and a detailed report of results and experimental apparatus will be published shortly.

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Oxidation of Tantalum Cluster Ions[1]

Sir:

We report here on the results of a study of the stoichiometry of oxidation of the tantalum cluster species $[Ta_6Cl_{12}]^{2+}$ by iron(III) in acidic solution, and on the kinetics and mechanisms of the reactions involved. To the best of our knowledge, this work constitutes the first example of studies of reaction mechanisms of heavy-metal cluster ions.

Stoichiometry Results. Earlier work[2] dealing with the stoichiometry established that a high concentration excess of iron(III) oxidizes $[Ta_6Cl_{12}]^{2+}$ to $[Ta_6Cl_{12}]^{4+}$. It was on the assumption that reaction 1 described the

$$[Ta_6Cl_{12}]^{2+} + 2Fe^{3+} = [Ta_6Cl_{12}]^{4+} + 2Fe^{2+} \qquad (1)$$

stoichiometry under all circumstances that work on the kinetics and mechanism was begun. A number of subsequent observations rendered this hypothesis untenable, and we now formulate this reaction as two one-electron oxidations in which $[Ta_6Cl_{12}]^{3+}$ occurs as a stable species. Several lines of evidence substantiate this formulation. At low concentrations (10^{-5}–10^{-4} M, Cl^- or ClO_4^- counterion), only 1 mole of iron(III) is reduced per mole of $[Ta_6Cl_{12}]^{2+}$ added; solutions in this concentration range with a iron(III):cluster ratio of 1–2 contained iron(III) in excess. Likewise, in solutions at similar concentration levels, but with <1.0 iron(III) per tantalum cluster, the concentration of $[Ta_6Cl_{12}]^{2+}$, estimated by its intense absorption band at 6370 A, decreased directly with added iron(III), falling essentially to zero at 1.0 mole ratio.

At higher iron(III) concentrations (0.001–0.1 M) further spectral changes were noted, especially in the near-infrared region. Solutions of $[Ta_6Cl_{12}]^{2+}$ in dilute perchloric acid were treated with chlorine, and the excess was removed in a stream of nitrogen. The spectrum of the product was the same as that produced at the very highest iron(III) concentrations.

We account for these observations in terms of two one-electron oxidations of $[Ta_6Cl_{12}]^{2+}$ in reactions 2 and 3. The equilibrium constant for reaction 3 under

$$[Ta_6Cl_{12}]^{2+} + Fe^{3+} = [Ta_6Cl_{12}]^{3+} + Fe^{2+} \qquad (2)$$

$$[Ta_6Cl_{12}]^{3+} + Fe^{3+} = [Ta_6Cl_{12}]^{4+} + Fe^{2+} \qquad (3)$$

these conditions is somewhat less than unity; only iron(III) concentrations greater than *ca.* 0.01 M substantially converted 10^{-5} M $[Ta_6Cl_{12}]^{2+}$ to $[Ta_6Cl_{12}]^{4+}$. This suggests reaction 3 should easily be reversed. When iron(II) was added to such solutions, or when it was added to $[Ta_6Cl_{12}]^{2+}$ prior to iron(III), the spectrum was identical with that observed in low iron(III) solutions, *i.e.*, $[Ta_6Cl_{12}]^{3+}$. The same spectrum resulted also when iron(II) was added to $[Ta_6Cl_{12}]^{4+}$ solutions obtained by oxidation of $[Ta_6Cl_{12}]^{2+}$ with chlorine.

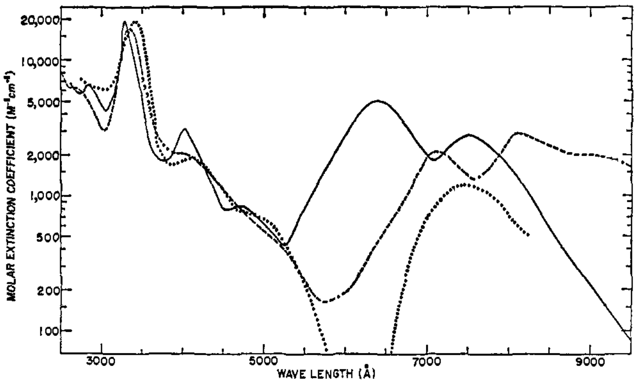

Figure 1. Absorption spectra of tantalum cluster ions; extinction coefficient (logarithmic scale) *vs.* wavelength. Spectra shown are: ——, $[Ta_6Cl_{12}]^{2+}$; – – – –, $[Ta_6Cl_{12}]^{3+}$; and . . . ., $[Ta_6Cl_{12}]^{4+}$.

