Kinetics & Mechanism of Oxidation of Aniline & Substituted Anilines by Tl(III)—A Change from Ionic to Radical Pathway in Presence of Ru(III)

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The kinetics of oxidation of aromatic primary amines by various oxidants have been studied by different workers. Yatsimirskii et al. reported Ru(III)-catalysed oxidation of anilines by Mn(III). The present communication deals with the kinetic aspects of uncatalysed and Ru(III)-catalysed oxidation of aniline and substituted anilines by thallium triacetate in aq. acetic acid medium in the presence of perchloric and sulphuric acids under homogeneous conditions, and to our knowledge this is the first kinetic report.

Materials and Methods

Aniline and substituted anilines were purified by redistillation or recrystallisation before use. Thallium triacetate was prepared and purified as reported earlier. Estimation of oxidant was done iodometrically. Solvent decomposition has been routinely checked and found to be negligible in Ru(III)-catalysed oxidations, whereas under uncatalysed experimental conditions Tl(III) has been found to be quite stable. The solution of ruthenium trichloride was prepared as per the procedure adopted by Singh et al. The values of $H_0$ for acetic acid-water mixtures in the presence of sulphuric acid were calculated by our previous method; Wiberg has determined $H_0$ for acetic acid-water mixtures in the presence of perchloric acid.

The solutions of the substrate and oxidant in the mixed solvent were equilibrated at the desired temperature and then mixed in a dark-coloured reaction vessel. Aliquots (5 ml) of the reaction mixture were quenched by adding potassium iodide solution at different time intervals and the liberated iodine titrated against standard thiosulphate.

Results and Discussion

Uncatalysed oxidation of anilines — The reactions are first order each in [substrate] and [oxidant]. The reaction is dependent on concentrations of perchloric and sulphuric acids and the order with respect to $H_0$ is unity. The plots of log $k_1$ versus $H_0$ are linear suggesting that $H_0$ is a more satisfactory measure of acidity of the medium than is the stoichiometric concentration of the acid (Table 1). The acid dependence is traced to the hydrolysis equilibria of the type:

$$\text{Tl(OAc)}_2 + \text{H}^+ \rightleftharpoons \text{Tl(OAc)}_2^- + \text{HOAc}$$

$$\text{Tl}^+(\text{OAc})_2^\text{ClO}_4^- + \text{H}^+ \rightleftharpoons \text{Tl(OAc)}_2^+ + \text{HClO}_4$$

In view of the above, the reaction of acid with substrates is negligible as reactions between inorganic species are instantaneous as compared to its reaction with weak bases. The data in Table 2 show first-order dependence on [aniline]. At a fixed [substrate] the [Tl(III) acetate] was varied. The constancy of the first-order rate constants clearly indicates a first order dependence on [Tl(III)] (Table 3).

<table>
<thead>
<tr>
<th>$[\text{HClO}_4]$ $M$</th>
<th>Aniline</th>
<th>$m$-Toluidine</th>
<th>$p$-Chloroaniline</th>
<th>$k_1 \times 10^3$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.37</td>
<td>0.65</td>
<td>0.14</td>
<td></td>
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<tr>
<td>1.5</td>
<td>1.00</td>
<td>1.15</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.51</td>
<td>1.70</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>—</td>
<td>—</td>
<td>0.38</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$[\text{H}_2\text{SO}_4]$ $M$</th>
<th>—</th>
<th>—</th>
<th>—</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.01</td>
<td>2.01</td>
<td>—</td>
</tr>
<tr>
<td>1.5</td>
<td>1.54</td>
<td>2.81</td>
<td>—</td>
</tr>
<tr>
<td>2.0</td>
<td>2.04</td>
<td>5.60</td>
<td>—</td>
</tr>
</tbody>
</table>
On the basis of these results the following rate expression is proposed.

$$-\frac{d[Tl(III)]}{dt} = k [S][H_0][Ti(III)]$$

The order of reactivity is p-toluidine > o-toluidine > m-toluidine > aniline > o-chloroaniline > p-bromoaniline > p-chloroaniline > m-chloroaniline > m-nitroaniline. This indicates that electron releasing groups enhance the reaction rate and electron withdrawing groups retard the rate (Table 4).

