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RUTHENIUM(III) DETERMINATION BY KINETIC-CATALYTIC METHOD USING THE NILE BLUE-ACIDIC CHLORITE REACTION

L.Q. Qwabe, B. Pare and S.B. Jonnalagadda*

School of Chemistry, University of KwaZulu-Natal, Westville Campus, Chiltern Hills, Durban, South Africa.

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ABSTRACT. The mechanism of the Ru(III) catalysed oxidation of Nile blue (3-amino-7-diethylamino-8,9-benzo-2-phenoxazine chloride, NB^+) by acidic chlorite were investigated by kinetic approach and using the stopped flow technique at 633 nm. The catalysed reaction had a first-order dependence on the concentrations of NB^+, H^+, ClO_2^- and catalyst. The pertinent mechanism, consistent with the experimental results is proposed. Based on the high sensitivity and selectivity of the reaction to the presence of Ru(III), using its catalytic efficiency on the oxidation of Nile blue (NB^+) by acidic chlorite, a fixed-time kinetic method is reported for Ru(III) determination. Interference studies confirm that the proposed method allows determination of Ru(III) in presence of wide range of cations, including Pd(II), Rh(II), Fe(III) and Os(VIII). The lowest detection limit for Ru(III) ions is 0.2 nmoles L^{-1} (2.0 ng mL^{-1}).

KEY WORDS: Ru(III) determination, Photometric, Kinetic method, Nile blue, Chlorite

INTRODUCTION

The six platinum group metals (PGMs) occur together in nature alongside nickel and copper. South Africa is the world's leading platinum producer and the second largest palladium producer after Russia [1]. Platinum and palladium have the greatest economic importance and are found in the largest quantities. The other four –iridium, rhodium, ruthenium and osmium are produced as co-products of platinum and palladium and are rarely mined for their own sake. Ruthenium's catalytic qualities make it a key element in catalysts for fuel cells. Due to its hardness and corrosion resistance, ruthenium is used to coat electrodes in the chloralkali process which produces chlorine and caustic soda for a wide range of industrial and domestic applications. In the future, the use of ruthenium in alloys for aircraft turbine blades will help reduce the CO_2 impact of air travel on the environment. If current prototypes are successful, their high melting points and high temperature stability will allow for higher temperatures and, therefore, a more efficient burning of aircraft fuel [1]. The existence of at least eight valence states, coupled with the tendency to complex with many ions, often results in the presence of several different complexes in a given solution. Ru(III) is easily oxidized to tetravalent state by air [2]. While ruthenium and osmium are in the same group, they differ in the fact that higher oxidation states of ruthenium are less stable, it has more similarities with iron [3].

There are number of instrument based methods using neutron activation analysis [4] and by AAS and ICP for the determination of Ru in ore samples [5]. In atomic absorption spectrometry, the presence of Rh, Ir, Pa or Pt interferes in Ru determination by enhancing the ruthenium signal. Procedures using the UV-VIS spectrophotometer, a common facility in all the analytical laboratories will be handy and affordable. The technique requires a quantitative conversion of the analytes into stable complexes that can act as the basis for photometric measurements. The high chemical similarity of noble metals resulting in the formation of complexes of similar compositions and properties, limits the direct application of UV-VIS spectrometry in the

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*Corresponding author. E-mail: jonnalagaddas@ukzn.ac.za analysis of multi-component samples. The developed methods are combined with separation procedures [5]. Separation and determination of ruthenium from Pt, Ir, Rh, Os, etc as RuO_4 in gravimetric method is known [6]. Ru(III) forms a red chelate with actylacetone in chloroform readily on heating at pH 4-6 and the red complex formed is measured at 505 nm. Preliminary extraction at pH 2 with the same solvent eliminates interference due to ion, vanadium, aluminum and titanium [7]. To overcome the interference problems, the difference in the kinetic rates of these elements with selected reagents can be exploited to develop kinetic rate based methods. Number of such methods have been reported in the literature including a spectrfluorometric method using 2-(α-pirydyl)thioquinaldinamide and photometric method involving Ru(III) catalysed reaction between indigocarmine and acidic iodate [8, 9].

