Kinetics and mechanism of oxidation of arylhydrazides by hexacyanoferrate(III) in alkaline medium

M M Al-Subu*, R Abu EL-Halawa & H M Abed
Department of Chemistry, An-Najah University, P.O. Box 7
Nablus, West Bank-Via Israel
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The kinetics of oxidation of a series of arylhydrazides, X-Ph.CO.NH.NHz (X = H, p-Cl, p-CH3 and o-NO2) by alkaline hexacyanoferrate(III) have been investigated. The reactions are first order each in [oxidant] and [substrate] and fractional order in [OH-]. The effects of added hexacyanoferrate(II) and other ions on the rate of oxidation have been investigated. The kinetics reveal a pronounced positive salt effect as well as specific ion effect. The temperature and solvent effects have also been studied. A suitable mechanism and a rate law consistent with the experimental results have been proposed.

Hexacyanoferrate(III), a one-electron oxidant in both acidic and basic media, has been widely used for the study of kinetics of oxidation of a variety of organic compounds1-3. However, very little work has been reported on the oxidation of arylhydrazides4. Hence, it is thought worthwhile to study the kinetics of the reaction between hexacyanoferrate(III) and some arylhydrazides in alkaline medium.

Experimental
All chemicals used were of the highest purity available. The kinetic runs were carried out spectrophotometrically using a 1 cm cell following the absorbance of hexacyanoferrate(III) at 414 nm until at least 70% reaction has been completed. The desired pH was maintained employing NaOH/(acetic acid, boric acid, phosphoric acid) buffer. NaCl was used to maintain a constant ionic strength.

The reported rate constant values were the average of replicated measurements which did not differ by more than 6%.

Results and discussion
The kinetics of oxidation of arylhydrazides by potassium hexacyanoferrate(III) in alkaline medium have resulted in the following features:

(i) The reaction followed first order dependence in [oxidant] as found from the slope of log(initial rate) versus log[Fe(CN)~3-] plots.

(ii) The order of the reaction in [hydrazide] as revealed from the slope of log(initial rate) versus log[hydrazide] plots was unity.

(iii) The rate increased with increase in pH. The plot of log(initial rate) versus log[OH-] was linear with a slope of approximately one half.

Table 1—Effect of varying [salt] on the rate of oxidation of benzoic acid hydrazide by Fe(CN)~3- in alkaline medium.

<table>
<thead>
<tr>
<th>10^3[Salt] mol dm^-3</th>
<th>10^3 × Rate mol dm^-3 s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.90</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.25 (0.95)</td>
</tr>
<tr>
<td></td>
<td>0.50 (0.99)</td>
</tr>
<tr>
<td></td>
<td>0.75 (1.03)</td>
</tr>
<tr>
<td></td>
<td>1.30 (1.05)</td>
</tr>
<tr>
<td></td>
<td>1.50 (1.10)</td>
</tr>
<tr>
<td>KF</td>
<td>0.50 (0.50)</td>
</tr>
<tr>
<td>KBr</td>
<td>0.50 (0.90)</td>
</tr>
<tr>
<td>I</td>
<td>0.50 (1.05)</td>
</tr>
<tr>
<td>KClO₃</td>
<td>0.50 (1.15)</td>
</tr>
<tr>
<td>KIO₃</td>
<td>0.50 (1.30)</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>(1.60)</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.60 (1.60)</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0.60 (1.65)</td>
</tr>
</tbody>
</table>

Values in parentheses are at 29°C.

Fig. 1—Plot of kobs versus [Fe(CN)~3-] at 20°C. [Fe(CN)~3-] = 1.0 × 10^-3 mol dm^-3, [benzoic acid hydrazide] = 2.0 × 10^-3 mol dm^-3.
Table 2—Activation parameters for oxidation of arylhydrazides by Fe(CN)₆³⁻ in alkaline medium.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eₐ (kJ mol⁻¹)</th>
<th>ΔS⁺ (J mol⁻¹ deg⁻¹)</th>
<th>ΔH⁺ (kJ mol⁻¹)</th>
<th>ΔG⁺ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid hydrazide</td>
<td>38.1</td>
<td>-6.2</td>
<td>35.6</td>
<td>37.4</td>
</tr>
<tr>
<td>p-Toluic acid hydrazide</td>
<td>44.2</td>
<td>12.0</td>
<td>41.8</td>
<td>38.2</td>
</tr>
<tr>
<td>p-Chlorobenzoic acid hydrazide</td>
<td>30.2</td>
<td>-31.9</td>
<td>27.7</td>
<td>37.3</td>
</tr>
<tr>
<td>α-Nitrobenzoic acid hydrazide</td>
<td>45.4</td>
<td>15.0</td>
<td>43.1</td>
<td>38.4</td>
</tr>
</tbody>
</table>

(iv) The observed rate constants increased with increase in [hexacyanoferrate(III)], added from outside up to 1.0 × 10⁻³ mol dm⁻³, thereafter a sudden decrease in the rate constant with increase in [hexacyanoferrate(III)] was observed (Fig. 1).

