

**1043.** *The Oxidation of Uranium(IV) by Thallium(III) over an Extended Concentration Range in Aqueous Perchloric Acid Solutions \**

By JAMES O. WEAR

The kinetics of the oxidation of uranium(IV) by thallium(III) have been examined in aqueous perchloric acid solution with the concentrations of reactants varied over a 2000-fold range. The orders with respect to uranium(IV) and thallium(III) were different in different concentration ranges. The data are explained on the basis of combinations of three paths involving hydrolytic species. The temperature was varied from 15° to 50°, and the activation energy found for each rate constant.

THE kinetics of the previously studied<sup>1-4</sup> reaction between uranium(IV) and thallium(III) have been studied in aqueous perchlorate medium. Harkness and Halpern<sup>1</sup> studied the reaction in the concentration ranges:  $[U^{IV}] = 3.5 \times 10^{-3}$ — $11.0 \times 10^{-3}M$ ,  $[Tl^{III}] = 5 \times 10^{-3}$ — $21 \times 10^{-3}M$ , and  $[H^+] = 0.50$ — $2.8M$ , with an ionic strength adjusted to 2.9 with sodium perchlorate. They found that the data could be explained by the expression:

$$-d[U^{IV}]/dt = k[U^{IV}][Tl^{III}][H^+]^{-1.4}$$

However, second-order plots had a small positive intercept. From a two-path mechanism the expression obtained was:

$$\begin{aligned} -d[U^{IV}]/dt &= [U^{4+}][Tl^{3+}](k_2[H^+]^{-1} + k_1[H^+]^{-2}) \\ &= [U^{IV}][Tl^{III}](k_2[H^+] + k_1)/([H^+] + K_1)([H^+] + K_2) \end{aligned}$$

where  $K_1$  and  $K_2$  are hydrolyses constants for  $U^{IV}$  and  $Tl^{III}$ , respectively. Other workers studied effects of solvent,<sup>2</sup> impurities,<sup>3</sup> and organic acids.<sup>4</sup> Jones and Amis<sup>2</sup> studied the reaction in various mixtures of methanol and water. As methanol was added, the orders changed drastically, but the general conclusions supported those of Harkness and Halpern.

The present study was undertaken to extend the concentration ranges and check procedures in the hope that this reaction might be used for studies in organic solvents. In expanding the concentration ranges, the orders in  $U^{IV}$  and  $Tl^{III}$  varied, and an attempt has been made to explain these phenomena.

The variation of orders was found outside the concentration regions studied by

\* Presented at the 19th Southwest Regional American Chemical Society Meeting, December 1963, Houston, Texas.

<sup>1</sup> A. C. Harkness and J. Halpern, *J. Amer. Chem. Soc.*, 1959, **81**, 3526.

<sup>2</sup> F. Jones and E. S. Amis, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1045.

<sup>3</sup> T. W. Newton, unpublished results.

<sup>4</sup> C. H. Brubaker, unpublished results.

Harkness and Halpern. This study supplements their work and supports their general conclusions. The variations in order can be attributed to the polymerisation of uranium(IV), or to a chain mechanism that becomes predominant at low concentrations.

### EXPERIMENTAL

Uranous perchlorate was prepared by electrolysis.<sup>5</sup> Thallous perchlorate dihydrate was dissolved in a perchloric acid solution, and the perchlorate was burned to the oxide and analysed spectrographically; only traces of iron (10 p.p.m.) were found. The thallic perchlorate concentration was determined by precipitation as the hydroxide, burning, and weighing the  $Tl_2O_3$ . Perchloric acid was titrated (phenolphthalein) with standard sodium hydroxide. Sodium perchlorate for adjusting ionic strength was prepared by treating reagent grade sodium carbonate with perchloric acid.

Distilled water from a Barnsted hard-water still was used. Permanganate distilled water was also used, and no difference was found. The distilled water was boiled and cooled with nitrogen bubbling through it. All solutions were prepared with oxygen-free distilled water, and nitrogen was passed through the stock solutions before analysis. The nitrogen was passed through a train consisting of pyrogallol solution, sulphuric acid, ascarite, and a water saturator.