The observations cited above require that the disproportionation equilibrium, reaction 4, favor the species of +3 charge. Solutions of $[Ta_6Cl_{12}]^{2+}$ and

$$[Ta_6Cl_{12}]^{2+} + [Ta_6Cl_{12}]^{4+} = 2[Ta_6Cl_{12}]^{3+} \qquad (4)$$

$[Ta_6Cl_{12}]^{4+}$, the latter prepared from chlorine oxidation, were mixed in equimolar amounts. The spectrum of this solution was definitely not that of a mixture of the two components and was identical with that observed in solutions of $[Ta_6Cl_{12}]^{3+}$ prepared from $[Ta_6Cl_{12}]^{2+}$ and low concentrations of iron(III). The absorption spectra of solutions of $[Ta_6Cl_{12}]^{3+}$ prepared in either manner remained unchanged during a 2-week period at room temperature. The spectra of the three tantalum cluster ions are shown in Figure 1. Solutions of $[Ta_6Cl_{12}]^{4+}$ were not stable. In the absence of excess chlorine, they reverted to $[Ta_6Cl_{12}]^{3+}$ after several hours at room temperature, presumably by disproportionation to the cluster +3 and to tantalum(V) oxide. In the presence of chlorine, a precipitate of tantalum(V) oxide was noted when such solutions were left to stand overnight.

Kinetics Results. Spectrophotometric kinetics studies were carried out on reaction 2, and on the forward and reverse of reaction 3.[3] Reaction 2 obeys the rate equation

$$-d[Fe^{3+}]/dt = k_{23}[[Ta_6Cl_{12}]^{2+}][Fe^{3+}] \qquad (5)$$

The reaction was studied with initial concentrations of iron(III) of 0.5–4 × 10^{-4} M, and of $[Ta_6Cl_{12}]^{2+}$ 1–3 × 10^{-5} M; each run was followed to at least 90% completion. At 15.0° and 0.020 M ionic strength, usually 0.020 F perchloric acid, k_{23} is 620 M^{-1} sec^{-1} (±32, standard deviation in 12 runs). The observed rate was independent of hydrogen ion.[4]

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1849.

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

[3] The procedures used in such studies and the specially constructed arrangement for precise temperature control have been described previously: J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[4] Low concentrations of chloride ion are without effect on the reaction rates. In some experiments solutions of $[Ta_6Cl_{12}]Cl_2 \cdot xH_2O$ were used directly, and, in others, anion exchange was used to replace anionic chloride with perchlorate. The tantalum cluster compound was prepared according to P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965). We are grateful to Mr. J. L. Meyer for carrying out this preparation.

The forward and reverse of reaction 3 were each studied at 15.0° and 0.100 M ionic strength. Concentrations were adjusted in an attempt to permit the two directions of reaction to be studied independently of one another.[5] The oxidation of $[Ta_6Cl_{12}]^{3+}$ by iron(III) follows the rate equation

$$d[Fe^{2+}]/dt = k_{34}[[TaCl_{12}]^{3+}][Fe^{3+}] \qquad (6)$$

with $k_{34} = 3.72\ M^{-1}\ sec^{-1}$ (±0.31, standard deviation in 10 runs). These studies covered the concentration range 0.0015–0.010 M iron(III). The rate law for the reaction of $[Ta_6Cl_{12}]^{4+}$ and iron(II) is

$$-d[Fe^{2+}]/dt = k_{43}[[Ta_6Cl_{12}]^{4+}][Fe^{2+}] \qquad (7)$$

with $k_{43} = 201\ M^{-1}\ sec^{-1}$ (±10, standard deviation in 10 runs). Initial iron(II) concentrations lay in the range 10^{-5}–$10^{-3}\ M$.

These data lead to a value for the equilibrium quotient of reaction 3, $Q_{34} = k_{34}/k_{43} = 0.018$ (±0.0025 standard deviation) at 15.0° and 0.100 M ionic strength. The equilibrium was also studied directly by spectrophotometry at 8100 A, where $[Ta_6Cl_{12}]^{3+}$ absorbs 3.4 times more intensely than does $[Ta_6Cl_{12}]^{4+}$. In four experiments covering 6–60% as the oxidized complex, we found $Q_{34} = 0.016 \pm 0.002$ at 0.100 M ionic strength and room temperature (22 ± 2°).

An attempt was made to study the rate of reaction of $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{4+}$ (reaction 4), but in every instance the reaction was apparently complete upon mixing. In a run $3 \times 10^{-5}\ M$ in each cluster ion, the first reading was taken 5 sec after mixing and indicated the reaction was >95% complete in this time; assuming a simple mixed-second-order rate law, a lower limit was placed that $k > 1 \times 10^5\ M^{-1}\ sec^{-1}$.

