Acridine orange and chlorite reaction — An indicator reaction for the trace determination of Ru(III)

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Catalysis by transition metal ions plays an important role in understanding the mechanistic aspects of a particular redox reaction. Ru(III) acts as an efficient and potential catalyst in many redox reactions. Hence the use of Ru(III) chloride as a homogeneous catalyst in acidic medium is of present interest. Based on the highly selective catalytic efficiency of Ru(III) on the oxidation of acridine orange (3,6-bis (dimethylamino) acridine zinc chloride double salt)(AO+) by acidic chlorite, a fixed-time kinetic analytical procedure for determination of Ru(III) is developed. The lowest determination limit attainable with the developed method is 1.01 ng/mL. The method allows determination of Ru(III) with no interference from a wide range of cations. Tolerance ratios have also been computed. With excess concentration of reactants, both un-catalyzed and catalyzed reactions follow a pseudo-first order kinetics in [AO+], fractional order kinetics in oxidant and first order kinetics in catalyst [Ru(III)]. The rate coefficient of the un-catalyzed reaction is $4.45 \times 10^{-4}$ s$^{-1}$ while the catalytic constant for the catalyzed reaction is $8.00 \times 10^{-4}$ s$^{-1}$. Retarding effect of increasing ionic strength suggests the involvement of oppositely charged species in rate determining step. A tentative mechanism has also been proposed based on the results of variation of various factors.

Keywords: Ruthenium(III) determination, Acridine orange, Acidic catalysis
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Kinetic analytical techniques are very popular in the field of trace determination of elements present in a system. A number of papers and reviews have been published till now1-5. These methods have an advantage of having very low detection limits with the help of simple instrumental facilities. Ru(III) is a well known catalyst used in the kinetic studies of various reactions6-9 and many of them have been used as an indicator reaction for the determination of Ru(III)10-15. In the present communication a procedure for kinetic-catalytic determination of Ru(III), using a fixed time method, in the range of $1.0 \times 10^{-8}$ to $9.0 \times 10^{-8}$ mol dm$^{-3}$ is reported. Acridine orange-acidic chlorite reaction is basically a very slow reaction. The observed catalytic effect of Ru(III) on the AO'-Chlorite reaction generated interest to investigate the suitability of the reaction as an indicator reaction for the determination of trace amounts of Ru(III). The detailed kinetics and mechanism of this reaction are also discussed.

Experimental Procedure

All the chemicals used were of analar grade (Aldrich/B.D.H.) and double distilled water was used to prepare solutions. Aqueous stock solution (M/1000) of AO' (Sigma) was prepared by dissolving 0.0369 g of AO' in 100 mL water. Working solution of chlorite was prepared by appropriate dilution of stock solution. Working solution was prepared by dissolving 0.28 g of chlorite (Aldrich) in 25 mL of water for M/10 solution. In order to avoid any error due to decomposition of the solution the aqueous solution of chlorite was prepared daily. Ru(III) stock solution (0.02 M) was prepared as reported earlier16.

Kinetic measurements

In all kinetic experiments, the pseudo-first-order kinetics with respect to acridine orange were monitored at 490 nm, using Systronix UV-VIS spectrophotometer. Beer's law was found to be valid for the measurements under the experimental conditions considered. No apparent interference from the other reagents, intermediates or products was noticed at 490 nm. In all the kinetic measurements the reaction solutions were maintained at constant temp. (25.0±0.1°C) and the total volume of the reaction mixture was always kept 10 mL. Reagent solutions were mixed in the order: requisite volumes of acridine orange, sulphuric acid, water, plus catalyst or other reagents wherever necessary. Separately thermostatted solution of sodium chlorite was added to commence the reaction. The solution was mixed vigorously before transferring to spectrophotometer cell. In all the experiments, the reactions were followed up to two half lives.
Results and Discussion

Method and calibration curve

For the calibration curves experiments were run in duplicate using fixed initial concentration of acridine orange \(=2.0 \times 10^{-5}\) mol dm\(^{-3}\); H\(_2\)SO\(_4\)=1.0×10\(^{-3}\) mol dm\(^{-3}\) and with varied concentration of Ru(III) in the range 1.0×10\(^{-8}\) to 9.0×10\(^{-8}\) mol dm\(^{-3}\). Keeping the total volume 10 mL, the reaction was started by the addition of chlorite=1.0×10\(^{-3}\) mol dm\(^{-3}\). Adopting the fixed time method, the absorbance values (490 nm) were measured at fixed times of 600 and 1200 s (Table 1). For the construction of calibration curve, log absorbance values at 600 and 1200 s were plotted against [Ru(III)]. The plots yield linear curves, \(Y=-0.0141X-0.1657\) (\(R^2=0.97\)) for 600 s and \(Y=-0.0204X-0.2162\) (\(R^2=0.94\)) for 1200 s, where Y stands for the log absorbance and X for [Ru(III)] (Fig. 1). The curve at 600 s was used to determine the [Ru(III)] from the measured values of absorbance.