The concentration of uranium(IV) was determined as a function of time with a Cary 14 spectrophotometer, using the 6475 Å peak with  $a_m = 60$ .<sup>2</sup> A two-pen recorder was used with either a 0—2 or 0—0.2 slide-wire. The temperature of the cell compartment was maintained to  $\pm 0.1^\circ$  by jacketed cell holders in a thermostatted compartment through which water was pumped from a bath. The temperature was monitored with a copper-constantan thermocouple, with a melting-ice reference and a K-3 potentiometer.

The reagents for each run were mixed in a 25-ml. volumetric flask by pipetting from stock solutions under nitrogen. All components were added except the thallium, and then the reaction solution and the thallium solution were allowed to come to thermal equilibrium in a bath before mixing. When one half of the thallium solution had been added, the stop-watch was started. The reaction mixture was transferred to a cell, and the recorder was always started within 2 min. of mixing (30 sec. on the fastest runs). The initial slope, or the slope at a certain per cent of reaction, was taken directly from the chart paper with a Gerber D-2 derivimeter. Where possible, least-square calculations were used. Calculations were made on a CDC 1604 computer.

### RESULTS AND DISCUSSION

In extending the concentration ranges, four different regions with respect to concentration were found (Table I). The order with respect to  $[H^+]$  (considering 100 per cent

TABLE I

Identification of concentration regions, and orders in each at  $25^\circ$ , with  $\mu = 2.9$

Region	$10^3[U^{VI}]$ (M)	$10^3[Tl^{III}]$ (M)	$[H^+]$ (M)	$U^{IV}$ order	$Tl^{III}$ order	$H^+$ order
I	0.5—50	1—50	0.25—2.75	0.88	0.90	-1.4
II	0.03—0.5	5.0	0.90	1.2	0.90	-1.4
III	6.3	0.02—1.0	0.90	0.88	0.67	-1.4
IV	0.07—0.22	0.12—0.36	0.50—1.90	1.6	0.38	-1.5

ionisation of perchloric acid, and taking hydrolysis into account) remained about -1.4 in all regions studied. The reaction character was insensitive to the addition of thallium(I) or uranium(VI) up to  $10^{-3}M$ . The rate doubled as the ionic strength was increased from 1.0 to 2.9 with sodium perchlorate.

The ionic strength was maintained at 2.9 in most cases; this maintained the perchlorate concentration constant to within 3%. This constancy of anion concentration is considered to provide the best conditions.<sup>6</sup> Of course, the ionic strength changes as the reaction proceeds, but the maximum change is 4%. These slight differences in composition could not account for the large changes in order.

<sup>5</sup> J. O. Wear, N. K. Shastri, and E. S. Amis, *J. Inorg. Nuclear Chem.*, 1965, in the press.

<sup>6</sup> F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1963, p. 22.

The four different regions will be discussed separately. Orders, and empirical and mechanistic rate expressions, will be presented for each.

*Region I.*—The method of initial rates <sup>7</sup> was used to determine orders, after an isolation method <sup>7</sup> and a standard second-order plot failed to yield consistent results. The method of initial rates, or instantaneous rates, was also used at 0.25, 0.5, 0.2, 0.4, and 0.6 reaction (with respect to the reagent whose initial concentration was being held constant). This method of instantaneous rates should be valid as long as the products have no effect on the reaction, as is so in the present case. The orders in this region are 0.88, 0.90, and -1.4, with respect to U<sup>IV</sup>, Tl<sup>III</sup>, and H<sup>+</sup>. The orders were obtained from the average of the slopes for the instantaneous-rate plots at various fractions of reaction and those for the initial-rate plots (Figures 1—3).

