Oxidation of Aroyl Hydrazines: Part VII—Kinetics of Oxidation of Benzoyl Hydrazines by Iron(III) in Presence of 1,10-Phenanthroline

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The title reaction is found to be first order in the [oxidant]. Evidences for the formation of a 1 : 1 complex of Fe(III) with the substrate and both 1:1 and 1 : 2 complexes with 1,10-phenanthroline have been obtained. H⁺ and HSO₄⁻ ions retard the rate and their influences on the rate have been quantitatively correlated. The effect of added methanol on the rate indicates that a dispersal of charge takes place in the transition state as also the participation of a water molecule in the reaction. The Hammett plot is a curve concave in shape. A mixed ligand complex between iron(III), substrate and 1,10-phenanthroline is postulated to explain the observed kinetics.

Materials and Methods

The benzoyl hydrazine solutions were prepared in aqueous methanol from Fluka AG's 'purum' samples. 1,10-phenanthroline solution was prepared in aqueous methanol from E. Merck's 'pro analysi' sample. Iron(III) sulphate solution was prepared by the literature method. Aqueous sulphuric acid and vanadium(V) were of AR grade.

The kinetics were followed by measuring the absorbance of ferroin formed at 510 nm using a Hilger UVISPEK spectrophotometer under pseudo-first order conditions. All other reactants were colourless at this wavelength. In all the runs, [Phen] was kept in sufficient excess to minimise complications due to its removal in the product. Beer's law was obeyed under the experimental conditions. The pseudo-first order rate constants (k₁) were evaluated from the slopes of the plots of log(Aₒ-Aₜ) versus t where Aₒ and Aₜ are the absorbances at time t and when the reaction was complete respectively. These plots were linear at least up to 50% completion of the reaction and the k₁ values were reproducible within ±3%.

Results

Stoichiometry and product analysis — Under the experimental conditions, [substrate]> [oxidant], one mol of the substrate was oxidised by 1.1-1.8 mol of oxidant. The analysis of the reaction mixture revealed that besides nitrogen, ammonia (Nessler's reagent test) and the corresponding benzoic acid were the products of oxidation. The formation of free radicals during the reaction was established by polymerisation of acrylamide present in the reaction mixture.

Effect of varying [oxidant] — The reaction is first order in [oxidant] as is evident from the linearity of the the plots of log(Aₒ-Aₜ) versus time. Also the k₁ value is independent of initial [iron(III)].

Effect of varying [substrate] — The rate increases with an increase in [substrate] in the range 2.5 × 10⁻⁴ to 7.5 × 10⁻³ M. The plot of 1/k₁ versus 1/[substrate] is linear with a positive intercept on the 1/k₁ axis up to [substrate] = 1.0 × 10⁻³ M. Beyond this concentration, the reaction shows a first order dependence on [substrate] (Fig. 1).

Effect of varying [1, 10-phenanthroline] — The effect of varying [1, 10-phenanthroline] on the rate was investigated at two different [H⁺] in order to characterise the nature of the oxidising species. At low [H⁺] (≈ 7.5 × 10⁻⁴ M), the rate increases with increase in [Phen] and the plot of 1/k₁ versus 1/[Phen] is linear up to [Phen] = 3.0 × 10⁻² M and beyond this concentration 1/k₁ varies linearly with 1/[Phen]² (Fig. 1), thus suggesting the successive formation of 1 : 1 as well as 1 : 2 complexes of iron(III) with 1,10-phenanthroline at low [H⁺]. However, at higher [H⁺] evidence for only 1 : 2 complex has been obtained, as indicated by the linearity of the plot of 1/k₁ versus 1/[phen]² (Fig. 1).

Effect of varying [H⁺] — The influence of varying [H⁺] on the rate was studied by varying [H₂SO₄] from 2.0 × 10⁻⁴ M to 2.4 × 10⁻³ M at constant [HSO₄⁻] and also keeping other variable parameters constant. The rate decreases with an increase in [H⁺] and the plot of 1/k₁ versus [H⁺] is linear up to [H⁺] = 8.0 × 10⁻³ M and thereafter 1/k₁ varies linearly with [H⁺]² (Fig. 1).
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Effect of varying [HSO₄⁻]—The effect of varying [HSO₄⁻] on the rate was investigated at constant [H⁺]. To nullify the influence, if any, due to change in the ionic strength when [HSO₄⁻] was varied, the ionic strength was maintained at 10⁻⁴ M, MeOH = 1% (v/v), I[HSO₄⁻] = 2.4 x 10⁻² M, [BAH] = 8 x 10⁻⁴ M, MeOH = 1% (v/v), [H⁺] = 1.275 x 10⁻¹ M.

Fig. 1—Plots of 1/10k₁ (min) versus 2/10⁴ [BAH] (M⁻¹) (curves A and A'); 1/5k₁ (min) versus 5/10⁴ [Phen] (M⁻¹) (curve B); 1/k₁ (min) versus 5/10⁴ [Phen] (M⁻¹) (curve B'); 1/5k₁ (min) versus 10⁻⁴ [H⁺] (M) (curve C); 1/20k₁ (min) versus 10⁻¹ [H⁺]² (M²) (curve C'); 1/80 k₁, (min) versus 2.5 x 10⁻¹ [HSO₄⁻] (M) (curve D') (A and A': [Phen] = 2 x 10⁻⁴ M; MeOH = 1% (v/v), [H⁺] = 1.375 x 10⁻¹ M, B and B': [BAH] = 1 x 10⁻⁴ M, MeOH = 20% (v/v), [H⁺] = 7.5 x 10⁻¹ M (B) and 1.275 x 10⁻¹ M (B'); C and C': [Phen] = 2 x 10⁻⁴ M, [BAH] = 1 x 10⁻³ M, MeOH = 1% (v/v), [HSO₄⁻] = 2.4 x 10⁻² M; D': [Phen] = 2 x 10⁻⁴ M, [BAH] = 8 x 10⁻⁴ M, MeOH = 1% (v/v), [H⁺] = 1.275 x 10⁻¹ M.

