

Analysis of Ruthenium(III) in Micro Amounts by Kinetic Method

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Ruthenium(III) catalyzed oxidation of As(III) by Ce(IV) in acid solution has been utilized to develop a kinetic method for the analysis of ruthenium(III) in the range of 0.04–0.065 $\mu\text{g cm}^{-3}$ by spectrophotometric technique. Interferences of various ions were also studied.

Key Words: Analysis, Ruthenium(III), Kinetic method.

INTRODUCTION

In the analysis of ruthenium by gravimetric method, there is no specific gravimetric reagent for ruthenium and all the gravimetric methods yield non-stoichiometric precipitates¹. There are only a few direct methods of analysis of ruthenium(III) such as chelatometric titration of ruthenium(III) with xylenol orange as indicator² are available in the literature. These methods suggest the analysis of ruthenium(III) to the 3.5 mg level. Methods of analysis of ruthenium(III) below this level are important in view of the presence of ruthenium in the earth crust with the abundance of about 10^{-4} ppm.

The kinetic method of analysis of inorganic and organic species in micro amounts is receiving considerable interest, since they are highly sensitive, selective, reproducible and less expensive. However, a small quantity of ruthenium is known to catalyze³ the reaction between cerium(IV) and arsenic(III). Such ruthenium catalysis may be the basis of a kinetic catalytic procedure for the estimation of ruthenium in the ppm range. In continuation with the kinetic method of analysis⁴, in the present study, ruthenium(III) has been utilized as a catalyst for the cerium(IV)-arsenic(III) reaction in the analysis of ruthenium(III) in micro amounts.

EXPERIMENTAL

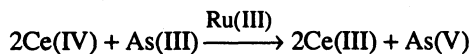
Reagent grade chemicals and double distilled water were used throughout. The cerium(IV) stock solution was made by dissolution of cerium(IV) ammonium sulphate (E. Merck) in dilute sulphuric acid and was standardized^{5b} with iron(II) ammonium sulphate (AnalaR) solution. The arsenic(III) stock solution was obtained by dissolving arsenic(III) oxide (BDH, AR) in 1 mol dm^{-3} sodium

hydroxide solution which was neutralized with acid and standardized^{5a} with potassium iodate solution. The ruthenium(III) stock solution was prepared by dissolving a known weight of ruthenium(III) chloride (S.D. Fine chem.) in 0.20 mol dm⁻³ HCl. Mercury was added to the ruthenium(III) stock solution to reduce any ruthenium(IV) formed during the preparation of ruthenium(III) stock solution and kept for a day. The ruthenium(III) concentration was assayed by EDTA titration². The stock solutions were diluted as required before use. Sodium sulfate (AnalaR) and sulphuric acid (AnalaR) were used to maintain the required ionic strength and acidity, respectively.

The kinetics was followed at 25 ± 0.1°C unless otherwise stated. Reaction was initiated by adding cerium(IV) solution, containing the required amounts of ruthenium(III), sulphuric acid and sodium sulphate, to the arsenic(III) solution. The reaction was followed under pseudo-first order conditions with the concentration of the reductant in excess over the cerium(IV) concentration, by measuring the absorbance of cerium(IV) in the mixture at 360 nm in a 1 cm cell placed in the thermostated compartment of a Hitachi 150-20 spectrophotometer. Kinetic runs involved variation of one of the variables at a time keeping the others constant. Beer's law had been verified earlier between 5.0 × 10⁻⁵ and 8.0 × 10⁻⁴ mol dm⁻³ of cerium(IV) at 360 nm under the reaction conditions ($\epsilon = 3300 \pm 25 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). All measurements were made at constant acidity and ionic strength. The pseudo-first order rate constants at constant acidity and ionic strength were found from the slopes of plots of log [Ce(IV)] vs. time. The first order plots were linear well beyond 80% completion of reaction. Rate constants were reproducible within ±5%. The standard deviations for analysis were calculated^{5c} from the known formula.