**Nucleophilicity** — Swain and Scott have shown that log $k/k_0 = S n$ where 'S' is the susceptibility factor and 'n' is the nucleophilicity constant. The $n$-values computed by us were plotted against log $k_2$, a linear plot showing the relationship between nucleophilicity and reactivity was obtained. The plot of log $k_2$ versus $pK_a$ was also found to be linear.

**Application of Edwards equation** — The Swain-Scott linear free energy relationship has been improved by Edwards by a four-parameter equation. It has been noted that the electrode potentials for many reactions, parallel the nucleophilicity of many ions. According to Edwards

$$\log k/k_0 = \alpha En + \beta H$$

where $\alpha$ and $\beta$ are the constants. The other parameters are defined as:

$$En = E_0 + 2.6$$

and

$$H = pK_a + 1.74$$

Using the kinetic data the values of $H$, $En$, $\alpha$ and $\beta$ for this oxidation in 20% HOAc, at 60° are computed for the first time with the help of partial multiple correlation theory. The accuracy of $En$ and $H$ values have been checked by plotting log $k_2$ versus $En$ and log $k_2$ versus $H$ respectively. The plots are linear indicating the general applicability of these values.

**Mechanism** — Based on these observations a mechanism depicted in Scheme I is suggested. **Ru(III)-catalysed oxidation** — Ruthenium(III) chloride catalysed oxidation of aniline and substituted anilines by thallium triacetate in the presence of perchloric acid in aqueous acetic acid medium indicates the reaction to be of first-order each with respect to substrate (Table 6), catalyst and oxidant (Table 5) but independent of perchloric acid (Table 7).
TABLE 6 — DEPENDENCE OF FIRST ORDER RATE CONSTANT ON [Substrate] IN Ru(III)-CATALYSED OXIDATION OF ANILINES BY Ti(III)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>k₁ (M⁻¹ min⁻¹)</th>
<th>Substrate</th>
<th>k₁ (M⁻¹ min⁻¹)</th>
<th>Substrate</th>
<th>k₁ (M⁻¹ min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>1.56</td>
<td>m-Toluidine</td>
<td>0.91</td>
<td>m-Chloroaniline</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>2.82</td>
<td></td>
<td>1.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.64</td>
<td></td>
<td>2.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.77</td>
<td></td>
<td>5.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Bromoaniline</td>
<td>1.40</td>
<td>p-Chloroaniline</td>
<td>0.98</td>
<td>p-Bromoaniline</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>2.65</td>
<td></td>
<td>1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.02</td>
<td></td>
<td>1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.89</td>
<td></td>
<td>4.02</td>
<td></td>
<td></td>
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</tbody>
</table>

TABLE 7 — DEPENDENCE OF RATE CONSTANTS ON ACIDITY IN THE Ru³⁺-CATALYSED OXIDATION OF ANILINES BY Ti(III)

<table>
<thead>
<tr>
<th>[HClO₃] M</th>
<th>Aniline k₂ (litr mol⁻¹ min⁻¹)</th>
<th>m-Toluidine k₂ (litr mol⁻¹ min⁻¹)</th>
<th>p-Chloroaniline k₂ (litr mol⁻¹ min⁻¹)</th>
<th>p-Bromoaniline k₂ (litr mol⁻¹ min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.12</td>
<td>2.30</td>
<td>1.70</td>
<td>1.92</td>
</tr>
<tr>
<td>1.5</td>
<td>2.02</td>
<td>2.54</td>
<td>1.30</td>
<td>1.63</td>
</tr>
<tr>
<td>2.0</td>
<td>2.03</td>
<td>2.63</td>
<td>1.29</td>
<td>1.69</td>
</tr>
<tr>
<td>3.0</td>
<td>2.03</td>
<td>2.63</td>
<td>1.29</td>
<td>1.69</td>
</tr>
</tbody>
</table>

It appears that the hydrolysis equilibria which leads to the dependence on acid is not important in the presence of Ru(III) as the reaction between Ti(III) and Ru(III) is fast leading to formation of active Ru(V). Due to the intervention of the inorganic oxidation step hydrolysis equilibria are of no significance and hence independence to acidity is observed.