Discussion

Iron(III) is known to form both 1:1 and 1:2 complexes with SO₄²⁻ ions. The 1:2 form predominates when [SO₄²⁻] > 0.01 M. At [H₂SO₄] = 7.5 x 10⁻⁴ M, the [SO₄²⁻] is very small since [SO₄²⁻] ~ [H₂SO₄] such that almost all the iron(III) will exist as Fe (SO₄)²⁺. In the presence of 1,10-phenanthroline the equilibria (1 and 2) exist:

Fe(SO₄)²⁺ + Phen ⇌ [Fe(SO₄) Phen]⁺  

1)
Thus evidence for the successive formation of 1:1 and 1:2 complexes of iron (III) with 1,10-phenanthroline at low $[\text{H}^+]$ i.e. at low $[\text{SO}_{4}^{2-}]$. Both the complex species may be reactive. However, at $[\text{H}_{2}\text{SO}_{4}]=1.275\times10^{-2}M$, the iron (III) mainly exists as $\text{Fe (SO}_{4}^{2-})$ and in the presence of excess 1,10-phenanthroline the equilibrium (3) exists:

$$\text{K}_1 \text{FeSO}_4^{2-}+2\text{Phen} \Leftrightarrow \text{Fe(Phen)}^{2+}+2\text{SO}_4^{2-} \quad \ldots (3)$$

Thus evidence for the 1:2 complex formation at higher acidities is explained. Also the observed inhibition of the rate with $[\text{HSO}_4^-]$ is in tune with equilibrium (3) since at constant $[\text{H}^+],[\text{SO}_4^{2-}]=\text{K}_1$ and the results on the variation of $k_1$ with $[\text{HSO}_4^-]$ correspond to a study of the variation of $k_1$ with $[\text{SO}_4^{2-}]$. The catalysis by 1,10-phenanthroline may be due to a more favourable electron transfer through its $\pi$-electron cloud.

In acidic solutions the substrates undergo protonation readily as shown in equilibrium (4). The observed decrease in rate with increase in $[\text{H}^+]$ can be explained as due to complexation of the unprotonated substrate only, with the oxidant (equilibrium 3.)

$$\text{PhCONHNH}_2 + \text{H}^+ \Leftrightarrow \text{PhCONHNH}_2^+ \quad \ldots (4)$$

At higher $[\text{H}^+]$, the 1,10-phenanthroline also gets protonated and because it takes up only one proton and since only one 1,10-phenanthroline molecule is involved in the oxidation at the [Phen] employed, this second order inhibition due to $[\text{H}^+]$ at higher acidities is also explained. The linearity of the plot of $1/k_1$ versus $1/\text{[substrate]}$ with a positive intercept on the $1/k_1$ axis indicates the formation of a 1:1 complex at low [substrate]. In order to explain the complex formation of iron (III) with both the substrate and 1,10-phenanthroline molecules, a mixed ligand complex as a transient intermediate is envisaged which breaks up in a rate-limiting step as indicated in Scheme 1.

The $\text{N}_2\text{H}_4$ radical that is formed may either dimerise to give $\text{N}_2\text{H}_6$ which decomposes (Eq. 5) as shown or is further oxidised (Eqs. 6 and 7) (all in fast steps):

$$2\text{N}_2\text{H}_3 \rightarrow \text{N}_2\text{H}_6 \rightarrow \text{N}_2 + 2\text{NH}_3 \quad \ldots (5)$$

$$\text{N}_2\text{H}_3 + \text{Fe(phen)}^{2+} \rightarrow \text{N}_2\text{H}_6 + \text{Fe(phen)}^{2+} + \text{H}^+ \quad \ldots (6)$$

$$\text{N}_2\text{H}_6 + 2\text{Fe(phen)}^{2+} \rightarrow \text{N}_2 + 2\text{Fe(phen)}^{2+} + 2\text{H}^+ \quad \ldots (7)$$

This simultaneous oxidation of the $\text{N}_2\text{H}_6$ radical accounts for the fractional stoichiometry observed.

The results of study on the influence of added methanol on the rate show that the reaction is favoured in a medium of low dielectric constant. This indicates that the transition state is stabilised due to a dispersal of charge and its formation is favoured in less polar solvents. However, the increase in rate is less pronounced when methanol is greater than 50% (vol/vol). This may be due to decrease in activity of the water molecule participating in the reaction. This is obvious in solutions of higher methanol content. The proposed mechanism leads to the rate law (8)

$$-\frac{d[\text{Fe(III)}]}{dt} = \frac{k_1 k_2 [\text{Fe(III)}]_0 [\text{Substrate}]_0 [\text{Phen}]^2}{K_1 K_2 [\text{Substrate}]_0 [\text{Phen}]^2 + \{K_1 [\text{Phen}]^2 + [\text{SO}_4^{2-}\}] \{1 + K_1 [\text{H}^+]\}} \quad \ldots (8)$$

This rate law demands that the plots of $1/k_1$ versus $1/[\text{Substrate}]$, $1/k_1$ versus $1/[\text{Phen}]$, $1/k_1$ versus $[\text{H}^+]$ and $1/k_1$ versus $[\text{HSO}_4^-]$ should all be linear with positive intercepts on the $1/k_1$ axis. This is actually found to be the case as shown in Fig. 1, supporting the plausibility of the proposed mechanism.

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References