RESULTS AND DISCUSSION

Different sets of concentration of reactants at constant ruthenium(III) concentration (2.0 × 10⁻⁶ mol dm⁻³) in 0.20 mol dm⁻³ sulphuric acid at constant ionic strength, 0.70 mol dm⁻³, were kept for over 8 h at 25°C in a closed container. When [Ce(IV)] > [As(III)], the remaining cerium(IV) concentration was assayed by measuring the absorbance at 360 nm, whereas under conditions [As(III)] > [Ce(IV)], when cerium(IV) had fully reacted, the remaining arsenic(III) concentration was determined with potassium iodate^{6a}. Cerium(III) was oxidized to cerium(IV) with peroxodisulphate and determined by spectrophotometry. The results showed that cerium(III) reacted with arsenic(III) in a 2 : 1 mole ratio.



Reaction Order

At constant ruthenium(III) concentration (2.0 × 10⁻⁶ mol dm⁻³), the order with respect to cerium(III) to cerium(IV) in the 5.0 × 10⁻⁵–5.0 × 10⁻⁴ mol dm⁻³ concentration range was nearly unity (0.98). First order plots under these conditions were linear to over 80% completion of reaction for different initial cerium(III) concentrations and the absence of any variation in rate constants with different cerium(III) concentrations confirms the unit order in [cerium(III)]. The

rate of the catalyzed reaction as a function of the arsenic(III) concentration was determined at a constant cerium(IV) concentration of 2.0×10^{-4} mol dm⁻³ and constant ruthenium(III) concentration in a 0.20 mol dm⁻³ sulphuric acid solution at 25°C. The rate was found to be independent of the arsenic(III) concentration.

At constant oxidant, reductant and acid concentrations of 2.0×10^{-4} , 1.0×10^{-3} and 0.20 mol dm⁻³, respectively and at $I = 0.70$ mol dm⁻³, the ruthenium(III) concentration was varied between 5.0×10^{-7} and 8.0×10^{-6} mol dm⁻³ (Table-1). The order in [ruthenium(III)] was unity. Variation in the concentration of sulphuric acid for 0.1–1.0 mol dm⁻³ at constant reactant and at constant catalyst concentrations, produced no change in the reaction rate.

TABLE-1
RUTHENIUM(III) CATALYZED Ce(IV)-As(III) REACTION AT 25°C

[Ce(IV)] = 2.0×10^{-4} ; [As(III)] = 1.0×10^{-3} ; [H₂SO₄] = 0.20; $I = 0.70$ /mol dm⁻³

[Ru(III)] × 10 ⁶ (mol dm ⁻³)	k ₁ × 10 ³ (s ⁻¹)
0.0	1.96
0.5	3.03
1.0	4.84
1.5	6.22
2.0	7.30
2.5	8.95
3.0	10.40
3.5	12.10
4.0	13.60
4.5	14.50
5.0	15.80
6.0	18.80
6.5	20.30
7.0	21.20
7.5	23.40
8.0	24.60

Effect of initially added products: The effect of initially added products, cerium(III) and arsenic(V), was studied in the 5.0×10^{-5} – 4.0×10^{-4} mol dm⁻³ and 1.0×10^{-4} – 6.0×10^{-4} mol dm⁻³ concentration ranges, respectively, keeping the ionic strength, reactant concentrations and other conditions constant. No significant effect on the reaction rate was observed in either case.

Effect of dielectric constant and ionic strength: At constant acidity and other constant conditions, decreasing dielectric constant (increasing acetic acid content in the reaction mixture) and increasing ionic strength did not have any significant effect on the reaction rate.