Apparently, simple bimolecular reaction mechanisms account satisfactorily for the reactions studied here, where second-order kinetics always were observed. No evidence was found for any complexities, such as reaction intermediates or hydrogen ion dependences. The reactions are quite rapid, which is consistent with the relative lack of molecular rearrangement accompanying electron transfer.

A study of the stoichiometry, kinetics, and mechanisms of electron-transfer reactions of these tantalum cluster complexes promises to provide some interesting results on these novel substances.

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(5) In the two series of experiments performed here, reduction of $[Ta_6Cl_{12}]^{4+}$ by iron(II) was calculated to be between 88 and 99.98% complete, and oxidation of $[Ta_6Cl_{12}]^{3+}$ by iron(III) between 78 and 95% complete. In this preliminary treatment of data, failure of the reactions to run to completion was ignored. A number of additional runs on the reaction of $[Ta_6Cl_{12}]^{3+}$ and iron(III), where the extent of equilibrium conversion was somewhat lower, are not reported here.

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Reaction of Free Carbon Atoms with Cyclopentadiene

Sir:

We have studied the interaction of free carbon atoms with gaseous cyclopentadiene. This system is of special interest in the development of a general mechanism for reactions of atomic carbon in organic systems.[1] Rearrangement and/or decomposition of the adducts ($C + C_5H_6$) formed can be predicted with an unusual degree of confidence, with only relatively few final products being expected to be formed in major yield. For this reason, the system provides an excellent test of our understanding of the fundamental mechanisms of carbon atom reactions. In addition, results provide a basis for comparison in attempting to understand the difficult problem of reaction of carbon with benzene.

Free carbon atoms were produced in the form of C^{11} (20.5 min) by nuclear techniques described in detail elsewhere.[1,2] Such atoms are expected, on the basis of certain theoretical considerations,[1c,3] to be in low-lying electronic states (^3P, ^1D, ^1S), an expectation consistent with all results obtained. Their reactions were studied both in unmoderated systems, in which products may be formed in "hot" reaction, and in mixtures moderated by sufficient neon so that virtually all the atoms reacted "thermally," *i.e.*, after removal of their excess kinetic energy.[4]

Table I.[a] Yields of C^{11}-Labeled Products from Reactions of C^{11} with Cyclopentadiene

Product	Hot system cyclopentadiene (30.0 cm)	Thermal system cyclopentadiene (4 cm)–neon (76 cm)
Carbon monoxide[b]	0.7 ± 0.3	1.6 ± 0.1
Acetylene	10.0 ± 1.0	2.9 ± 0.1
Vinylacetylene	3.8 ± 0.1	2.2 ± 0.1
Diacetylene	8.9 ± 0.3	3.2 ± 0.1
Bicyclo[1.3.0]hexene-3[c]	1.2 ± 0.3	<0.2
Fulvene[d]	3.0[d]	1.2[d]
Benzene	8.6 ± 0.3	11.2 ± 0.5
cis-1,3-Hexadien-5-yne	2.1 ± 0.2	5.2 ± 0.8
trans-1,3-Hexadien-5-yne	1.2 ± 0.1	3.3 ± 0.4
Low mol wt minor products	2.0	Not detn
Polymer[e]	59 ± 5.0	70 ± 5.0

[a] All yields given in per cent absolute activity. Total volatile activity for unmoderated sample is about 55%, for moderated sample 35%. (This includes unidentified but volatile material classified as "polymer." See footnote *e* below.) [b] Results from reaction with oxygen impurity. [c] Probably results from reaction of CH_2 with cyclopentadiene. [d] Both the hot and thermal yields reported here are for samples with oxygen scavenger present and with a $C_5H_6:O_2$ ratio of 19:1. We believe that these are the significant yields for fulvene. In the absence of oxygen, fulvene is difficult to recover and yields are erratic. Apparently fulvene is particularly susceptible to destruction by reaction with radicals produced in the radiation field. Oxygen scavenges such radicals efficiently and permits recovery of fulvene. [e] Represents polymer, defined here as material containing more than six carbon atoms.

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(1) For recent reviews, see (a) C. MacKay and R. L. Wolfgang, *Science*, **148**, 899 (1965); (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 210 (1964); (c) R. L. Wolfgang, *Progr. Reaction Kinetics*, 3, 99 (1965).

(2) J. Durbin, C. MacKay, M. L. Pandow, and R. L. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964). Experimental details were largely as described in this work and in ref 5.

(3) M. Marshall, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964).

(4) The results of the experiments with neon moderation indicate that even at 95% moderation hot reactions play a minor role in determining the product spectrum. At this concentration, the sum yield