

steps can be and still be resolved. Just as shown in the previous work (4), the minimum peak separation required is about 150 to 200 mV if concentration ratios up to 100:1 for $2e^-$ reduction steps are to be resolved quantitatively.

The data for the $[Tl(I)]-[Pb(II)]$ system (Table III) show that no significant difference exists between the interrupted sweep and non-interrupted sweep experimental values for small concentration ratios. However, the data obtained without interrupt are several per cent high because of the overlap distortion described earlier. For the 100:1 system, no peak was detected for the non-interrupted sweep case while good analytical data were obtained using the interrupted sweep. The advantage of using the interrupted sweep can be seen in Figure 5 for the 100:1 mixture. Note that considerable faradaic interference exists even at an E_p'' separation of 280 mV for a $[1e^-]-[2e^-]$ reduction system, without interrupted sweep.

When the data just presented are compared with those taken in the previous work (4), several observations can be made. First, no data are shown for a 1000:1 mixture in this work. This is because the hardware device will not detect a peak at a 1000:1 concentration difference with either of the two systems used. Second, the data for the $[Pb(II)]-[Cd(II)]$ system were taken in 0.1M KCl rather than in 2M $NH_4OAc-HOAc$ electrolyte because the hardware device would not detect reduction steps as close as 150 mV. This is a result of the way reduction peaks are detected with the 1st-derivative in the hardware device. Also, it must be pointed out that no provision was made for potential delay with the hardware device in contrast to the software-oriented approach.

The limitations mentioned above reflect the objective of

hardware development. The device was built to handle most situations with a minimum of operator manipulations. It does this very well, but some sacrifice in performance results from this approach. However, the strong advantage of this approach is that it provides a simple, reliable, easy to use automatic instrument that will perform the desired analysis for almost all cases at a cost of less than \$2000. It is much simpler to operate than the computer-oriented approach because only the initial cell potential, amplifier gain, and sweep mode (with or without sweep interrupt) need to be specified by the operator before an experiment. In addition, it offers one other distinct advantage over the software approach. The sweep rate of the software system was limited by the time necessary to perform the real-time calculations which must be done serially. This amounted to about 800 μ sec between data points, which limited the data rate to about 1 KHz. If data are taken at each millivolt during the sweep, this limited the sweep rate to about 1 V/sec. In the hardware device, this limitation does not exist as the hardware makes decisions and performs logical operations in parallel. This allows much faster possible operation. With proper modifications to the potentiostat, current follower, differentiators, and filters, the interrupted-sweep experiment could be run at sweep rates of 100 V/second. With appropriate scaling of τ , this would allow much shorter experimental times and might be useful for the analysis of unstable systems.

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Kinetics and Analytical Applications of the Ruthenium Catalyzed Reaction between Cerium(IV) and Arsenic(III) in Sulfuric Acid Medium

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The oxidation-reduction reaction between Ce(IV) and As(III) as catalyzed by ruthenium has been studied in 2M sulfuric acid. The reaction is first order in Ru(VIII) over a wide concentration range. The Ce(IV) dependency is complex with regions of first and second order being observed. An As(III) dependency of a maximum of half order has been observed. Behavior under different types of order of addition of reagents is discussed. A rate equation which satisfies a portion of the experimental observations is presented. The information presented is utilized for the combined analysis of Ru(VIII) and Os(VIII) without prior separation. Results are presented for analysis of mixtures down to $2 \times 10^{-10}M$. Most relative errors and standard deviations are in the range of 3%.

APPLICATION OF KINETIC methods of analysis to the determination of trace constituents has become a promising area of investigation. These determinations are often based on the catalytic effect of the trace constituents on an oxidation-reduction reaction. Yatsimirskii has recently discussed the utility of these reactions for determinations at part per

billion levels (1). In addition, Margerum and coworkers have reported the application of a ligand exchange reaction for the determination of metals at $10^{-7}M$ levels (2, 3).

A major problem encountered in the application of these reactions arises from the fact that in many cases more than one element acts as a catalyst. Therefore, the selectivity of these reactions may be poor. The solution to this problem has usually involved a prior separation of the catalytic species or a masking of the interfering substances (2, 4). A recent report described the use of the Ce(IV)-As(III) reaction to determine mixtures of osmium and iodide using silver(I) or mercury(II) to mask the iodide (5). Another approach which has been

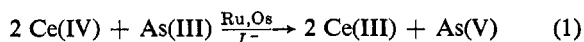
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used recently is the exploitation of kinetic differences for each catalytic species to carry out the determination without a prior separation. Yatsimirskii and coworkers have reported the determination of zirconium and hafnium using a change in pH to bring about kinetic differences (6).

Initial interest in the application of catalytic reactions for the simultaneous determination of mixtures in this laboratory resulted from work reported by Sandell *et al.* on the Ce(IV) and As(III) reaction (4, 7, 8).



These authors reported on the application of this reaction to the determination of osmium and ruthenium mixtures, but only after a separation had been performed. Kinetic information reported by these authors indicated that a determination without a prior separation might be possible based on differences in kinetic behavior (4, 7, 8). The osmium-catalyzed reaction was reported to be dependent only on the As(III) and osmium concentrations (7). The ruthenium-catalyzed reaction was reported to be dependent only on the Ce(IV) and ruthenium concentrations (4, 8). It was postulated therefore that changes in either As(III) or Ce(IV) concentrations should allow simultaneous determination without a prior separation (9, 10). When work was begun on the system, it was apparent that the kinetics were more complex than previously indicated and, therefore, further kinetic studies were necessitated for both catalytic systems.

The osmium(VIII)-catalyzed reaction between Ce(IV) and As(III) was found to be a function of both reactant concentrations (10). It was noted that the ratio of Ce(IV) to As(III) determines the type of dependence observed. At high Ce(IV) to As(III) ratios, the reaction is first order in As(III) and zero order in Ce(IV). At low ratios of Ce(IV) to As(III), the reaction is zero order in As(III) and first order in Ce(IV). The region around unity ratios is characterized by complex Ce(IV) behavior. The reaction was found to be independent of the products and order of mixing of reagents and catalyst. The reaction was first order in osmium over the entire region examined. A reaction mechanism and rate expression which agree with the experimental observations over a wide range of reaction conditions were proposed and are discussed below in relation to results observed for the ruthenium-catalyzed reaction.