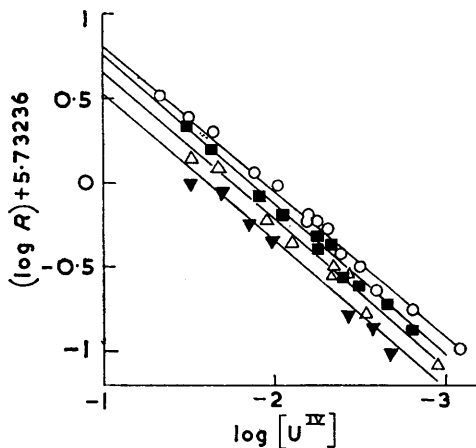


FIGURE 1. Determination of order with respect to uranium(IV)

○ Initial. ■ 0.2 Reaction. △ 0.4 Reaction. ▼ 0.6 Reaction

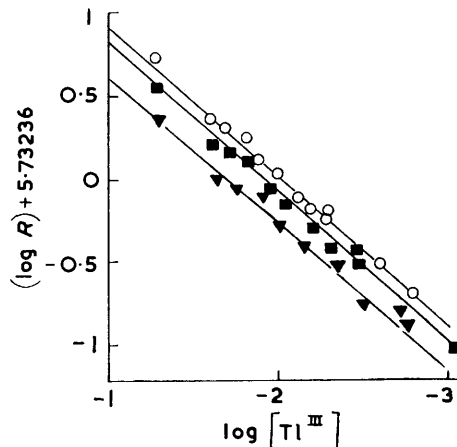


FIGURE 2. Determination of order with respect to thallium(III)

○ Initial. ■ 0.25 Reaction. ▼ 0.5 Reaction.

The orders of 0.86 and 0.90 cannot be rounded off to unity since they have an average deviation of less than  $\pm 1\%$ . If the values are rounded to unity then  $k' = 3 \times 10^{-2}$  min.<sup>-1</sup>, which is not greatly different from Harkness and Halpern's value of  $4 \times 10^{-2}$ ; but the deviation is over  $\pm 15\%$  instead of  $\pm 4.4\%$ .

The negative 1.4 order with respect to H<sup>+</sup> indicates at least two paths, one involving two and the other one hydrolytic species. No paths could be written that would give the fractional orders with respect to U<sup>IV</sup> and Tl<sup>III</sup> and also reproduce the observed rate. The closest fit was given by two paths which assumed that the orders with respect to U<sup>IV</sup> and Tl<sup>III</sup> were those which give the expression:

$$R = k_1[\text{TlOH}^{2+}][\text{UOH}^{3+}] + k_2[\text{TlOH}^{2+}][\text{U}^{4+}] \quad (1)$$

Using the following hydrolysis: <sup>8,9</sup>

$$K_1 = \frac{[\text{UOH}^{3+}][\text{H}^+]}{[\text{U}^{4+}]} = 2.1 \times 10^{-2} \quad (2)$$

$$K_2 = \frac{[\text{TlOH}^{2+}][\text{H}^+]}{[\text{Tl}^{3+}]} = 7.3 \times 10^{-2} \quad (3)$$

<sup>7</sup> E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd edn., Oxford University Press, London, 1947, p. 48.

<sup>8</sup> K. A. Kraus and F. Nelson, *J. Amer. Chem. Soc.*, 1950, **72**, 3901.

<sup>9</sup> G. Biederman, *Arkiv Kemi*, 1953, **5**, 441.

where  $K_1$  and  $K_2$  are given for  $25^\circ$  and  $\mu = 2.9$ , the following is obtained from eqn. (1):

$$R = \frac{k_1'[\text{Tl}^{\text{III}}][\text{U}^{\text{IV}}]}{(K_1 + [\text{H}^+])(K_2 + [\text{H}^+])} + \frac{k_2'[\text{Tl}^{\text{III}}][\text{U}^{\text{IV}}][\text{H}^+]}{(K_1 + [\text{H}^+])(K_2 + [\text{H}^+])} \quad (4)$$

where  $k_1' = k_1K_1K_2$  and  $k_2' = k_2K_2$ .