The chemistry of chlorite ion has been the subject of extensive studies due to its exotic non-linear kinetic patterns [10] and because of its applications as disinfectant and in water treatment [11]. Nile blue (7-amino-3-diethylamino-8,9-benzo-2-phenoxazine sulphate, NB^+) is a phenoxazine class of non-toxic and water soluble dye (λ_{max} at 633 nm, absorption coefficient, $\varepsilon = (5.22 \pm 0.05) \times 10^4\ M^{-1}\ cm^{-1}$) used in staining. The reaction between Nile blue and chlorite in presence of acid is known to follow first-order kinetics with respect to Nile blue, chlorite and acid [12]. Preliminary experiments showed that among wide range of cations, with exception of Fe(III) and Ru(III), very few had any significant influence on the rate of the reaction between Nile blue and acidic chlorite. Based on the high sensitivity and selectivity of Ru(III) on the reaction between Nile blue (NB^+) by acidic chlorite, the scope of the title reaction as an indicator reaction for the kinetic-catalytic determination of Ru(III) is explored. In this communication, we report a kinetic-catalytic method for determination Ru(III), using it's selective catalytic efficiency to catalyse the oxidation of Nile blue by acidic chlorite.

EXPERIMENTAL

Reagents

Sodium chlorite (BDH) was recrystallized before the use and Nile blue sulfate (λ_{max} = 633 nm) (Aldrich) was used as it is [13]. All the other reagents used were of Analar grade or high purity. All the solutions were made in deionized double distilled water. The ruthenium trichloride trihydrate (Aldrich) was evaporated with concentrated hydrochloric acid three times to remove traces of Ru(IV), following the procedure described by Connick and Fine [14]. Ru(III) stock solution (0.02 M) was prepared by dissolving 0.207 g of Ru(III) chloride trihydrate (Aldrich) into 50 mL of 0.10 M sulfuric acid and small amount of metallic mercury is added to reduce the residual Re(IV), if any. The solution obtained was dark green in color. The green color changed to red brown in a few days at room temperature. All the experiments are carried out with the filtered red-brown solution, which was kept air-tight. This stock solution responded negatively to a starch-iodide test indicating the absence of Ru(IV) [15]. The solution had $\varepsilon = 7.5 \times 10^2\ M^{-1}\ cm^{-1}$ and λ_{max} = 295 nm. The Ru(III) concentration in the stock solution was determined by EDTA titration method.[16]. All the other cation solutions for the study were prepared by standard methods and mostly using the sulfate or chloride salts.

Kinetic measurements

In all the experiments the pseudo-first-order kinetics with respect to Nile blue were monitored at 633 nm, using Varian-Cary UV-VIS double beam spectrophotometer. Beer's law was valid for the measurement under the experimental conditions considered. No interference from the reagents, intermediates or products observed at 633 nm. The total initial volume of the reaction mixture was always kept 10 mL and at (298 ± 0.1 K). In all the experiments, the reactions were followed up to two half lives.

RESULTS AND DISCUSSION

With excess concentrations of other reactants, both uncatalysed and Ru catalysed reactions had *pseudo*-first-order kinetics with respect to Nile blue (NB^+). The uncatalysed reaction had first-order dependence on chlorite and H^+ concentrations [12]. The Ru(III) catalysed reaction had first-order dependence on both chlorite and catalyst, and a fractional order with respect to $[H^+]$. Based the observed high sensitivity and selectivity of Ru(III) on the title reaction, the Ru(III) catalysed kinetics and scope of the it as an indicator reaction are investigated. Figure 1 shows the typical absorbance *versus* time kinetic profiles, the depletion of NB^+ in presence of varied concentrations of Ru(III). The plots of ln absorbance *versus* time data gave good straight line with $R^2 = 0.998$ confirming the first-order dependence of rate on the Nile blue concentration. The plot of the *pseudo* first-order rate constants, k" *versus* [Ru(III)] gave excellent straight line with slope = 4.63×10^{-3} and $R^2 = 0.998$ indicating the order is unity with respect to the catalyst. The ln k' *versus* ln $[ClO_2^-]$ gave good straight line with gradient 1.03 and $R^2 = 0.99$ and the k' *versus* ln $[H^+]$ gave good straight line with gradient 0.93 and $R^2 = 0.99$. The slope indicates that reaction is first-order with respect to chlorite and it is slightly lower than one with respect to acid. The kinetic data, showing the effect of change in the concentrations of H^+, ClO_2^- and Ru(III) on the k" values is provided in Table 4 as additional information. Further, the reaction displayed negative kinetic salt effect. When the ionic strength is increased from 0.40 to 1.82, corresponding k" values, decreased from 1.37×10^{-3} s^{-1} to 1.22×10^{-3} s^{-1} (Table 4). In the current studies, the changes in ionic strength of the reaction mixture are very small, as the concentration of cations used are in the range of 10^{-8} to 10^{-4} M, which had marginal effect on ionic strength of the magnitude of 0.40. Based on the experimental results and assuming the oxidation reaction proceeds simultaneously through both uncatalyzed and catalyzed paths, the following rate law is proposed for the catalysed reaction.