The kinetic behavior of the ruthenium-catalyzed reaction has been examined in some detail earlier (8). It was reported that the reaction exhibited zero-order dependence on As(III) concentration, first-order dependence on ruthenium concentration, and complex-order dependence on Ce(IV) concentration. In addition it was reported that the reaction rate is dependent upon the manner in which catalyst is mixed with reactants. For example, if Ru(IV) or Ru(VIII) are mixed with Ce(IV) prior to the addition of As(III), or if Ru(VIII) is added to a well stirred solution of As(III), then a maximum limiting rate for that set of concentrations of catalyst and reactants is observed. However, if Ru(IV) is mixed with As(III) initially, or if Ru(VIII) is mixed with an unstirred solution of As(III), then the resulting rate after the

addition of Ce(IV) is lower than the limiting rate. The limiting rate data were summarized into a rate expression given in Equation 2 in which the rate has units of moles/liter · minute. In addition to the zero As(III) dependence and first-order Ru dependence

$$\text{Rate} = \frac{4 \times 10^{10} [\text{Ce(IV)}]^{2.5}}{1 + 2.1 \times 10^3 [\text{Ce(IV)}]^{1.5}} [\text{Ru}] \quad (2)$$

this equation predicts high order Ce(IV) dependence at low concentrations of Ce(IV) ($[\text{Ce(IV)}] < 5 \times 10^{-3} M$) and intermediate to first-order Ce(IV) dependence at higher Ce(IV) concentrations ($[\text{Ce(IV)}] \geq 5 \times 10^{-3} M$). Effects of other variables such as acid concentration, temperature, and ionic strength were discussed.

This report describes the results of a more extensive study of this reaction than has been carried out before. Experimental results are in good agreement with those of Reference 8 for the same reactant concentration ranges. However, results obtained outside the concentration ranges examined by them demonstrate that the rate equation given by them is valid only for a narrow range of experimental conditions. Results of this study are summarized in a rate expression which is applicable over a wide range of experimental conditions.

The kinetic data obtained in this work are used with those reported earlier for the osmium-catalyzed reaction (10) to develop an analytical method for mixtures of ultratrace concentrations of the ruthenium and osmium without prior separation of the two. For example, a mixture containing $3 \times 10^{-10} M$ osmium and $1 \times 10^{-7} M$ ruthenium is analyzed with errors of -2.7% for osmium and -0.9% for ruthenium. These and other data are reported.

EXPERIMENTAL

Instrumentation. A stabilized Spectronic 20 colorimeter modified as described earlier (10) and an optical feedback stabilized spectrophotometer (11) were used for the kinetic measurements. Performance characteristics of both photometers have been discussed earlier (10, 11). The reaction cells are thermostated at $25.00 \pm 0.02^\circ \text{C}$ by circulating water controlled at this temperature through thermostating jackets surrounding the cells. The contents of the cells are mixed by a glass stirring rod rotated at 3200 rpm above the light path.

Solutions. All solutions are prepared in 2M sulfuric acid prepared from distilled, deionized (Amberlite MB-3 column) water and reagent grade sulfuric acid. It was confirmed that the use of deionized water yields results identical to those obtained when using triply distilled water.

Ce(IV) solution (0.1M). Ceric ammonium nitrate (G. F. Smith & Co.) is dried at 85°C for 2 hours. Exactly 54.826 grams of the dried salt is dissolved in a small amount of water, and an amount of concentrated sulfuric acid to make the final concentration 2M is added and the solution is diluted to 1 liter.

As(III) solution (0.025M). Arsenic trioxide of 99.999% purity (Electronic Space Products) is dried for 1 hour at 100°C . Exactly 2.4725 grams of the dried As_2O_3 is dissolved in 100 ml of water containing NH_4OH . The solution is neutralized, an amount of concentrated sulfuric acid to make the final concentration 2M is added, and the solution is diluted to 1 liter.

Ruthenium tetroxide. Ruthenium tetroxide was obtained from K and K Laboratories and dissolved in 2M H_2SO_4 . The solution is standardized by measuring the absorbance

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of the solution at 385 nm and 310 nm and the concentration computed using the extinction coefficients of Connick and Hurley (12). Results at these two wavelengths agree to within $\pm 1\%$.

Osmium tetroxide. Reagent grade osmium tetroxide (United Mineral and Chemical Corp.) is weighed and dissolved in $2M$ H_2SO_4 .

Lower oxidation states of ruthenium. The appropriate ruthenium salts were dissolved in $2M$ H_2SO_4 and standardized by precipitation of the hydrated ruthenium oxide at pH 6, followed by reduction to metal by hydrogen at $600^\circ C$ and weighing of the metal (13).

Carbon tetrachloride. Spectral grade CCl_4 was cleaned according to procedures of Surasiti and Sandell (4). It is stored in the dark in a container wrapped in aluminum foil to retard decomposition.

Working solutions of the desired final concentrations were prepared by dilutions of these stock solutions with $2M$ H_2SO_4 .

Kinetic Measurements. All solutions were equilibrated to $25.00^\circ C$ for one-half hour. Solutions were transferred to the cell using glass syringes equipped with Teflon (Du Pont) needles. All syringes were equilibrated to $25^\circ C$ before solutions were transferred with them. The absorptivity of the $Ce(IV)$ - $As(III)$ mixtures were determined in the absence of catalysts. Rate measurements were made by following the disappearance of $Ce(IV)$. The measurements were made by following transmittance or absorbance as a function of time on a potentiometric recorder. Initial rates were taken from these recorded curves.

RESULTS

The results discussed below are for reactions in $2M$ H_2SO_4 . Also the reaction rates quoted are initial rates. All results and discussion pertain to the use of ruthenium tetroxide as catalyst unless stated otherwise.

The following comments apply to all figures. All points on the figures refer to experimental data. The solid symbols apply to situations in which the catalyst is mixed with $Ce(IV)$ prior to the addition of $As(III)$ and the open symbols apply to situations in which the catalyst is mixed with $As(III)$ prior to the addition of $Ce(IV)$. The solid lines in these figures represent computed rates based upon the rate equation presented below. The broken lines represent curves drawn through experimental points obtained in this work.