*Region II.*—This region is where  $[\text{U}^{\text{IV}}] < 5 \times 10^{-4}\text{M}$  and  $[\text{Tl}^{\text{III}}] > 10^{-3}\text{M}$ . The  $[\text{Tl}^{\text{III}}]$

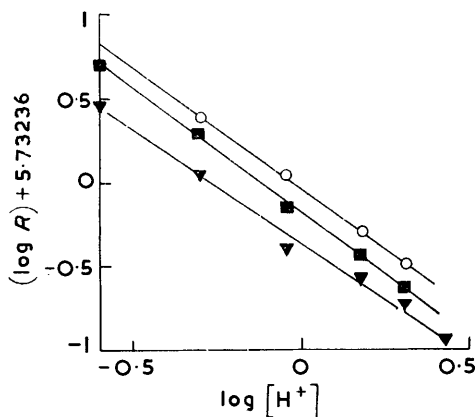


FIGURE 3. Determination of order with respect to  $\text{H}^+$

○ Initial. ■ 0.25 Reaction. ▼ 0.5 Reaction

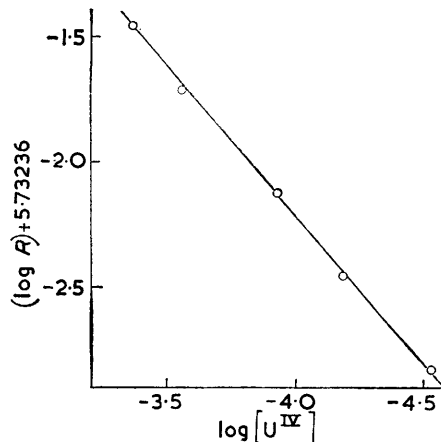


FIGURE 4. Determination of order with respect to uranium(IV)

was made 100 times the  $[\text{U}^{\text{IV}}]$ , and a fractional-life plot<sup>10</sup> indicated an order of 1.2 with respect to  $\text{U}^{\text{IV}}$ . As a further check, the order in  $\text{U}^{\text{IV}}$  was determined by the method of initial rates (Figure 4) and found to be 1.2. The orders with respect to  $\text{Tl}^{\text{III}}$  and  $\text{H}^+$  were 0.90 and 1.4, respectively.

The 1.2 order with respect to  $\text{U}^{\text{IV}}$  can be explained by one path involving two uranium(IV) atoms and a second path with only one such atom. Since a similar combination of paths is necessary to explain the  $\text{H}^+$  dependence, the following rate expression can be written:

$$R = k_1[\text{TlOH}^{2+}][\text{UOH}^{3+}] + k_2[\text{TlOH}^{2+}][\text{U}^{4+}] + k_3[\text{UOH}^{3+}]^2 \quad (5)$$

$$\text{or } R = \frac{k_1'[\text{Tl}^{\text{III}}][\text{U}^{\text{IV}}]}{(K_1 + [\text{H}^+])(K_2 + [\text{H}^+])} + \frac{k_2'[\text{Tl}^{\text{III}}][\text{U}^{\text{IV}}][\text{H}^+]}{(K_1 + [\text{H}^+])(K_2 + [\text{H}^+])} + \frac{k_3'[\text{U}^{\text{IV}}]^2}{[\text{H}^+] + K_1^2} \quad (6)$$

where  $k_1' = k_1K_1K_2$ ,  $k_2' = k_2K_2$ , and  $k_3' = k_3K_1^2$ . Path  $k_3$  is reasonable since uranium(IV) does form polymers of this type, but it would also be expected to be important at high concentrations. Since  $[\text{U}^{\text{IV}}]$  is low and the main reaction slow, perhaps path  $k_3$  has become important although it is too slow to be important at higher concentration.

*Region III.*—When  $[\text{U}^{\text{IV}}] > 10^{-3}\text{M}$  and  $[\text{Tl}^{\text{III}}] < 10^{-3}\text{M}$ , order with respect to  $\text{Tl}^{\text{III}}$  was found by the method of initial rates (Figure 5) to be 0.67; the orders with respect to  $\text{U}^{\text{IV}}$  and  $\text{H}^+$  remained 0.86 and  $-1.4$ , respectively.