The observed reaction orders with respect to AO\(^+\) and chlorite is unity and fractional, respectively, while the role of acid is complex. The negative salt effect suggests that the rate-determining step is the reaction between two, singly, oppositely charged species. Further, the plot of 1/k versus 1/[oxidant] was found to be linear with non-zero intercept, which is an evidence of the formation of an intermediate complex. Thus, a reaction mechanism\(^{15}\) may be proposed as shown in scheme 1.

The organic intermediate is further oxidised in steps involving various chloro and oxychloro species to give the final reaction products. On the basis of well studied chemistry of acidic chlorite reactions, the following reactions need to be considered\(^{17-19}\).

\[
\begin{align*}
H^+ + ClO_2^- & \rightarrow HClO_2 \quad \ldots(1) \\
HOCl + Cl^- + H^+ & \rightarrow Cl_2 + H_2O \quad \ldots(2) \\
Cl_2 + 2 ClO_2^- & \rightarrow 2 ClO_2 + 2 Cl^- \quad \ldots(3) \\
ClO_2^- + 2 ClO_2^- + 2 H^+ & \leftrightarrow 2ClO_2 + 2HOCl \quad \ldots(4) \\
HClO + ClO_2^- & \leftrightarrow ClO_2 + H_2O \quad \ldots(5) \\
HClO_2 + Cl^- + H^+ & \rightarrow 2HOC1 \quad \ldots(6) \\
AO^+ + 2HOC1 & \rightarrow X^+ + HCl \quad \ldots(7) \\
X^+ + H^+ + ClO_2^- & \rightarrow P + (CH_3)_2N ^+OH + CH_3CH_2OH + HOCl \quad \ldots(8) \\
I + 2HOCl & \rightarrow P + 2HCl \quad \ldots(9) \\
\end{align*}
\]

Mechanism for Ru(III) catalyzed reaction

The observation that in absence of oxidizing agent, Ru(III) does not oxidize AO\(^+\) in a direct reaction confirms that reduction of Ru(III) to lower oxidation states does not happen. Higher oxidation states of ruthenium are involved in the catalytic cycle. Analogous to literature reports, it is suggested that Ru(III) forms complex with acidic chlorite in a rapid reaction and gets oxidized to Ru(V). The rate limiting step for the catalyzed reaction is the reaction between the binary complex and the organic substrate to form ternary complex, in which Ru(V) abstracts electrons from substrate and transfers to the chlorite in the complex\(^{20-22}\). It is possible that Ru ion acts as an electron mediator only within the ternary complex\(^{23-25}\).

\[
\begin{align*}
Ru(III) + ClO_2^- & \rightarrow [Binary complex]\quad \ldots(10) \\
[Binary complex] + AO^- & \rightarrow[Ternary complex]\quad \ldots(11) \\
[Ternary complex] + H^+ & \rightarrow Ru(III) + AO^- + HOCl \quad \ldots(12) \\
\end{align*}
\]

Table 1 — Absorbance values of acridine orange at fixed time for variation in Ru(III)

<table>
<thead>
<tr>
<th>[Ru(III)](\times 10^8) mol (^{-1}) dm(^{-3})</th>
<th>Absorbance 600 s</th>
<th>Absorbance 1200 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0.685</td>
<td>0.620</td>
</tr>
<tr>
<td>1.0</td>
<td>0.664</td>
<td>0.606</td>
</tr>
<tr>
<td>3.0</td>
<td>0.615</td>
<td>0.545</td>
</tr>
<tr>
<td>5.0</td>
<td>0.585</td>
<td>0.487</td>
</tr>
<tr>
<td>7.0</td>
<td>0.546</td>
<td>0.448</td>
</tr>
<tr>
<td>9.0</td>
<td>0.517</td>
<td>0.411</td>
</tr>
</tbody>
</table>

*Mean of duplicate results

\[Fig. 1 — Calibration graph\]
The chemistry of remaining reaction scheme is same as for the uncatalyzed reaction.