Order of Reagent Addition. Under certain conditions to be discussed below, the reaction rate is dependent upon the order in which the reactants are mixed with the catalyst. As it will be necessary to refer to data obtained by two modes of mixing throughout this report, an abbreviated notation is utilized in the text. Situations in which $Ce(IV)$ is mixed with catalyst prior to adding $As(III)$ are referred to as "Ce first addition." Situations in which $As(III)$ is mixed with the catalyst prior to the addition of $Ce(IV)$ are referred to as "As first addition."

The data in Figure 1 illustrate the dependence upon order of mixing. For $Ce(IV)$ concentrations below about $5 \times 10^{-3} M$, the reaction rate for Ce first addition is always faster than the reaction rate for As first addition. For the time scale of these observations (a few seconds to an hour), the reaction rate is not dependent upon the time the catalyst is in contact with the first reagent prior to the addition of the second. For $Ce(IV)$ concentrations above $5 \times 10^{-3} M$, the reaction rate is relatively independent of the order of mixing catalyst and reactants.

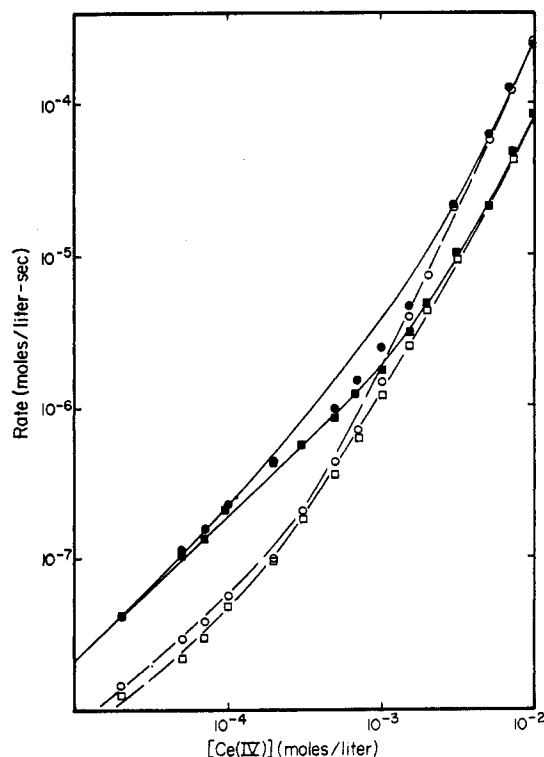


Figure 1. Rate dependency on $Ce(IV)$

- $[Ru(VIII)] = 1.31 \times 10^{-7} M$
 \bullet, \circ $[As(III)] = 1.0 \times 10^{-2} M$
 \blacksquare, \square $[As(III)] = 1.0 \times 10^{-3} M$
 \bullet, \blacksquare $As(III)$ added to $Ce(IV)$ - $Ru(VIII)$ mixture
 \circ, \square $Ce(IV)$ added to $As(III)$ - $Ru(VIII)$ mixture

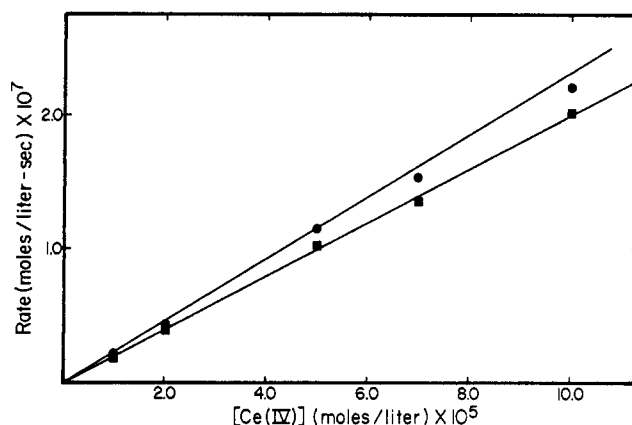


Figure 2. First-order dependency on $Ce(IV)$

- \bullet $[As(III)] = 1.0 \times 10^{-2} M$, $[Ru(VIII)] = 1.31 \times 10^{-7} M$
 \blacksquare $[As(III)] = 1.0 \times 10^{-3} M$, $[Ru(VIII)] = 1.31 \times 10^{-7} M$
 \bullet, \blacksquare $As(III)$ added to $Ce(IV)$ - $Ru(VIII)$ mixture

The data in Figure 1 represent initial rates. If the reactions for $[Ce(IV)] < 5 \times 10^{-3} M$ and Ce first addition are monitored for extended periods of time, it is observed that the rate eventually becomes equal to that for the same Ce concentration and As first addition.

In addition the $As(III)$ dependence and activation energy are functions of the order of mixing of catalyst and reactants. These points are discussed in more detail below.

Rate Dependence on Reactants, Products, and Catalysts. $Ce(IV)$. The rate dependence on $Ce(IV)$ is represented in Figure 1 for $As(III)$ concentrations of $1.0 \times 10^{-2} M$ and $1.0 \times 10^{-3} M$. The log-log plots present an overview of

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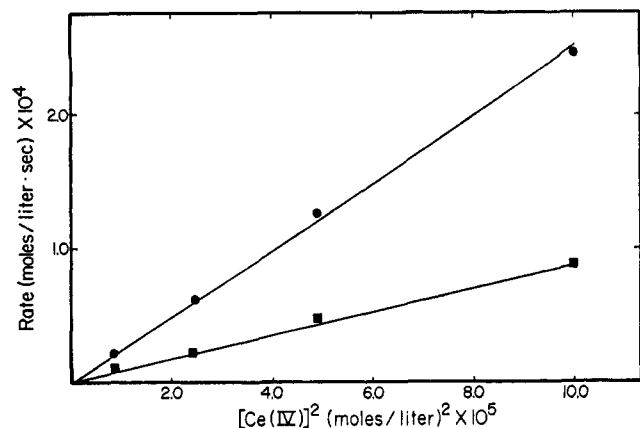


Figure 3. Second-order dependency on Ce(IV)