$$-d[NB^+]/dt = \underbrace{k_0 [ClO_2^-][H^+] [NB^+]}_{\text{uncatalyzed path}} + \underbrace{k_C [ClO_2^-][H^+][Ru(III)][NB^+]}_{\text{catalyzed path}} \qquad (1)$$

k_0 and k_C are the rate coefficients for the uncatalyzed and catalyzed reactions, respectively. Under excess chlorite and acid concentrations the above equation reduces to,

$$- d[NB^+]/dt = k'' [NB^+]$$

and the overall pseudo first-order rate constant, $k'' = \{k_0' + k_C' [Ru(III)]\}$ (2)

where $k_0' = k_0 [ClO_2^-][H^+]$. k_0' and k_C' are the *pseudo* first-order rate constant for the uncatalyzed reaction and the catalytic constant respectively for the reaction, for chosen chlorite and acid conditions. If the equation 2 holds good, a plot of the *pseudo* first-order rate constant for the catalysed reaction, (k") *versus* [Ru(III)] should give a straight line with the intercept equal to k_0'. With [chlorite] = 0.05 M and $[H^+]$ = 0.10 M, the plot of k" versus [Ru(III)] gave a good straight line with gradient equal to $(4.63 \pm 0.3) \times 10^4$ M^{-1} s^{-1}. Thus, for the chosen conditions of reactants, the catalytic constant, k_C' for Ru(III) is $(4.63 \pm 0.3) \times 10^4$ M^{-1} s^{-1}. Furthermore, the intercept value 1.44×10^{-3} s^{-1} agreed well with the *pseudo* first-order rate constant 1.53×10^{-3} s^{-1} for the uncatalyzed reaction under similar conditions [12]. The overall catalytic constant, $k_C = k_C'/\{[ClO_2^-][H^+]\}$, for the reaction is quite large and is equal to 4.63×10^4 M^{-1} s^{-1}/ (0.05 M x 0.1 M) = 9.26×10^6 M^{-3} s^{-1}.

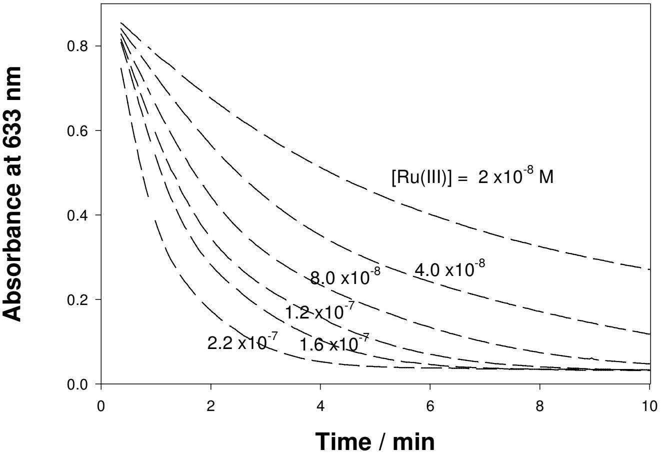

Figure 1. Typical kinetic curves ($[NB^+] = 2.0 \times 10^{-5}$ M, $[H^+] = 0.10$ M and $[ClO_2^-] = 0.05$ M, Temp. (298 ± 0.1) K, $[Ru(III)] = 2 \times 10^{-8}$ M to 2.2×10^{-7} M).