**Rate laws**

The un-catalyzed reaction between $\text{AO}^+$ and acidic chlorite can be represented by Eq. (13)

$$-\frac{d[\text{AO}^+]}{dt} = k_0 [\text{AO}^+] [\text{ClO}_2^-]^{1/2} \quad \ldots (13)$$

when $[\text{ClO}_2^-]$ is in excess, Eq. (13) reduces to

$$r = k' \ [\text{AO}^+] \quad \ldots (14)$$

where the pseudo first order rate constant for un-catalyzed reaction is $k' = k_0 [\text{ClO}_2^-]^{1/2}$

In the presence of catalyst, the oxidation proceeds through both catalyzed and un-catalyzed pathways. Therefore, the following represents the rate of degradation of $\text{AO}^+$ in presence of catalyst under excess chlorite and acid concentration.

$$-\frac{d[\text{AO}^+]}{dt} = \{k' + k_c'[\text{Ru(III)}]\} [\text{AO}^+]$$

where $k_c' = k_c[\text{ClO}_2^-]^{1/2}$

$$= k'' \ [\text{AO}^+] \quad \ldots (15)$$

where $k'' = \{k' + k_c'[\text{Ru(III)}]\}$

$$= \{k' + k_0 [\text{ClO}_2^-]^{1/2}\} \quad \ldots (16)$$

**Interference studies**

To investigate the influence of various cations and anions on the procedure and to set the tolerance limits, the effect of varied concentration of selected cations and anions on the reaction rate were investigated. Table 2 summarises the tolerance ratio of various cations investigated. To mask the interference of Fe(III) disodium pyrophosphate $[\text{Na}_2\text{H}_2\text{P}_2\text{O}_7]$ showed high selectivity without diminishing the catalytic activity of Ru(III). Disodium pyrophosphate has no effect on the reaction rate. A similar selective masking effect of Fe(III) by $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ in the kinetic determination of Mn(II) using methylene green-iodate reaction was reported by Vinas et al.\textsuperscript{26}. The tolerance ratio is given as the

<table>
<thead>
<tr>
<th>Interferent</th>
<th>Tolerance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>10</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>100</td>
</tr>
<tr>
<td>Cr(III), Hg(II), Ce(IV), I$^-_{}$</td>
<td>1000</td>
</tr>
<tr>
<td>Ni(II), Rh(II), Pb(II), Pd(II)</td>
<td>10000</td>
</tr>
<tr>
<td>Se(IV), Cu(II), Mn(II)</td>
<td>100000</td>
</tr>
<tr>
<td>Co(II), NO$<em>2^-</em>{}$</td>
<td>1000000</td>
</tr>
<tr>
<td>Re(V)</td>
<td>1000000</td>
</tr>
<tr>
<td>Os(VIII), V(V), Mo(VI), Ir(III)</td>
<td>1000</td>
</tr>
</tbody>
</table>
ratio of concentration of interferent to the catalyst. Table 3 summarises the results obtained for the determination of Ru(III) in synthetic mixtures using this method.

Scope as kinetic-catalytic indicator reaction

In order to find lower limit of determination a fixed time method is proposed. The scope of the title reaction as the catalytic indicator reaction is very promising. In this fixed time method the lowest determination limit is found to be 1.01 ng/mL. The plot of log abs. (for a fixed time) versus [Ru(III)] yields a good straight line. Kinetic runs were carried out at (25 ± 0.1)°C in duplicate with fixed concentration of substrate i.e. acridine, acid and oxidant and varied concentration of Ru(III) in the range of 1.0 × 10⁻⁸ to 9.0 × 10⁻⁵ mol dm⁻³.

Conclusion

Acridine orange, a water-soluble dye having sharp absorption peak in visible range shows no shift due to pH change. The reaction of AO⁺ with acidic chlorite provides a sensitive method for the trace determination of Ru(III) (1.01 × 10⁻⁶ mg/mL). Fe(III) interference is successfully masked by Na₂H₂P₂O₇, thus making the proposed method quite sensitive as well as selective. The results are highly reproducible when stock solutions of the same batch are used for analysis, but vary marginally when new solutions are made. The errors due to variation in absorbance value of AO⁺ were minimised by reading the absorbance at two fixed times rather than depending on single value. Further, fixed time procedure is easy to adopt and suitable, particularly when the spectrophotometer cell is not thermostated.

Table 3 — Determination of Ru(III) in synthetic mixtures

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Synthetic mixtures/µ M</th>
<th>Os(VIII)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
<th>Pd(II)</th>
<th>Fe(III)</th>
<th>Ru(III)</th>
<th>Ru(III) found/µ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000</td>
<td>2000</td>
<td>200</td>
<td>200</td>
<td>0.80</td>
<td>0.20</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>1000</td>
<td>100</td>
<td>100</td>
<td>0.10</td>
<td>0.40</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>50</td>
<td>0.20</td>
<td>0.60</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>50</td>
<td>0.80</td>
<td>0.80</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>50</td>
<td>0.80</td>
<td>0.100</td>
<td>0.103</td>
<td></td>
</tr>
</tbody>
</table>

*With 1.0 × 10⁻⁴ mol dm⁻³ Na₂H₂P₂O₇ as a masking agent for Fe(II).
@ Mean of triplicate experiments with standard deviation less than 3%.
#Tap water spiked with cations.

References