- [Ce(IV)] = 0 to $1 \times 10^{-3}M$
- [As(III)] = $1.0 \times 10^{-2}M$, [Ru(VIII)] = $1.31 \times 10^{-7}M$
- [As(III)] = $1.0 \times 10^{-3}M$, [Ru(VIII)] = $1.31 \times 10^{-7}M$
- As(III) added to Ce(IV)-Ru(VIII) mixture

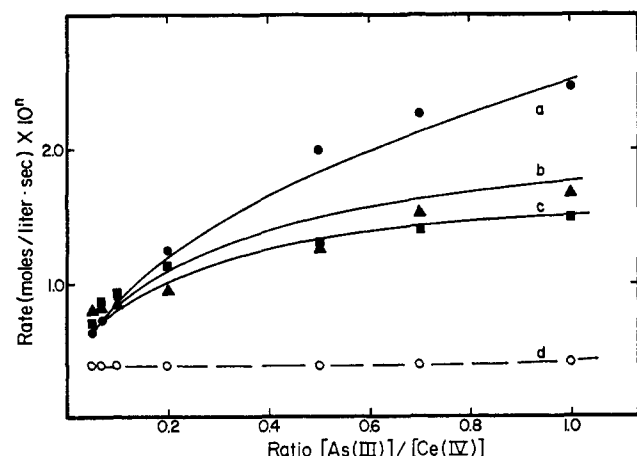


Figure 4. Rate dependency on As(III) at low ratios of As(III) to Ce(IV), [Ru(VIII)] $\times 10^{-7}M$

- a. ● [Ce(IV)] = $1.0 \times 10^{-2}M$, 0.388 normalized to 1.31
- b. ■ [Ce(IV)] = $1.0 \times 10^{-3}M$, 0.960 normalized to 1.31
- c. ▲ [Ce(IV)] = $1.0 \times 10^{-4}M$, 1.31
- d. ○ [Ce(IV)] = $1.0 \times 10^{-4}M$, 1.31
- , ■, ▲ As(III) added to Ce(IV)-Ru(VIII) mixture
- Ce(IV) added to As(III)-Ru(VIII) mixture

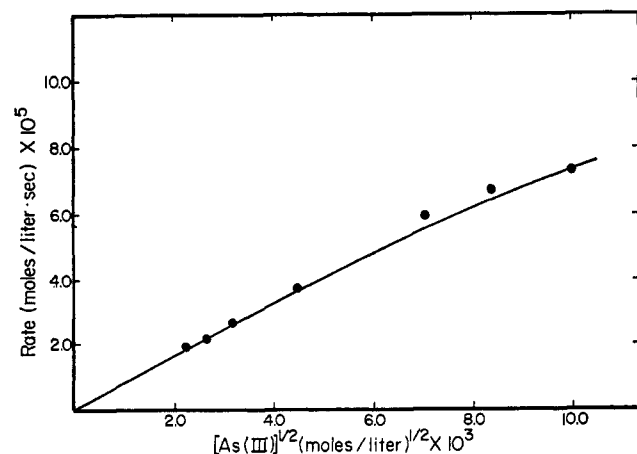


Figure 5. Rate dependency on As(III) at high [Ce(IV)]

- [Ce(IV)] = $1.0 \times 10^{-2}M$, [Ru(VIII)] = $3.88 \times 10^{-8}M$
- As(III) added to Ce(IV)-Ru(VIII) mixture

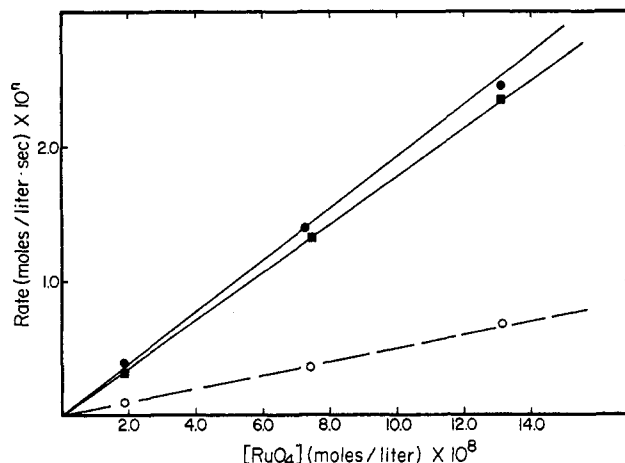


Figure 6. Rate dependency on Ru(VIII)

- [Ce(IV)] = $1.0 \times 10^{-2}M$, [As(III)] = $1.0 \times 10^{-2}M$, $n = 4$
- [Ce(IV)] = $1.0 \times 10^{-4}M$, [As(III)] = $1.0 \times 10^{-2}M$, $n = 7$
- [Ce(IV)] = $1.0 \times 10^{-4}M$, [As(III)] = $1.0 \times 10^{-2}M$, $n = 7$
- , ■ As(III) added to Ce(IV)-Ru(VIII) mixture
- Ce(IV) added to As(III)-Ru(VIII) mixture

the Ce(IV) dependence over a 10^3 fold concentration range of Ce(IV) as well as the dependence upon order of addition of reagents. It is easily shown from these plots that in passing from a low to a high Ce(IV) concentration the Ce(IV) dependence changes from first to second order.

The linear coordinate plots in Figures 2 and 3 illustrate more clearly first- and second-order regions on an expanded scale for Ce first addition and also show clearly the magnitude of the As(III) dependence at different Ce(IV) concentrations. It is apparent that a finite As(III) dependence exists over the full range of Ce(IV) concentrations examined ($1 \times 10^{-3}M$ to $1 \times 10^{-2}M$). It is observed that the Ce(IV) dependence is independent of the As(III) concentration and dependent only on the absolute Ce(IV) concentration. This observation applies also when the reactions are observed continuously from zero time to greater than 90% completion. If the initial Ce(IV) concentration is high enough, the reaction starts off second order in Ce(IV) and eventually falls off to first order in Ce(IV) as the Ce(IV) concentration is depleted.

As(III). The As(III) dependence is represented in Figure 4 for three different concentrations of Ce(IV). The upper three curves apply for Ce first addition. Curves a and b in this figure have been normalized to a RuO₄ concentration of $1.31 \times 10^{-7}M$. It is observed that the As(III) dependence is finite (but less than first order) throughout the range examined and approaches zero order as the ratio [As(III)]/[Ce(IV)] approaches unity for Ce first addition. It is apparent that the As(III) dependence is more a function of the absolute concentrations of As(III) and Ce(IV) than the ratio of the concentrations.