This region can also be explained by eqn. (6). As the reaction becomes slower because of lower  $[\text{Tl}^{\text{III}}]$ , path  $k_3$  will become more important and the order with respect to  $\text{Tl}^{\text{III}}$  will decrease. However, the data do not obey eqn. (6) very well, so a better explanation is required.

<sup>10</sup> A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd edn., Wiley, New York, 1961, p. 43.

*Region IV.*—When  $[Tl^{III}] < 10^{-3}M$ ,  $[U^{IV}] < 5 \times 10^{-4}M$ ,  $[H^+] = 0.25-2.0M$ , and  $\mu = 2.9$ , the orders, determined by the method of initial rates (Figures 6 and 7), were 1.6, 0.38, and  $-1.5$  for  $U^{IV}$ ,  $Tl^{III}$ , and  $H^+$ , respectively. The paths used to explain Region II can be used to explain this region.

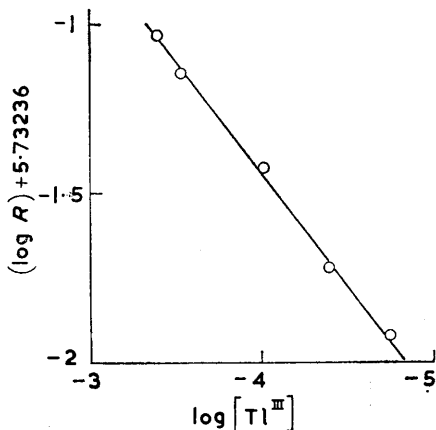


FIGURE 5. Determination of order with respect to thallium(III)

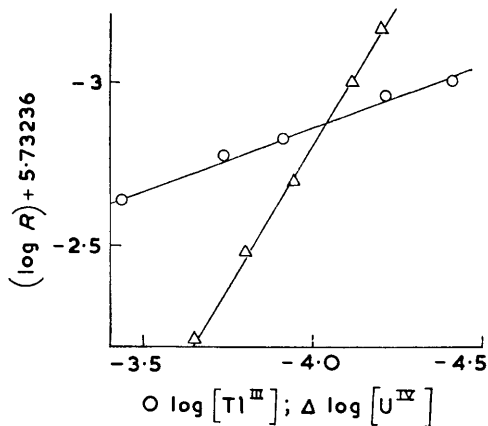


FIGURE 6. Determination of order with respect to uranium(IV) and thallium(III)

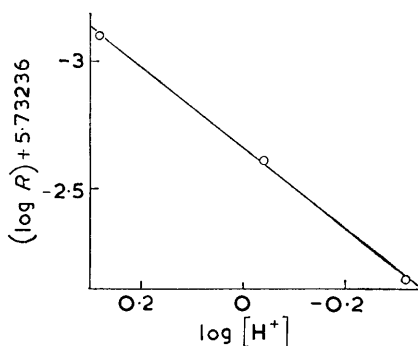


FIGURE 7. Determination of order with respect to  $H^+$

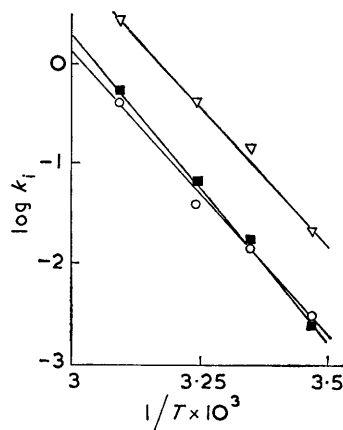
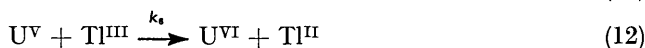
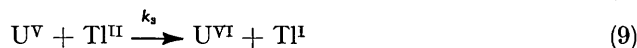
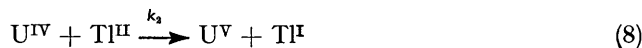
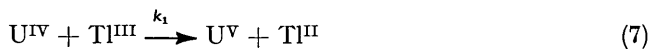


FIGURE 8. Determination of activation energies

○  $k_1'$ . ■  $k_2'$ . ▽  $k_3'$ .

