{-5}$ *M* in most experiments. [b] The uncertainty in this quantity represents the average deviation in k_{exptl} from duplicate determinations or in the number of runs given in parentheses. [c] Calculated values from the least-squares parameters for the fit to eq 3.

Scavenging Experiments.—Tests are often applied for the possible presence of intermediates such as Cr(V) and Cr(IV).[8] The detection of Cr(V) by its reaction with iodide ions is an example of this method.[7,8] Attempts were made to use the induced oxidation of I^- to learn whether Cr(V) is an important intermediate. However, the equilibrium

$$3I^- + 2Ta_6Br_{12}^{3+} = I_3^- + 2Ta_6Br_{12}^{2+} \qquad (4)$$

is established in less than 50 sec under the conditions studied and consequently renders this application unsuitable.

An alternative scavenging agent, V^{3+}, was added in some experiments. Kinetic studies[7b] have shown V^{3+} reacts much more rapidly with both Cr(V) and Cr(IV) than it does with Cr(VI), whereas the reaction rates of $Ta_6Br_{12}^{2+}$ and V^{3+} with $HCrO_4^-$ are comparable. After correcting for the VO^{2+} produced in the Cr(VI) step, additional quantities of VO^{2+} were formed along with $Ta_6Br_{12}^{3+}$. The qualitative interpretation of this observation is that evidence is provided for the existence of some chromium intermediate(s), Cr(V) and/or Cr(IV), with which the two reducing agents can react. Because the number of possible reactions is large, the data do not allow a determination of what intermediates are reacting at either stage.

Experiments with $Ta_6Cl_{12}^{2+}$.—A smaller number of kinetic experiments were carried out on the reaction of the chloride cluster ion, which reacts more rapidly than the bromide. The experiments covered a narrow range

---

(8) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

(9) J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **75**, 6180 (1953).

of $[HCrO_4^-]$, (3.8–4.8) $\times 10^{-5}$ *M*, with $Ta_6Cl_{12}^{2+}$ the limiting reagent at *ca.* 1×10^{-5} *M*. The kinetic data are consistent with the rate law

$$-d[Ta_6Cl_{12}^{2+}]/dt = k_3[Ta_6Cl_{12}^{2+}][HCrO_4^-][H^+] \quad (5)$$

with $k_3 = (28 \pm 1) \times 10^3\ M^{-3}\ sec^{-1}$. The range of $HCrO_4^-$ concentrations was too narrow, however, to claim a strictly first-order dependence on $[HCrO_4^-]$, although that result would follow by analogy to eq 3.

Reaction Mechanism.—The rate law given in eq 3 indicates the reaction occurs by two parallel pathways, which can be represented by the net activation processes[10]

$$Ta_6Br_{12}^{2+} + HCrO_4^- + H^+ = [(Ta_6Br_{12})H_2CrO_4^{2+}]^{\ddagger} \quad (6)$$

$$Ta_6Br_{12}^{2+} + 2HCrO_4^- + H^- = [(Ta_6Br_{12})H_3Cr_2O_8^{+}]^{\ddagger} \quad (7)$$

By analogy to other chromium(VI) oxidations,[7,9,11] a mechanism consisting of a sequence of three one-electron steps can be proposed for the first pathway. In this case, the first step would be

$$Ta_6Br_{12}^{2+} + HCrO_4^- + H^+ \xrightarrow{k_1} Ta_6Br_{12}^{3+} + H_2CrO_4^- \quad (8)$$

with the two subsequent steps, reduction to Cr(IV) and to Cr(III), being rapid.