(v) A positive salt effect was observed with increase in added [NaCl] (Table 1).

(vi) Added ions affected the rate in the following order:

IO₅⁻ > ClO₄⁻ > I⁻ > Br⁻ and NH₄⁺ > Na⁺ > K⁺ (Table 1).

(vii) The rate of the reaction decreased with increase in the percentage of ethanol in the solvent medium. For example, under the conditions [benzoic acid hydrazide] = 2.0 × 10⁻³ mol dm⁻³; [Fe(CN)₆³⁻] = 1.0 × 10⁻³ mol dm⁻³; u = 0.28 and temp. = 30°C, kₘₐₓ decreased from 1.00 to 0.60 mol dm⁻³ s⁻¹ when % ethanol was increased from 10 to 50.

(viii) The substituent effect was found to follow the order: p-Cl > H > p-Me > α-NO₂. The average values of the calculated activation parameters are shown in Table 2.

On the basis of the above results and those reported by Kalb and Gross¹, the oxidation of arylhydrazides by alkaline hexacyanoferrate(III) may be written as

2Ph.COH.NH₂ + 2Fe(CN)₆³⁻ + 2OH⁻ → Ph.CO-NH-N = CH-Ph + N₂ + 3H₂O + 2Fe(CN)₆⁴⁻

To account for the observed kinetics the following mechanism in Scheme 1 is postulated:

In the mechanism in Scheme 1 it has been assumed that the imide nitrogen (-CO-NH-) is more susceptible to oxidation than the terminal nitrogen (-NH₂) in accordance with reported activity sequence for the oxidation of amines by Fe(CN)₆⁴⁻ (Refs 6, 7). The first step in the proposed mechanism is similar to en-ol and imine-enamine tautomerization and explains the observed reactivity order of arylhydrazides employed in this study: p-Cl > H > p-CH₃ > α-NO₂, which is also in accordance with their electron-withdrawing strength. The relatively lower rate of oxidation of α-nitrobenzoic acid hydrazide has been attributed to the possibility of intramolecular H-bonding in the α-nitrobenzoic acid hydrazide solution. The observed substituent effect agrees also with the reported pKₐ-values of the hydrazides under investigation. In the second step, i.e., rate-determining step, the abstraction of the first electron by hexacyanoferrate(III) from the imine-enol form results in the formation of the hydrazide radical cation [III]. The formation of radical cation has also been reported⁷⁻¹¹ for the oxidation of amines, hydrazines and other electron-rich organic compounds by hexacyanoferrate(III). The observed cationic and solvent effects and the calculated activation parameters are similar to other hexacyanoferrate(III) reactions where the slow step is assumed to involve an electron abstraction by Fe(CN)₆³⁻. The reversibility of
this step has been assumed to explain the dependence of rate upon addition of Fe(CN)$\text{III}^-$ (refs 10, 11). The hydrazide radical cation loses a proton, followed by the loss of another electron by a second Fe(CN)$\text{III}^-$ to produce the acyldiimide cation (V) which loses another proton to produce the acyldiimide intermediate (VI). The acyldiimide can react to give different products depending on the reaction conditions. In the present study the intermediate (VI) reacts with another arylhydrazide species to produce the arylhydrazone (VII) through the formation of the aldehyde.

Mechanism in Scheme 1 leads to rate Eq. (8).

$$\frac{-d[\text{Fe(CN)}_{\text{III}}^-]}{dt} = k_1[\text{II}][\text{Fe(CN)}_{\text{III}}^3]$$

$$- k_{-1}[\text{III}][\text{Fe(CN)}_{\text{VI}}^-] \quad \ldots (8)$$

From reaction (1)

$$[\text{II}] = K_{eq} [\text{I}] \quad \ldots (9)$$

After applying steady state treatment with respect to [III], rate law (10) is obtained

$$\frac{-d[\text{Fe(CN)}_{\text{VI}}^-]}{dt} = k_{obs}[\text{II}][\text{Fe(CN)}_{\text{VI}}^3]$$

$$\times \frac{k_2[\text{OH}^-]}{k_{-1}[\text{Fe(CN)}_{\text{VI}}^-] + k_2[\text{OH}^-]} \quad \ldots (10)$$

Where, $k_{obs} = K_{eq} k_1$.

The derived rate law agrees well with the experimental results.

Acknowledgement
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References
5 Kalb C & Gross D, Chem Ber, 59 (1926) 727.