*An Alternative Mechanism.*—Another possible mechanism would be a chain reaction involving the following steps (hydrogen-ion dependence has been ignored):



This assumes that all the back-reactions are not important which may not be the case, at least with eqn. (10).

Since the reaction has been studied by observing the decrease in  $U^{IV}$  with time, the following rate equation would be obeyed:

$$-d[U^{IV}]/dt = k_1[U^{IV}][Tl^{III}] + k_2[U^{IV}][Tl^{II}] - k_4[U^V]^2 \quad (13)$$

Since  $[Tl^{II}] \propto [Tl^{III}]$  and  $[U^V] \propto [U^{IV}]$ , eqn. (13) would have a form similar to eqn. (6) if  $[Tl^{II}]$  and  $[U^V]$  could be specified.

A chain mechanism would explain why this reaction is so sensitive to impurities such as silver, iron, and other cations. Jones and Amis<sup>2</sup> also proposed a chain mechanism to explain salt effects. No method is at present available to distinguish between the two mechanisms.

*Specific Velocity Constants and Activation Energy.*—Taking in account the specific velocity constants and expressions involving specific velocity constants determined in each of the regions, the average values of the specific velocity constants were found (Table 2)

TABLE 2  
Hydrolysis constants and specific velocity constants at different temperatures for  $U^{4+}$  and  $Tl^{3+}$ , and activation energy for each

	$k_1'$ (moles/l. sec.)	$k_2'$ (sec. <sup>-1</sup> )	$k_3'$ (moles/l. sec.)	$K_1$	$K_2$
15°	0.00307	0.00237	0.0201	0.011	0.038
25	0.0143	0.0151	0.134	0.021	0.073
35	0.0382	0.0624	0.408	0.038	0.133
50	0.411	0.500	2.80	0.088	0.308
$\Delta H^*$ (kcal.)	25.9	28.0	25.0	—	—

for 25°. The rates were calculated by using the determined specific velocity constants in eqns. (4) and (6), and the calculated rates are within 10% of those observed in most cases.

To determine activation energy of each of three specific velocity constants, runs were made at 15°, 35°, and 50°, as well as at 25°. The orders remained constant with variation of temperature. In order to use eqns. (4) and (6) to determine specific velocity constants at each temperature, values of  $K_1$  and  $K_2$  had to be calculated. An enthalpy of hydrolysis<sup>11,12</sup> of 11 kcal./mole was used for both  $U^{4+}$  and  $Tl^{3+}$ . The calculated hydrolysis constants are listed in Table 2. The activation energies in Table 2 were determined graphically from Figure 8.

*Conclusions.*—In studying the kinetics of the oxidation of  $U^{IV}$  by  $Tl^{III}$ , the concentrations have been varied over a 2000-fold range and the orders have been found to change with concentration. This study extends and in general supports the work of Harkness and Halpern.<sup>1</sup> The variation in orders can be explained by the polymerisation of  $U^{IV}$ .

As  $[U^{IV}]$  and  $[Tl^{III}]$  are lowered below  $10^{-3}M$ , the order for  $U^{IV}$  increases from 0.88 to 1.6, and that for  $Tl^{III}$  decreases from 0.90 to 0.38. The hydrogen-ion order remains constant at 1.4.

A chain mechanism involving  $Tl^{II}$  and  $U^V$  can also be used to explain the data qualitatively. Since  $[Tl^{II}]$  and  $[U^V]$  cannot be calculated, no quantitative treatment is possible.

This work was performed under the auspices of the U.S. Atomic Energy Commission. The author appreciates the interest and critical discussions of Dr. E. S. Amis, Dr. N. K. Shastri, Dr. E. A. Moelwyn-Hughes, and Dr. T. W. Newton.

SANDIA LABORATORY, ALBUQUERQUE, NEW MEXICO.

[Received, May 5th, 1964.]

<sup>11</sup> R. H. Betts, *Canad. J. Chem.*, 1955, **33**, 1775.

<sup>12</sup> K. A. Kraus and F. Nelson, *J. Amer. Chem. Soc.*, 1955, **77**, 3721.