Effect of temperature: The reaction was studied at different temperatures by keeping all other conditions constant and the plot of $\log k_1$ vs. $1/T$ was found to be linear. The activation parameters are listed in Table-2. These experimental results can lead to the following mechanism:

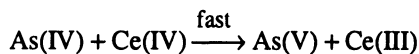
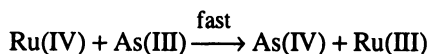
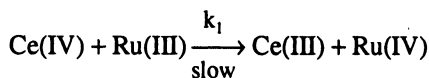


TABLE-2
EFFECT OF TEMPERATURE ON RUTHENIUM(III) CATALYSED
Ce(III)-As(III) REACTION

$[\text{Ce(IV)}] = 2.0 \times 10^{-4}$; $[\text{As(III)}] = 1.0 \times 10^{-3}$; $[\text{Ru(III)}] = 2.0 \times 10^{-6}$; $[\text{H}_2\text{SO}_4] = 0.20$;
 $I = 0.70/\text{mol dm}^{-3}$

Temperature (K)	$k_1 \times 10^3$ (s^{-1})	Activation parameters
298	7.30	$E_a = 46 \pm 2 \text{ kJ mol}^{-1}$
303	9.54	$\Delta H^\ddagger = 43 \pm 2 \text{ kJ mol}^{-1}$
308	12.90	$\log A = 6.0 \pm 0.2$
313	17.30	$\Delta S^\ddagger = 144 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$ $\Delta G^\ddagger = 86 \pm 4 \text{ kJ mol}^{-1}$

The results suggest that cerium(IV) reacts with ruthenium(III) in a rate determining step to give the cerium(III) product and the intermediate ruthenium(IV). The intermediate ruthenium(IV) reacts in a fast step to give another intermediate, arsenic(IV) and ruthenium(III) being regenerated. The intermediate arsenic(IV) formed reacts in a further fast step with another molecule of cerium(IV) to give the products, arsenic(V) and cerium(III).

Scheme-1 leads to the following rate law:

$$\frac{-d[\text{Ce(IV)}]}{dt} = k_1[\text{Ce(IV)}][\text{Ru(III)}]$$

The modest activation energy and sizeable entropy of activation supports **Scheme-1**.

A calibration curve k_1 vs. $[\text{Ru(III)}]$ under a known set of conditions of concentrations of oxidant, substrate, acid and temperature (as in Table-1) is made. The reaction is repeated under similar conditions in presence of the solution of ruthenium(III) of unknown concentration and the resulting value of k_1 , used to obtain the concentration of ruthenium(III) from the calibration curve. Alternatively, under the conditions of the reaction after definite intervals of time (say 10, 20, 30, 60 s) one of the concentrations, in this case that of cerium(IV), measured both in the presence and absence of known amount of the catalyst. Such data, again, lead to a calibration curve as shown in Fig. 1 and the unknown concentration of ruthenium(III) can be obtained from such a graph.

For routine measurements, the latter procedure is recommended. However, as shown in Fig. 1, for concentrations higher than around $6.5 \times 10^{-6} \text{ mol dm}^{-3}$, under