Other possibilities must be considered among which is a mechanism involving a rate-determining two-electron step

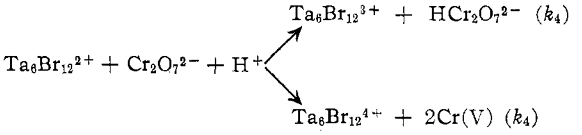
$$Ta_6Br_{12}^{2+} + HCrO_4^- + H^+ \xrightarrow{k_1} Ta_6Br_{12}^{4+} + Cr(IV) \quad (9)$$

$$Ta_6Br_{12}^{2+} + Cr(IV) \longrightarrow Ta_6Br_{12}^{3+} + Cr(III) \quad (fast) \quad (10)$$

$$Ta_6Br_{12}^{2+} + Ta_6Br_{12}^{4+} \longrightarrow 2Ta_6Br_{12}^{3+} \quad (fast) \quad (11)$$

Provided the first step is the slowest, this is not kinetically distinguishable from the one-electron mechanism. Winograd and Kuwana[12] have studied the rate of reaction 11, finding $k = 9 \times 10^7\ M^{-1}\ sec^{-1}$, which is sufficiently rapid to satisfy that condition. The distinctions that could be made using specific chemical scavenging for Cr(V) and Cr(IV) were not sufficient because of other reactions occurring in this system, as discussed above.

The pathway with a second-order dependence on $[HCrO_4^-]$ is probably accounted for by the reaction of dichromate ion, by either of reactions 12 or 13, where



$$\begin{tikzcd}[column sep=small] & Ta_6Br_{12}^{3+} + HCr_2O_7^{2-}\ (k_4) \quad (12) \\ Ta_6Br_{12}^{2+} + Cr_2O_7^{2-} + H^+ \arrow[ur] \arrow[dr] & \\ & Ta_6Br_{12}^{4+} + 2Cr(V)\ (k_4) \quad (13) \end{tikzcd}$$

$HCr_2O_7^{2-}$ represents a mixed Cr(VI)–Cr(V) species. On that basis $k_4 = k_2K_d^{-1} = 3.8 \times 10^5\ M^{-2}\ sec^{-1}$. Comparing eq 8 (or 9) and 12 (or 13), which have the same form, it is seen $Cr_2O_7^{2-}$ is considerably more reactive than $HCrO_4^-$, which is not usually the case.[9,13]

The oxidation of $Ta_6Cl_{12}^{2+}$ occurs more rapidly than that of $Ta_6Br_{12}^{2+}$ by a factor of *ca.* 3. This rate difference is in accord with the chloride cluster ion being the stronger reducing agent by *ca.* 0.1 V.[3]

---

[10] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

[11] J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

[12] N. Winograd and T. Kuwana, *J. Amer. Chem. Soc.*, **92**, 224 (1970).

[13] (a) J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963); (b) M. Nicol and D. R. Rosseinsky, *J. Chem. Soc. A*, 2812 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, AND THE LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA 94720

Chemical Shifts in Core Electron Binding Energies for Some Gaseous Nitrogen Compounds

BY PATRICIA FINN, RICHARD K. PEARSON, JACK M. HOLLANDER, AND WILLIAM L. JOLLY*

Received June 17, 1970

Chemical shifts in core electron binding energies for gaseous nitrogen compounds are compared with values estimated by various theoretical and empirical methods. The relative merits of these methods are discussed.

X-Ray photoelectron spectroscopy is of great interest to chemists because the measured core electron binding energies are a function of the chemical environment of the atoms—that is, the binding energies show chemical shifts. Experimental binding energies for compounds of a given element can be estimated from (1) correlations with calculated atomic charges,[1–6] (2) thermodynamic data based on the approximation that the energy of core electron capture by a nucleus is independent of chemical environment,[7–9] (3) empirical parameters characteristic of the directly bonded groups,[8] and (4)

---

* To whom correspondence should be addressed at the Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, Calif. 94720

[1] K. Siegbahn, *et al.*, "ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, 1967.

[2] J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968).

[3] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

[4] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

[5] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **9**, 612 (1970).

[6] K. Siegbahn, *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

[7] W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **92**, 1863 (1970).

[8] W. L. Jolly, *ibid.*, **92**, 3260 (1970).

[9] J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, **3**, 193 (1970).