Reactivity order in substituted anilines — Amongst the various substituted anilines studied the observed order of reactivity is, p-toluidine > o-toluidine > m-toluidine > aniline > p-bromoaniline > o-chloroaniline > p-chloroaniline > m-chloroaniline > m-nitroaniline. It clearly indicates that electron releasing groups accelerate the reaction and electron withdrawing groups retard the reaction rate. The reaction rates for the catalysed reaction are almost 80 to 90 fold more than that for uncatalysed reaction showing thereby the specific catalytic nature of Ru(III). The second order rate constants of different substituted anilines are recorded in Table 8.

ρ-a-relationship — A plot of log k₂ versus ρ is linear (correlation coefficient = 0.98) and the ρ value has been found to be -0.76 which establishes that oxidation of amines by Ti(III) in Ru(III)-catalysed reaction proceeds through a radical process, whereas in uncatalysed reaction it proceeds through a cationic centre. This is the novelty in the present study, where Ru(III) participates in the reaction sequence and changes the mechanism from ionic to radical mechanism.

Nature of Ru(III) species — It has been confirmed by electronic spectral studies¹⁴ that Ru(III) chloride exists in the hydrated form as [Ru(H₂O)]³⁺. The plot log k₁ versus log [Ru³⁺] is linear with a unit slope.

Solvent effect — An increase in the percentage of acetic acid decreases the reaction rate. For aniline, the values of k₁ at 20, 40, and 60% HOAc are 2.12, 1.87, and 1.50 x 10⁻² min⁻¹ respectively.

Mechanism — It has been stated earlier that the reaction involves a radical pathway. Arguments in favour of the radical process are:

(i) In the NBS bromination of toluenes Pearson and Martin¹⁵ have reported the reactions of a radical type. The plot of log k₂ (NBS bromination of toluenes) versus log k₂ [Ti(III) oxidation of anilines] is linear indicating the operation of identical mechanisms in both the reactions. Hence, the present reaction also occurs by a radical process.

(ii) The plot of log k₂ [V(V) oxidation of anilines¹] versus log k₂ [Ti(III) oxidation of anilines] is fairly linear confirming the reactions proceeding through a similar radical mechanisms.

(iii) The effect of acid is reversed from one of dependence to independence in the presence of Ru(III) indicating a change of mechanism.

(iv) Drummonds and Waters¹⁶ tests for radical process are positive especially the test of acrylonitrile.

As stated earlier, in Ru(III)-catalysed oxidation electron transfer takes place from Ru(III) to Ti(III) to give intermediate Ru(V) and Ti(I). The Ru(V) functions as an active oxidising species. Such participation of intermediate Ru(V) species in the oxidation processes has been invoked by Yatsimirskii¹⁷ in the Ru(III)-catalysed oxidations by Ce(IV), Ru(IV) reacts with aniline to give ArNH, Ru(IV) and a proton. The intermediate Ru(IV) then reacts with another molecule of aniline to give ArNH. These two free radicals dimerise to give hydrazo-benzene which is further oxidised by another molecule of Ti(III)-Ru(III) couple to give azobenzene.
A sequence of reaction is shown in Scheme 2 which explains the observed experimental results.

Product analysis — In the present Ti(III) oxidation of anilines the products azobenzenes obtained were isolated and characterized by the literature method

Acknowledgement

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References