Scope as kinetic-catalytic indicator reaction

In view of the high value of catalytic constant for ruthenium(III), the scope of the title reaction as the catalytic indicator reaction is promising. Under excess concentration of H^+ and chlorite concentration, in presence of varied concentrations of Ru(III) the ln abs *versus* time plots, which give the k", are good straight lines confirming the reaction follows *pseudo* first-order kinetics. Thus, for the ease of the analytical procedure, the plot of difference of ln Abs (at 633 nm for a fixed times 60 s and 180 s) *versus* [Ru(III)] were plotted (Figure 2).

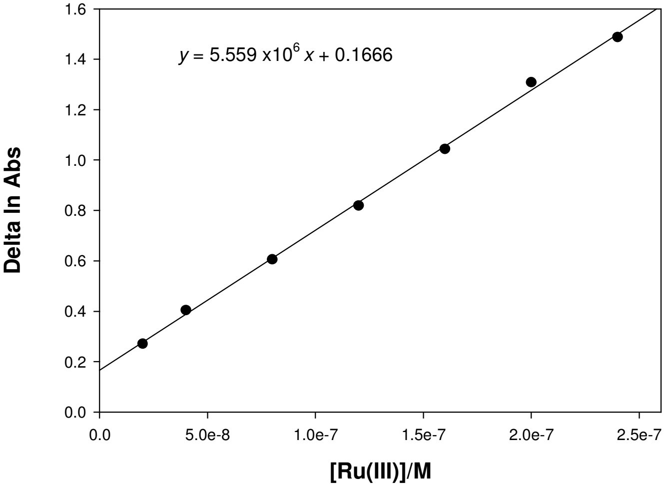

Figure 2. Δ ln Abs versus [Ru(III)] plot- calibration curve ($[NB^+] = 2.0 \times 10^{-5}$ M, $[H^+] = 0.10$ M and $[ClO_2^-] = 0.05$ M, Temp. (298 ± 0.1) K, $[Ru(III)] = 2 \times 10^{-8}$ M to 2.4×10^{-7} M).

Calibration curve

Reagent solutions thermostatted at (298 ± 0.1) K were mixed in the order: 2.0 mL each of 1.0 x 10^{-4} M Nile blue and 0.25 M sulfuric acid; requisite volume of water plus catalyst and other reagents, where necessary. Separately thermostatted solution of sodium chlorite, 2.0 mL of 0.25 M was added to start the reaction. Total volume was maintained at 10.0 mL. After vigorous mixing, mixture was transferred to thermostatted spectrophotometer cell (298.0 ± 0.1 K). Kinetic runs were carried out in triplicate with fixed initial concentrations of $[NB^+]$ = 2.0 x 10^{-5} M, $[H^+]$ = 0.10 M and [chlorite] = 5.0 x 10^{-3} M and varied concentrations of Ru(III) in the range (2.0 x 10^{-8} to 2.4 x 10^{-7} M). The absorbance at 633 nm was measured at fixed times of 60 s and 180 s (Table 1). Figure 2 illustrates the Δ ln Abs *versus* [Ru(III)] plot, which is a good straight line with R^2 = 0.999. The gradient and intercept values were 5.559 x 10^6 and 0.168 respectively.

Table 1. Absorbance values of Nile blue at fixed time for Ru(III) variation.
($[NB^+]$ = 2.0 x 10^{-5} M, $[H^+]$ = 0.1 M, $[ClO^-_2]$ = 0.05 M, Temperature = 298.0 ± 0.1 K).