The lower plot in this figure shows that for low As(III) and Ce(IV) concentrations and for As first addition, the reaction rate is independent of the As(III) concentration.

Figure 5 represents the As(III) dependence at high Ce(IV) and low As(III) concentrations. It is observed that the reaction rate is proportional to the square root of the As(III) concentration under these conditions. This is the highest order (1/2) dependence observed for As(III). At these concentrations, the As(III) dependence is independent of the order of addition of reactants.

Ce(III) and As(V). The dependence of the reaction rate on product concentrations was investigated at Ce(IV) and

Table I. Rates for Ruthenium Chloride Salts

Conditions: $[\text{Ce(IV)}] = 1.24 \times 10^{-4}M$; $[\text{As(III)}] = 1.0 \times 10^{-3}M$;
 $[(\text{NH}_4)_2\text{RuCl}_6] = 2.34 \times 10^{-7}M$

Age Ru soln, hr	Rate, moles/liter \cdot sec $\times 10^7$
1	0.74
24	3.0
60	3.7

Conditions: $[\text{Ce(IV)}] = 1.0 \times 10^{-3}M$; $[\text{As(III)}] = 1.0 \times 10^{-3}M$;
 $[\text{RuCl}_3] = 1.04 \times 10^{-7}M$

Mixing order: $\text{Ce(IV)} + \text{RuCl}_3 + \text{Delay} + \text{As(III)}$

Delay, sec	Rate (moles/liter \cdot sec) $\times 10^7$
20	5.24
30	5.24
60	7.60
300	10.3
600	11.5

Table II. First-Order Dependency on $[\text{Ce(IV)}]$ and $[\text{Ru(VIII)}]$ ^a

$[\text{Ce(IV)}]$ (moles/liter) $\times 10^4$	$[\text{As(III)}]$ (moles/liter) $\times 10^3$	$[\text{Ru(VIII)}]$ (moles/liter) $\times 10^7$	Rate (moles/liter) sec $\times 10^7$	Rate/ $[\text{Ce(IV)}]$, $[\text{Ru(VIII)}]$, sec ⁻¹ $\times 10^3$
1.0	1.0	4.65	1.38	2.97
1.0	2.0	4.65	1.37	2.95
1.0	1.0	1.31	3.99	3.04
1.0	2.0	1.31	3.97	3.03
2.0	1.0	1.31	7.95	3.04
0.70	1.0	1.31	2.65	2.90

Av 2.99

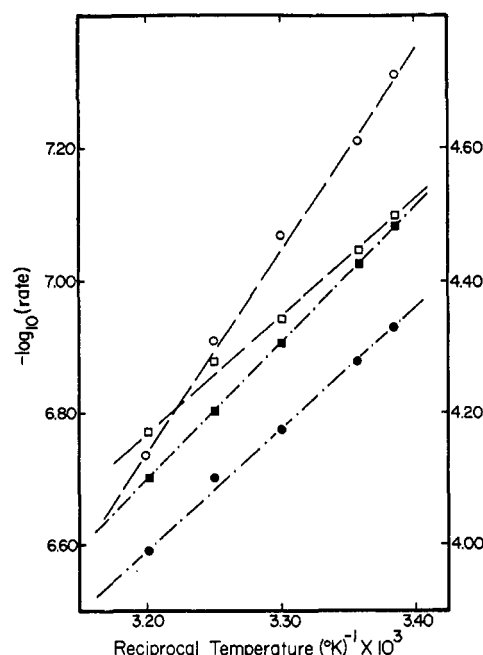
^a Ce(IV) added to $\text{As(III)}\text{--Ru(VIII)}$ mixture.

As(III) concentrations of $1 \times 10^{-3}M$ and a Ru(VIII) concentration of $1.54 \times 10^{-7}M$ and for both orders of mixing catalyst and reactants. The reaction rate is independent of product concentration for ratios of product to reactant concentration up to ten for the conditions described above. The previous report (8) indicated no product dependence at higher Ce(IV) and As(III) concentrations.

Ruthenium. Figure 6 presents data illustrating the reaction dependence on RuO_4 concentration. It is observed that the reaction rate is proportional to Ru(VIII) for all conditions examined, including the reduced rates for As first addition. Ruthenium solutions prepared from ruthenium sulfate salts give essentially the same results for Ce first addition as solutions prepared from ruthenium tetroxide. However ruthenium chloride salts exhibit significantly different behavior. Typical results for chloride solutions are given in Table I. These data indicate some very slow kinetic processes are involved with the ruthenium chlorides making the age of solutions and the time of exposure to reactants important parameters. The use of As first addition with these lower oxidation states leads to markedly lower rates.

The region of greatest simplicity occurs at low Ce(IV) and As(III) concentrations with As first addition. Table II illustrates the behavior observed in this region. The ratio of rate to the product of $[\text{Ce(IV)}]$ and $[\text{Ru(VIII)}]$ indicates that the reaction rate is first order in each of these species.

Temperature and Other Considerations. The effects of temperature changes on the reaction rate are represented in Figure 7 for low and high Ce(IV) concentrations. It is observed that at low Ce(IV) concentrations there is a marked difference in the slope of the plots for different orders of addition of catalyst and reactants. The plots at high Ce(IV)

**Figure 7. Temperature dependency of reaction rate**

$[\text{As(III)}] = 1.0 \times 10^{-3}M$, $[\text{Ru(VIII)}] = 1.81 \times 10^{-8}M$

○,● $[\text{Ce(IV)}] = 5.0 \times 10^{-4}$, left ordinate

□,■ $[\text{Ce(IV)}] = 1.0 \times 10^{-3}M$, right ordinate

■,● As(III) added to $\text{Ce(IV)}\text{--Ru(VIII)}$ mixture

□,○ Ce(IV) added to $\text{As(III)}\text{--Ru(VIII)}$ mixture

concentration exhibit slightly different slopes implying that even at the high Ce(IV) concentrations different mechanisms may be involved. The activation energies computed from the data are 9.15 kcal and 8.45 kcal for high and low Ce(IV) concentrations for Ce first addition. The values for As first addition are 8.0 kcal and 13.7 kcal, respectively, for high and low Ce(IV) concentrations. The previous work reports a value of 9.77 kcal (8).

