

the rate of the fragmentation solvolysis,¹⁴ whereas the Franck-Condon principle makes it of vital importance in the electronic excitation.

(14) C. A. Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Letters*, 2901 (1964).

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Received November 13, 1965

Internal Reflection Spectroscopic Observation of Electrode-Solution Interface

Sir:

We wish to report the use of internal reflection spectroscopy to *directly observe* and *monitor in situ* the *surface* concentration of the product of an electrochemical reaction. An optically transparent glass electrode coated with tin oxide was used. The optical configuration was similar to those previously described.¹

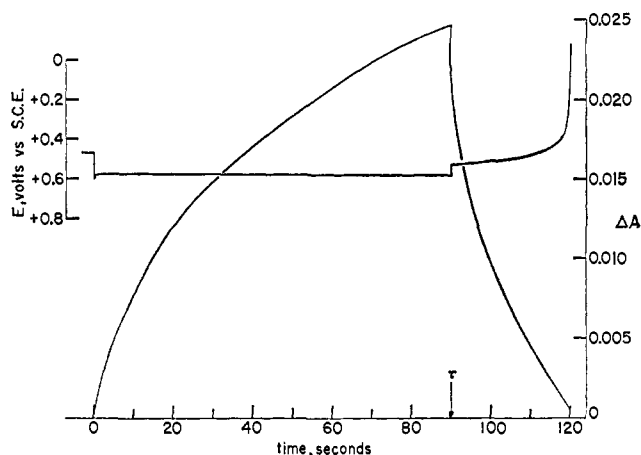
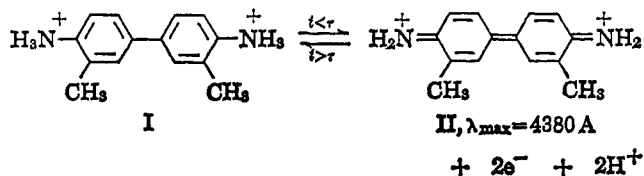


Figure 1. $E - t$ and $\Delta A - t$ behavior for solution 5 mF in *o*-toluidine and 0.1 F HCl. The electrolysis current of 1.0 ma results in the oxidation of I to II at the electrode surface to time τ , when current reversal causes reduction of II to I. The electrode area is approximately 13 cm².

The absorption of the oxidation product (II) of *o*-toluidine (I) in 0.1 F HCl solution was monitored at 4380 Å. Simultaneous electrochemical and normal transmittance spectroscopic studies of *o*-toluidine at tin oxide coated glass electrodes have been carried out.²



Plots of the voltage-time and absorbance-time characteristics during constant-current electrolysis (chronopotentiometry) are shown in Figure 1. To

(1) W. N. Hansen and J. A. Horton, *Anal. Chem.*, **36**, 783 (1964).

(2) T. Kuwana, R. K. Darlington, and D. W. Leedy, *ibid.*, **36**, 2025 (1964); F. A. Schultz and T. Kuwana, to be published.

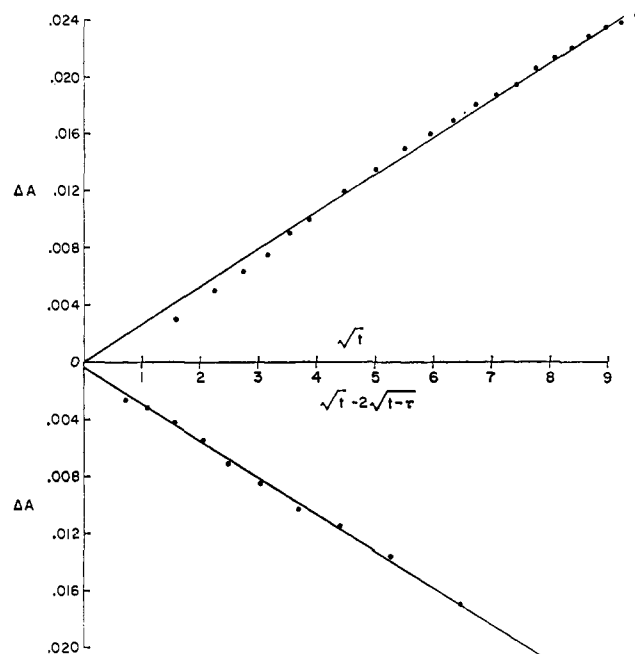


Figure 2. Plot of ΔA vs. \sqrt{t} and $\sqrt{t} - 2\sqrt{t - \tau}$. Abscissa units are sec^{1/2}; slopes are 0.0026 and 0.0027 sec^{-1/2} for ΔA vs. \sqrt{t} and $\sqrt{t} - 2\sqrt{t - \tau}$, respectively.

time τ the oxidation of *o*-toluidine results in the formation of II at the electrode surface; at time τ the current is reversed and reduction of the *product* II now occurs. The surface concentration of product II for time $t < \tau$ is proportional to $t^{1/2}$, and for time $t > \tau$ is proportional to the quantity $[t^{1/2} - 2(t - \tau)^{1/2}]$.³ From the linearity of the plots of these quantities in Figure 2, it is clear that only a region *very close* to the electrode surface is being observed. It is estimated that the penetration depth into the solution from the surface of the electrode is *ca.* 2000 Å. The penetration depth is here defined as the distance in solution at which the square of the amplitude of the electric field has decreased to 10% of its value at the surface.