Ru(III)/10^{-7}M	Absorbance at 633 nm*		Δ ln Abs**	Estimated #
	60 s	180s		(Ru(III) ± SD)/10^{-7}M
0.20	0.7696	0.5866	0.2718	0.190 ± 0.004
0.40	0.7270	0.4851	0.4045	0.429 ± 0.012
0.80	0.6577	0.3588	0.6062	0.792 ± 0.015
1.20	0.5890	0.2596	0.8195	1.175 ± 0.023
1.60	0.5336	0.1881	1.0440	1.579 ± 0.031
2.00	0.4575	0.1236	1.307	2.053 ± 0.047
2.40	0.3783	0.0851	1.488	2.379 ± 0.063

*Typical values in single run shown. **Mean of the difference of ln of absorbance values at 60 s and 180 s from triplicate experiments.

#Eqn. Y = 5.559 x 10^6 x + 0.166 is used, where y and x are Δ ln abs and [Ru(III)], respectively.

Interference studies

The metals that are associated with ruthenium in ores and that belong to the same group in periodic table, normally interfere in the analytical methods due to the similarities in chemical properties. Rh, Ir, Pa, Pt etc., are known to interfere in atomic absorption spectrometric determination of Ru by enhancing the ruthenium signal. Hence, the elements which may potentially interfere in the determination procedure are investigated. Initially, the effect of initial addition of various concentrations of each cation in the range (10^{-8} to 10^{-4} M) on the uncatalyzed and the Ru(III) catalyzed reaction was investigated, by estimating the k_0'and k" values in duplicate runs. As long as the k" values deviated by ≤ 4 % of the control value, the system is considered tolerant and has no interference. Tolerance ratios are estimated as the ratio, which gives deviations less than 4 % of the expected value for Ru(III). Taking the highest tolerance ratio for each cation, kinetic runs were repeated in triplicate runs together with 6.0 x 10^{-8} M Ru(III) and measuring the absorbance values at fixed times 60s and 180 s. From the Δ ln abs values the [Ru(III)] in the sample is estimated. None of the cations tested have any significant interference except Fe(III), which is a known catalyst in acidic chlorite oxidation. Fe(III) interfered even at 1:10 ratio to Ru(III). Table 2 summarizes the tolerance ratios for the presence of each individual species. The results on interference studies show that wide range of cations including Os(VIII), a known to interferant in kinetic-catalytic determination of Ru(III), has no effect on the studied reaction. To minimize the interference of Fe(III), the capability of citrate, tartarate, acetate, oxalate, EDTA, fluoride, ascorbic acid, potassium ortho-phosphate, etc. as masking reagents were investigated. All the reagents masked the catalysis by both Ru(III) and Fe(III) ions to different extent. The disodium pyrophosphate ($Na_2H_2P_2O_7$) solution effectively masked Fe(III) interference, without any impact on the catalytic efficiency of Ru(III). In a synthetic mixture containing Ru(III):Fe(III), in the tolerance ratio of 1:100, the addition of 1.0×10^{-4} M of $Na_2H_2P_2O_7$ masked Fe(III) effectively and completely. Vinas *et al.* reported similar masking effect of $Na_2H_2P_2O_7$ on Fe(III), during their studies on Mn(II) catalyzed periodate oxidations [17]. Further, to investigate the synergic effects of various ions on the determination of Ru(III), synthetic mixtures of Ru(III) were prepared with varying amounts of five selected cations and again with literature reported ore compositions[18]. The analyte concentration in such mixtures was determined in triplicate runs, using the described fixed time method. The disodium pyrophosphate was used as masking agent for Fe(III). Table 3 summarizes the composition of the synthetic mixtures and the Ru(III) concentrations determined. To probe the suitability of the method in analysis of the real samples, synthetic mixture was prepared spiking the tap water with Ru(III) and known amounts of different cations (Table 3, sample 6). The obtained analytical results data had less than 4 % standard deviation and agreed well with the predicted values, suggesting that results are reproducible. The analytical data summarized in Table 3, clearly show that proposed kinetic-catalytic method is reliable and has far higher tolerance limits.

Table 2. Interference and tolerance ratios.
($[NB^+] = 2.0 \times 10^{-5}$ M, $[H^+] = 0.10$ M, $[ClO^-_2] = 0.05$ M. Temperature = 298.0 ± 0.1 K).

