Oxidation of Lysine by Ferricyanide in Presence of Osmium(VIII)

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Osmium(VIII) catalysed oxidation of lysine by ferricyanide in excess ferrocyanide shows a complex kinetics. The order in lysine falls from 1 to 0 while that in ferricyanide increases from 0 to 2 with large increase in lysine concentration. The rates were directly proportional to [Os(VIII)] and $\{Const. + [Fe(CN)_6^4]\}$. A suitable mechanism is proposed and discussed.

Oxidation von Lysin mittels Ferricyanid in der Gegenwart von Osmium(VIII)

Die von Os(VIII) katalysierte Oxidation von Lysin mit Ferricyanid in überschüssigem Ferrocyanid zeigt eine komplexe Kinetik. Bei starker Steigerung der Lysinkonzentration fällt die Ordnung bezüglich Lysin von 1 auf 0, während bezüglich Ferricyanid eine Erhöhung von 0 auf 2 festzustellen ist. Die Geschwindigkeitskonstanten waren direkt proportional zu [Os(VII)] und $\{Const. + [Fe(CN)_6^4]\}$. Es wird ein möglicher Mechanismus vorgeschlagen und diskutiert.

Introduction

Earlier studies on the osmium(VIII) catalysed oxidation of α-amino acids by ferricyanide have shown a strong ferrocyanide ion autocatalysis. However, in presence of excess ferrocyanide these autocatalytic effects could be avoided and steady state conditions could be achieved. In the present communication, the results of the kinetics of osmium(VIII) catalysed oxidation of lysine by ferricyanide in excess ferrocyanide are reported and examined mechanistically.

Experimental

Aqueous solutions of lysine monohydrochloride were freshly prepared from BDH samples of the reagent, Potassium ferrocyanide solutions were freshly

prepared from a recrystallised reagent. All other solutions were prepared by the same procedure as reported earlier[1].

The kinetics were followed by examining aliquot portions of the reaction mixture for ferricyanide spectrophotometrically using a Bausch and Lomb Spectronic-20 spectrophotometer. Measurements were made at 420 nm where absorbance due to ferrocyanide was negligible.

The reaction mixture containing a known excess of ferricyanide over lysine was kept at 40° in presence of $0.1M$-NaOH, $3.90 \times 10^{-6}M$-osmium(VIII) and $5.0 \times 10^{-3}M$-Fe(CN)$_6^{4-}$ for six hours.

The keto acid as the product was detected by spot tests[2] which is in agreement with the earlier work[3] on the oxidation of lysine by osmium(VIII).

The oxidation process can be represented by the following stoichiometric equation $[R = NH_2(CH_2)_4]$:

$$RCHNH_2COOH + 2\,Fe(CN)_6^{3-} + 2\,OH^- =$$
$$= RCOCOOH + NH_3 + H_2O + 2\,Fe(CN)_6^{4-}$$
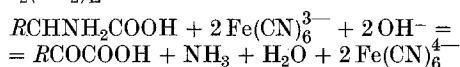
Results

[Fe(CN)$_6^{3-}$] — Time plots were found to be linear approximately up to 75% of the reactions and therefore, pseudo-zero order rate constants in ferricyanide (k_0) were obtained for various concentration of the reactants (Table 1).

Table 1. *Effect of concentration of* [Fe(CN)$_6^{3-}$] *and* [lysine] *on the rate constant[a] at 35°*

[Fe(CN)$_6^{3-}$]$M \times 10^4$	[lysine]$M \times 10^3$	$k_0 \times 10^5$ mol l^{-1} min^{-1}
3.0	4.0	2.08
3.5	4.0	2.18
4.0	4.0	2.08
4.5	4.0	2.18
5.0	4.0	2.25
5.0	1.6	1.31
5.0	2.4	1.70
5.0	3.2	1.98
5.0	5.6	2.54
5.0	8.0	2.66

[a] $[OH^-] = 0.1M$, $[Fe(CN)_6^{4-}] = 5.0 \times 10^{-3}M$ and $[Os(VIII)] = 3.90 \times 10^{-6}M$.