The effects of changes in ionic strength, acid concentration, and sulfate concentrations on the reaction rate were not investigated in this work. The previous report (8) indicates that moderate variation in these variables have virtually no effect on the reaction rate. Finally the $\text{Ce(IV)}\text{--As(III)}$ reaction proceeds at a very slow rate in the absence of added catalyst. The contribution of this "uncatalyzed rate" to the reaction rates reported in the work is negligible.

Qualitative Observations. In an attempt to determine possible oxidation states of ruthenium involved in catalysis, several macrolevel redox experiments were performed on Ru(VIII) . Titration of the golden yellow RuO_4 solution with one equivalent of As(III) produced a green solution. The solution is thought to contain Ru(VI) (14). Addition of another equivalent of As(III) produces a change in color from green to a green-brown and finally to a reddish brown. The reddish brown solution is reported to be Ru(IV) (8, 15–17). The further addition of As(III) does not change the color of this solution. This is in agreement with the observations of Surasiti and Sandell (8). The addition of

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(17) F. Brito and D. Lewis, *Ark. Kemi*, **26**, 401 (1966).

RuO_4 to an excess of As(III) (corresponding to As first addition) produces the straw yellow color of Ru(III) (8, 15, 16). The absorption spectrum of this solution was found to be similar to that previously reported for Ru(III) (18) and was substantially different from that of RuO_4 . During these reductions, the pink color attributed to Ru(II) (16, 17) was not observed.

The titration of the solutions thought to be Ru(III) , Ru(IV) , and Ru(VI) with Ce(IV) led to reformation of golden yellow color of RuO_4 . During the course of oxidation of Ru(III) by Ce(IV) , a gray-green color was observed instead of the expected reddish brown of Ru(IV) . The reason for this behavior is not known at this time. The conclusion can be drawn that oxidation states of ruthenium between III and VIII can exist during the course of the Ce(IV) - As(III) reaction.

The solutions believed to contain Ru(III) and Ru(IV) were diluted to catalytic concentrations, and reaction rates were measured using these solutions as catalysts. Results were compared to rates measured using a Ru(VIII) solution of the same concentration as catalyst. The Ru(III) solution yields the same rate as the Ru(VIII) solution for high Ce(IV) concentrations and both modes of reagent addition. At low Ce(IV) concentration, the Ru(III) solution gives the same rate as the Ru(VIII) solution for As first addition while the rate for Ce first addition is about half that of a Ru(VIII) solution. The Ru(IV) solution gives the same rates as the Ru(VIII) solution for Ce first addition at high Ce(IV) concentrations. Under all other conditions the rates for the Ru(IV) solution were markedly lower than rates for the Ru(VIII) solution. These results are in agreement with the previous report (8) which indicated that Ru(IV) can show reduced activity under certain conditions.

DISCUSSION

The results reported above indicate that two types of chemical behavior or reaction pathways exist. These different pathways are determined by the absolute concentrations of Ce(IV) . For Ce(IV) concentrations below about $5 \times 10^{-4}M$, the reaction is first order in Ce(IV) , has a slight As(III) dependency for Ce first addition, and is almost independent of As(III) for As first addition. The maximum dependence on the mode of reagent addition is observed under these conditions. At Ce(IV) concentrations above about $2 \times 10^{-3}M$, the reaction enters a region characterized by a second order dependence on Ce(IV) , a half-order dependence on As(III) , and very slight dependency on the mode of reagent addition. The reaction is first order in ruthenium in both of these regions.

It is difficult to ascertain the oxidation states of ruthenium involved at the levels used for catalysis. The small As(III) dependency observed in most cases would seem to indicate that the rates of reduction of higher oxidation states of ruthenium by As(III) are faster than the rates of oxidation of ruthenium to these states by Ce(IV) forcing the ruthenium into the lower oxidation states during the course of the reaction. A further indication that this may occur is the fact that at low Ce(IV) and As(III) concentrations the rates for Ce(IV) first addition approach those of As first addition as the reaction goes to completion.

The two distinct types of chemical behavior as well as the different activation energies observed are strong indications of two or more reaction pathways. The apparent dependence

on the absolute Ce(IV) and As(III) concentrations may indicate that one reaction pathway involves a fast equilibrium step prior to the rate determining step. This equilibrium would probably not involve the products of the reaction since no effect on reaction rate was observed when As(V) or Ce(III) was added to the reaction mixture. The exact nature of any intermediate involved is difficult to ascertain because of the concentrations involved.

Using these observations, many attempts were made to devise a mechanism for which a rate expression could be generated to fit the experimental data. To date, the attempts to arrive at such a mechanism have been unsuccessful. After failure to develop a rate expression based upon a reasonable mechanism, emphasis was shifted to the development of an empirical expression which would accurately describe the experimental observations. The development of a rate expression which would satisfy both modes of reagent addition was found to be an exceedingly difficult task. It was decided that effort should be devoted to the development of a rate expression which fit the Ce first addition data since these are the maximum obtainable rates.

Numerous rate expressions were investigated in the effort to find a suitable expression. The expressions were evaluated by their "best" fit to the experimental data using a nonlinear regression analysis computer program. Expressions composed of the sum of first- and second-order Ce(IV) terms were found to be inadequate. Complex expressions limited to the use of first-order powers of As(III) would not fit the half order in As(III) dependency observed at high Ce(IV) . The expression which was found to give the best fit is given below

$$v = \frac{1.0 \times 10^6 [\text{Ce(IV)}][\text{As(III)}]^{1/2} [\text{Ru(VIII)}] (5.6 + 3.50 \times 10^4 [\text{Ce(IV)}][\text{As(III)}]^{1/2} + 1.71 \times 10^6 [\text{Ce(IV)}]^2)}{1.0 + 3.20 \times 10^2 [\text{As(III)}]^{1/2} + 7.77 \times 10^3 [\text{Ce(IV)}]} \quad (3)$$

This expression correctly predicts the first- and second-order region in Ce(IV) concentration as well as half-order dependency of As(III) concentration. The expression holds only for Ce first addition and the use of Ru(VIII) as catalyst. The solid lines in the figures are the rates predicted by this expression and in most cases fit the experimental data to within $\pm 10\%$. The region of poorest fit is for intermediate Ce(IV) concentration at very high As(III) .