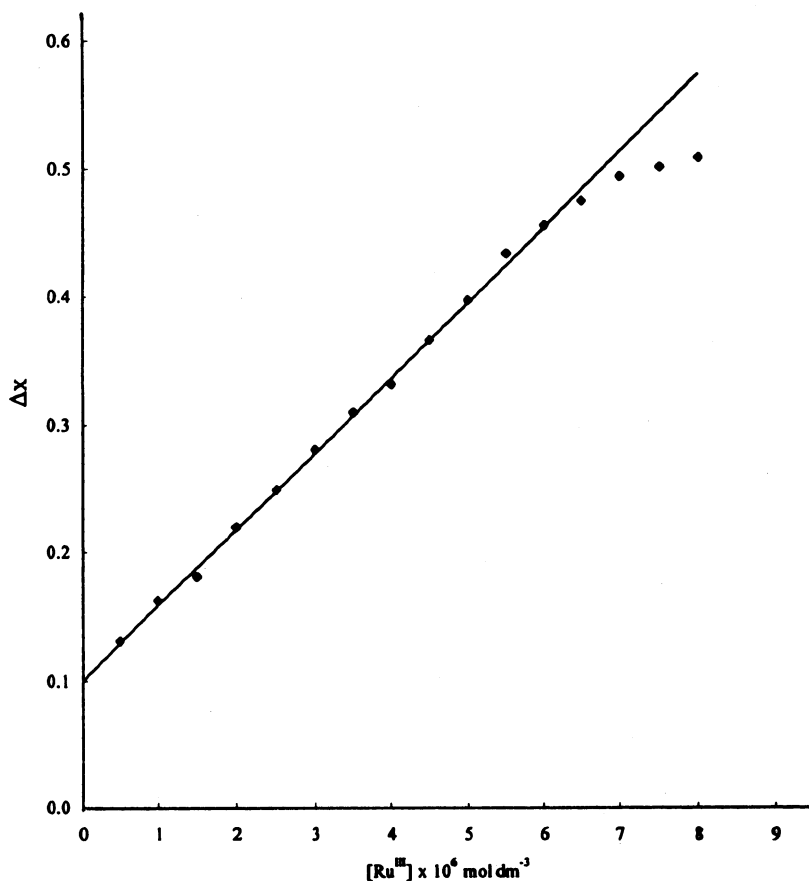


Fig. 1. Calibration curve for analysis of Ru(III) by kinetic method

the conditions of Table-1, deviations from linearity occur and the method is not satisfactory. The deviations are caused presumably because of the lack of excess concentrations of substrate whereby the conditions of total ruthenium(III) taking part in the catalytic cycle do not obtain. Furthermore, apparently a higher oxidant concentration than has been used for calibration purposes needs to be used as this concentration almost matches the ruthenium(III) concentration. In the determination of ruthenium(III), small variations in substrate and acid concentration do not affect the method. However, oxidant concentration should be the same. It is noteworthy that this method enables determination of sizable quantities of ruthenium(III) ranging from 0.04–0.65 $\mu\text{g cm}^{-3}$.

Method recommended for analysis: A set comprising of known concentrations of Ce(IV), As(III) H_2SO_4 and Ru(III) (2.0×10^{-4} , 1.0×10^{-3} , 0.20 and 2.0×10^{-6} mol dm⁻³, respectively as in Table-1) is thermostated and mixed. The absorbance of cerium(IV) at 30 s is taken at 360 nm. With the same concentration of reactants and acid, the concentration of ruthenium(III) is varied, the reading at 30 s being taken in each case. Taking the difference in absorbance between the catalyzed and uncatalyzed reactions as Δx , a calibration curve of Δx vs. [Ru(III)] is plotted (Fig. 1). This plot is then used for determining unknown concentrations of ruthenium(III). The results of such an analysis are shown in Table-3.

TABLE-3
 RESULT OF KINETIC METHOD OF ANALYSIS OF RUTHENIUM:
 RUTHENIUM(III) CATALYZED Ce(IV)-As(III) REACTION AT 25°C

Ru(III) ($\mu\text{g cm}^{-3}$)		S.D.
Taken	Found*	
0.046	0.043	± 0.01
0.101	0.107	± 0.02
0.172	0.179	± 0.04
0.233	0.241	± 0.04
0.293	0.289	± 0.03
0.354	0.348	± 0.03
0.430	0.438	± 0.02
0.470	0.483	± 0.01
0.505	0.496	± 0.03
0.556	0.546	± 0.02
0.586	0.581	± 0.02
0.632	0.629	± 0.01

*Average of five sets.

The interference of some ions was also tested in the method of analysis of ruthenium(III). Apart from the reductants which reduce Ce(IV) and the oxidants which oxidize As(III), it was found that Co(II), Ni(II), Zn(II), Fe(III), sulphate do not interfere, while cyanide, thiocyanate, acetate, iodide, bromide, Cu(II), Mn(II), Hg(I), Ag(I), Cr(III), V(V), Mo(II), Hg(II), Tl(I), Os(VIII) and Pd(II) interfere. In all the cases, interferences were examined up to a concentration of 5.0×10^{-4} mol dm⁻³ of the diverse ions.

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