Cation	Tolerance ratio*
Ni(II), Co(II), Mn(II), Cu(II), W(VI), Ce(IV), Pd(II), Pt (II), Se(IV)	10 000
Mo(VI), V(V), Ir(III), Ru(II), Pt(IV)	1 000
Os(VIII)	100
Fe(III)	10

* With single cation and no masking agent.

Table 3. Determination of Ru(III) in synthetic mixtures of varied compositions.#
($[NB^+] = 2.0 \times 10^{-5}$ M, $[H^+] = 0.1$ M, $[ClO^-_2] = 0.05$ M, Temperature = 298.0 ± 0.1 K).

Sample	Synthetic mixtures/10^{-8} M*						Analytical results		
	Os(VIII)	Ir(III)	Pt(II)	Pd(II)	Fe(III)	Ru(III)	Δ ln abs@ 60s-180s	Ru(III) Found@	% Recovery
1	20.0	20.0	20.0	20.0	10.00	6.00	0.5035	6.072	101.2
2	80.0	80.0	600	600	100	8.00	0.6042	7.883	98.54
3	100	80.0	600	600	500	8.00	0.6046	7.890	98.63
4	100	80.0	600	600	500	8.00	0.6175	8.123	101.5
5	400	200	10.0	0.0	0.0	40.0	0.3927	40.78	101.2
6	360	600	0.0	60.0	0.0	60.0	0.4919	58.62	97.70
7	420	720	0.0	60.0	0.0	60.0	0.4952	59.23	98.72

*All the samples were spiked with 1.0×10^{-4} $Na_2H_2P_2O_7$ as a masking agent for Fe(III).
@ Mean of triplicate experiments with standard deviation less than 4%.
\# Eqn. $y = 5.559 \times 10^6 x + 0.166$ is used, where y and x are Δ ln abs and [Ru(III)], respectively.
Sample 4 is prepared with tap water. Samples 5, 6 and 7 are the compositions of the osmiridium ore compositions from South Africa, Columbia and Australia respectively and were diluted by a factor of 10 [16].

Additional information on kinetic Data

Table 4. Effect of chlorite and acid concentrations on the overall rate constants.
($[NB^+] = 2.0 \times 10^{-5}$ M and temperature = 298.0 ± 0.1 K).

$[H^+]$/M	$[ClO_2^-]$/M	Ru(III)/10^{-8} M	k”/10^{-3} s^{-1}
0.1	0.02	4.0	1.37
0.1	0.04	4.0	2.68
0.1	0.05	4.0	3.36
0.1	0.06	4.0	4.13
0.1	0.07	4.0	4.80
0.1	0.08	4.0	5.32
0.1	0.09	4.0	6.14
0.1	1.00	4.0	7.01
			$\mu = 0.40$
$[H^+]$/M	$[ClO_2^-]$/M	Ru(III)/10^{-8} M	k”/10^{-3} s^{-1}
0.1	0.02	4.0	1.22
0.2	0.02	4.0	2.41
0.3	0.02	4.0	3.53
0.4	0.02	4.0	4.49
0.5	0.02	4.0	5.42
0.6	0.02	4.0	6.65
			$\mu = 1.82$
$[H^+]$/M	$[ClO_2^-]$/M	Ru(III)/10^{-8} M	k’’/10^{-3} s^{-1}
0.1	0.05	2.0	2.26
0.1	0.05	4.0	3.37
0.1	0.05	8.0	5.05
0.1	0.05	12. 0	6.83
0.1	0.05	16.0	8.70
0.1	0.05	20.0	10.91
0.1	0.05	24.0	12.41
			$\mu = 0.36$

CONCLUSIONS

The reaction of Nile blue dye with acidic chlorite reaction, provide a selective and sensitive method for the determination of Ru (III) ions at as low concentration as 20 nmoles per litre or 2 ng per mL. Os(VIII), which is known to interfere in determination of Ru(III), has no interference even at 100 fold excess. Most of the other cations studied have negligible influence on Ru(III) determination. The Fe(III) interference is successfully masked by use of sodium dihydrogen pyrophosphate, thus making the proposed method, quite sensitive as well as selective for the determination of Ru(III) in real samples. Considering the high sensitivity and selectivity of the reaction, it could also be used in flow injection systems for determination of Ru(III).

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