It is desirable to compare these results with those reported by Surasiti and Sandell (8). A comparison of the reported rates of these authors with rates predicted in this work over a common range of conditions is shown in Figure 8. The agreement is generally good until the higher Ce(IV) concentrations are reached. In this region the data obtained in this work exhibit a second-order dependence on Ce(IV) whereas the previous report indicates the Ce(IV) dependency falls to first order. One possible explanation for this may be that the mixing techniques used in the earlier work did not permit the accurate measurement of initial rates. The reactions are rapid, and fast mixing times (as short as 2 seconds in this work) become important.

Two major areas of disagreement between this work and the previous report do exist. The authors indicate that no As(III) dependency was observed and predict through a rate expression that the reaction should be 2.5 order in Ce(IV) at low Ce(IV) concentrations. This work indicates a real As(III) dependency with a maximum order of 0.5 and a first-order dependency on Ce(IV) at low Ce(IV) concentrations. One possible explanation for these differences is the

(18) A. S. Wilson, *J. Inorg. Nucl. Chem.*, **7**, 149 (1958).

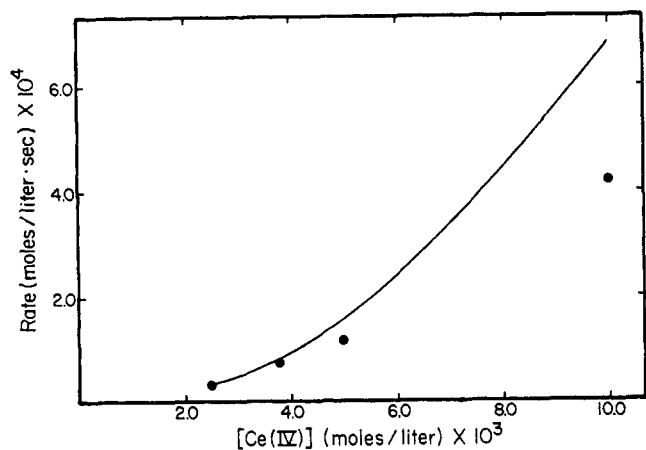


Figure 8. Comparison of predicted rates with literature values

[As(III)] = $4.0 \times 10^{-2}M$, [Ru(VIII)] = $1.98 \times 10^{-7}M$

● Rate reported by Surasiti and Sandell (8)

— Rate predicted by this work

limited range of experimental conditions examined in the previous report. The lowest [As(III)] to [Ce(IV)] ratio used in the previous report was 0.4 while the lowest Ce(IV) concentration investigated was $1.25 \times 10^{-3}M$.

The initial goal of a thorough study of the ruthenium catalyzed reaction, to obtain analytically useful information, has been accomplished and the results allow a critical comparison with the iodide and osmium catalyzed reactions (10, 19). All three reactions have regions of first-order dependence on Ce(IV) concentration with only the ruthenium catalyzed reaction having a higher order dependency (second order). The iodide and osmium catalyzed reactions have regions in which the reaction rate has a first-order dependence on As(III) concentration. The maximum dependence on As(III) concentration for the ruthenium-catalyzed reaction is half order. The reactant dependencies for the osmium-catalyzed reaction are a function [Ce(IV)] to [As(III)] ratios whereas the iodide- and ruthenium-catalyzed reactions are more dependent on the absolute concentrations of the reactants.

A dependence on the order of addition of reagents is observed for the iodide- and ruthenium-catalyzed reaction while the osmium-catalyzed reaction is independent of order of addition. For high Ce(IV) and low As(III) concentrations, the iodide-catalyzed reaction is not a linear function of iodide concentration due to oxidation to catalytically inactive iodate by Ce(IV). Under most other conditions, the reaction rate is a linear function of iodide concentration. The ruthenium- and osmium-catalyzed reactions are proportional to catalyst concentration under all reactant conditions. A comparison of the maximum limiting rate under a wide range of conditions indicates that on a molar basis, iodide is always the least effective catalyst. A comparison between ruthenium and osmium requires a specification of the reactant concentrations. At low Ce(IV) concentrations, the osmium is a more effective catalyst than ruthenium, while at high Ce(IV) concentrations, the ruthenium becomes a more effective catalyst.

In addition, the iodide-catalyzed reaction is completely inhibited by slight excesses of Ag(I) and Hg(II) while the ruthenium- and osmium-catalyzed reactions are not affected by these species.

(19) P. A. Rodriguez and H. L. Pardue, *ANAL. CHEM.*, **41**, 1369 (1969).

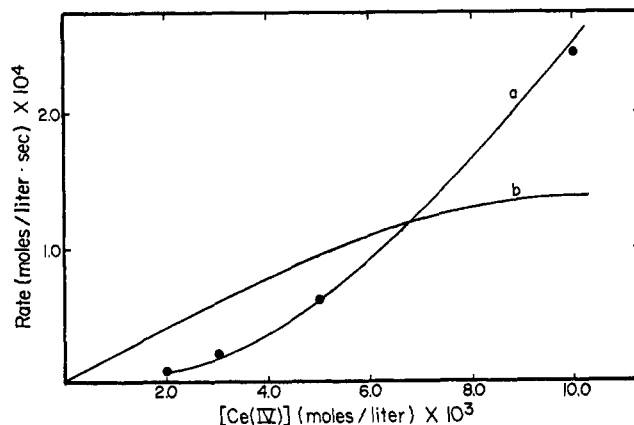


Figure 9. Rate dependency on Ce(IV) for osmium and ruthenium as catalysts

[As(III)] = $1.0 \times 10^{-2}M$, [catalyst] = $1.31 \times 10^{-7}M$

a. Ru(VIII)

b. Os(VIII)

As(III) added to Ce(IV)-catalyst mixture

The results of these kinetic studies indicate that the osmium-catalyzed reaction is the simplest of three catalyzed reactions and coupled with the high catalytic activity of osmium, supports the widespread use of osmium as a catalyst for applications of the Ce(IV)-As(III) reaction in titrimetric analysis.