The calculated "effective" path length of between 24,000 and 28,000 Å for the multiple reflection cell used agrees well with a value of *ca.* 25,000 Å obtained from the experimental absorbancy using a molar absorptivity of 50,000 l./mole/cm for product II at a wavelength of 4380 Å.²

The possible application of internal reflection spectroscopy to electrochemistry suggested earlier⁴ was recently investigated in the infrared region using germanium electrodes.⁵ The work reported here is, however, to our knowledge the first in which it has been conclusively demonstrated that the *surface* concentration, well within the diffusion layer, may be directly observed. Results from chronoamperometry and sweep voltammetry using this technique support our conclusion. Further experimental work is in progress

(3) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 8.

(4) W. N. Hansen, L. Lynds, and R. A. Osteryoung, "Infrared Reflectance Study of Gas-Solid Interaction," Final Summary Report, Oct 1962, Contract No. DA-44-009, U. S. Army Engineers Research and Development Laboratories, Fort Belvoir, Va.; Proceedings of the ARPA Fuel Cell Conference, Whiting, Ind., Feb 1962.

(5) H. B. Mark, Jr., and B. S. Pons, *Anal. Chem.*, **38**, 119 (1966).

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

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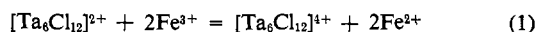
Received January 6, 1966

Oxidation of Tantalum Cluster Ions¹

Sir:

We report here on the results of a study of the stoichiometry of oxidation of the tantalum cluster species $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ 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.

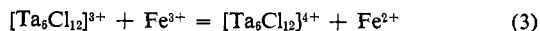
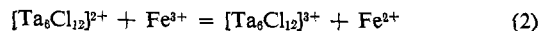
Stoichiometry Results. Earlier work² dealing with the stoichiometry established that a high concentration excess of iron(III) oxidizes $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ to $[\text{Ta}_6\text{Cl}_{12}]^{4+}$. It was on the assumption that reaction 1 described the



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 $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ 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 $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ added; solutions in this concentration range with an 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 $[\text{Ta}_6\text{Cl}_{12}]^{2+}$, estimated by its intense absorption band at 6370 Å, 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 $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ 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 $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ in reactions 2 and 3. The equilibrium constant for reaction 3 under



these conditions is somewhat less than unity; only iron(III) concentrations greater than *ca.* 0.01 M substantially converted 10^{-5} M $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ to $[\text{Ta}_6\text{Cl}_{12}]^{4+}$. This suggests reaction 3 should easily be reversed. When iron(II) was added to such solutions, or when it

(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).

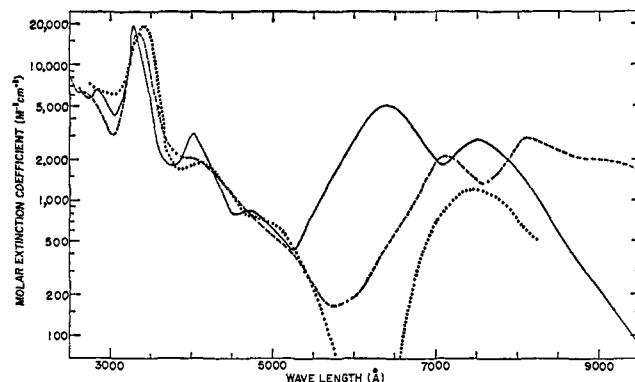
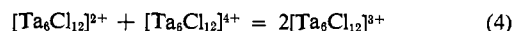


Figure 1. Absorption spectra of tantalum cluster ions; extinction coefficient (logarithmic scale) vs. wavelength. Spectra shown are: —, $[\text{Ta}_6\text{Cl}_{12}]^{2+}$; ---, $[\text{Ta}_6\text{Cl}_{12}]^{3+}$; and . . . , $[\text{Ta}_6\text{Cl}_{12}]^{4+}$.

was added to $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ prior to iron(III), the spectrum was identical with that observed in low iron(III) solutions, *i.e.*, $[\text{Ta}_6\text{Cl}_{12}]^{3+}$. The same spectrum resulted also when iron(II) was added to $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ solutions obtained by oxidation of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ with chlorine.

The observations cited above require that the disproportionation equilibrium, reaction 4, favor the species of +3 charge. Solutions of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and



$[\text{Ta}_6\text{Cl}_{12}]^{4+}$, 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 $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ prepared from $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and low concentrations of iron(III). The absorption spectra of solutions of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ 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 $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ were not stable. In the absence of excess chlorine, they reverted to $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ 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

$$-d[\text{Fe}^{3+}]/dt = k_{23}[[\text{Ta}_6\text{Cl}_{12}]^{2+}][\text{Fe}^{3+}] \quad (5)$$

The reaction was studied with initial concentrations of iron(III) of 0.5 – 4×10^{-4} M, and of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ 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

(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 $[\text{Ta}_6\text{Cl}_{12}]\text{Cl}_2 \cdot x\text{H}_2\text{O}$ 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.