ANALYTICAL APPLICATIONS

The results of this and previously reported kinetic studies (10, 19) indicate that sufficient kinetic differences exist between the ruthenium- and osmium-catalyzed reactions to carry out the determination of these elements without a prior separation. In the discussions below, the comparisons of catalytic activity are based on equimolar concentrations of the catalysts. The differences in dependence on Ce(IV) concentration for the two catalysts is shown in Figure 9. The OsO_4 data have been calculated using the rate expression previously reported (10). This curve shows that at high Ce(IV) concentrations, RuO_4 is the more effective catalyst. At $1 \times 10^{-2}M$ Ce(IV) and As(III), ruthenium is almost twice as effective a catalyst as osmium. Reduction of the Ce(IV) concentration changes the behavior of the reactions and the osmium becomes a more effective catalyst. At $1 \times 10^{-4}M$ Ce(IV) and $1 \times 10^{-2}M$ As(III), the osmium rate is twelve times that of the ruthenium. This rate ratio holds in general any time the reactions are in the regions of first-order dependence on Ce(IV) concentration. The use of As first addition further suppresses the ruthenium activity at these low Ce(IV) concentrations and increases the ratio of the catalytic activity of osmium relative to that of ruthenium.

The ratio of ruthenium-catalytic activity to that of osmium can be increased through changes in As(III) concentration. For [As(III)] to [Ce(IV)] ratios below 0.5, the osmium-catalyzed reaction becomes first order in As(III). A similar change at high Ce(IV) concentrations for the ruthenium-catalyzed reaction yields only a half-order dependence on As(III). Therefore, reduction of the As(III) concentration has a greater effect on the osmium-catalyzed reaction than the ruthenium-catalyzed reaction. As previously indicated, the ruthenium rates are twice those of osmium at $1 \times 10^{-2}M$ Ce(IV) and As(III). The reduction of As(III) to $1 \times 10^{-3}M$ changes the rates so that the ruthenium-catalyzed rate is almost ten times the osmium-catalyzed rate. Thus selectivity toward osmium is obtained at high As(III) and low Ce(IV)

Table III. Determination of Ruthenium(VIII)–Osmium(VIII) Mixtures without a Prior Separation

Os (moles/liter) $\times 10^8$		Ru (moles/liter) $\times 10^8$		Error, %	
Taken	Found	Taken	Found	Os	Ru
9.38	9.52	0.0220	0.0458	+1.5	+108
0.0290	0.0282	11.0	10.9	−2.7	−0.9
8.66	8.72	0.440	0.437	+0.7	−0.7
5.80	5.95	4.40	4.37	+2.6	−1.1
0.580	0.583	8.80	8.58	+0.5	−1.4

concentrations while selectivity toward ruthenium is obtained at high Ce(IV) and low As(III) concentrations. The obvious limitation to the latter approach is the small amount of Ce(IV) consumed and the resulting difficulty in obtaining an accurate measurement of the reaction rate.

Using this information, the analysis of mixtures of RuO_4 and OsO_4 was performed. The conditions chosen for selectivity toward ruthenium are $5 \times 10^{-3}M$ Ce(IV) and $1 \times 10^{-3}M$ As(III). Under these conditions the reaction rate is given by:

$$v_1 = 240[\text{RuO}_4] + 90.4[\text{OsO}_4] \quad (4)$$

The conditions chosen for selectivity for osmium are $5 \times 10^{-4}M$ Ce(IV) and $1 \times 10^{-3}M$ As(III). In addition, As first addition is used to further suppress the ruthenium-catalyzed rate. The resulting rate equation is:

$$v_2 = 2.69[\text{RuO}_4] + 78.0[\text{OsO}_4] \quad (5)$$

These expressions apply for initial rates. As can be seen from these expressions, the analysis is more favorable for osmium than for ruthenium.

Using these two sets of conditions and the corresponding equations, mixtures of RuO_4 and OsO_4 in the concentration range from $2 \times 10^{-10}M$ to $1 \times 10^{-7}M$ were determined. The results are given in Table III. The relative standard deviations range from 0.51 to 4.1%. The errors are quite low considering the levels of concentration involved. As would be expected the errors in the determination of ruthenium in the presence of large amounts of osmium are rather large. The results do indicate that the measurement approach can compete very favorably with activation analysis. Chung and Beamish report on the use of activation analysis for the simultaneous determination of osmium and ruthenium (20). Relative standard deviation of 2 to 7% was reported for mixtures with ratios of 4 to 0.3 osmium to ruthenium at $10^{-7}M$ levels. The samples were irradiated for three days before measurement. The analysis time in this work is about 15 minutes. Thus the kinetic analysis approach provides an accurate, simple, inexpensive, and relatively

rapid measurement method for mixtures of ruthenium and osmium at the nanomolar level.

It has been noted that neither Ag(I) nor Hg(II) affect the catalytic activity of ruthenium or osmium while both completely inhibit the iodide activity. Previous work (5) has demonstrated that this behavior can be utilized for the selective determination of iodide and osmium in mixtures of iodide, osmium and ruthenium can be resolved using the methodology suggested in that report combined with the information contained in this report. No attempt was made to confirm this experimentally in this work.

The principles outlined in this report would take on more practical significance if a reliable method for separating the catalytic species from potential redox interferences were available. Several attempts were made to determine lower oxidation states of osmium and ruthenium by oxidation to the tetroxides, extraction into an organic solvent, and re-extraction into an aqueous phase containing a suitable reductant. Experiments utilizing Ag(II) as the oxidant, carbon tetrachloride as the organic phase, and As(III) or sulfite as reductants were unsuccessful. Recoveries of added catalyst ranged between 75 and 95% in most cases and were not reproducible.

In summary, this report contains kinetic information and an empirical rate expression which permit an accurate prediction of the behavior of the reaction over a wide range of reaction conditions. Unfortunately, to this point it has not been possible to develop a mechanism which is consistent with all of the experimental observations. The analytical data reported clearly demonstrate the power of catalytic oxidation–reduction reactions for selective analyses at the ultratrace level when rate data of high reliability are combined with a detailed knowledge of reaction kinetics. The application of this information to the analysis of practical samples requires additional attention to the problems of separating the catalyst from potential interferences.

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(20) K. S. Chung and F. E. Beamish, *Anal. Lett.*, 1(2), 45 (1967).