A change in ferricyanide concentration had no effect on the k_0 values (Table 1) thus establishing zero order dependence in ferricyanide. The order in osmium(VIII) was obtained as unity (Fig. 1, A).
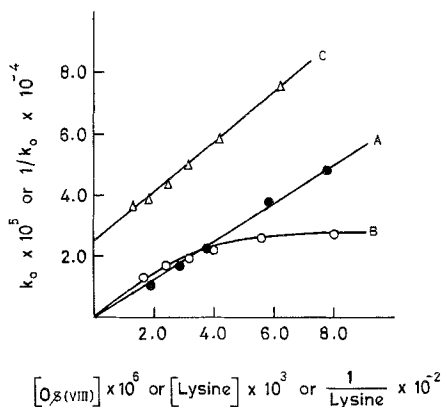
Fig. 1. A: plot of k_0 vs. [Os(VIII)] at 35°; [OH$^-$] = $0.1M$, [Fe(CN)$_6^{3-}$] = 5.0 $\times$ $10^{-4}M$, [Fe(CN)$_6^{4-}$] = $5.0 \times 10^{-3}M$ and [lysine] = $4.0 \times 10^{-3}M$. B: plot of k_0 vs. [lysine] at 35°; [OH$^-$] = $0.1M$, [Fe(CN)$_6^{3-}$] = $5.0 \times 10^{-4}M$, [Fe(CN)$_6^{4-}$] = $5.0 \times 10^{-3}M$ and [Os(VIII)] = $3.90 \times 10^{-6}M$. C: plot of $1/k_0$ vs. $1/$[lysine] at 35°, conditions as in B
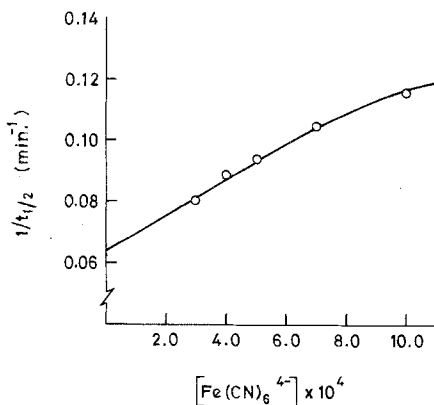

Fig. 2. Plot of [Fe(CN)$_6^{4-}$] vs. $1/t_{\frac{1}{2}}$ at 35°; [OH$^-$] = $0.2M$, [Os(VIII)] = 3.90 $\times 10^{-6}M$, [Fe(CN)$_6^{3-}$] = $5.0 \times 10^{-4}M$ and [lysine] = $4.0 \times 10^{-3}M$

The plot of k_0 vs. [lysine] (Fig. 1, B) showed a deviation from straight line behaviour at higher concentrations of lysine suggesting that the order in lysine falls from unity to zero.

At low ferrocyanide ion concentration the concentration—time plots were curves with increasing slope, the half life periods ($t_{\frac{1}{2}}$) of the reaction dropping sharply. A plot of [Fe(CN)$_6^{4-}$] vs. $1/t_{\frac{1}{2}}$ ($\alpha\, k_0$) gave a

straight line with positive intercept (Fig. 2) which suggests that the rate was proportional to $\{Const. + [Fe(CN)_6^{4-}]\}$. At higher concentration of ferrocyanide the concentration—time plots were linear with the k_0 values, first levelling off and then showing a decreasing trend (Table 2).

A tenfold change in NaOH concentration (0.02 to 0.20M) showed a slight increasing effect on the rate constant (1.40 to 3.05 × × 10^{-5} mol l^{-1} min^{-1}). Measurements were made at 35°, 40°, 45° and 50° to investigate the effect of temperature. The energy of activation was evaluated from the *Arrhenius* plots as 11.53 ± 0.05 kcal mol^{-1}.
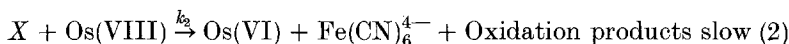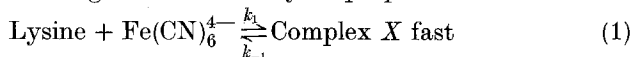
Table 2. *Effect of* $[Fe(CN)_6^{4-}]$ *on the rate constant*[a] *at 35°*

$[Fe(CN)_6^{4-}]/M \times 10^3$	1.0	2.0	3.0	4.0	5.0	10.0
$k_0 \times 10^5$/mol l^{-1} min^{-1}	1.83	2.20	2.34	2.38	2.25	1.81

[a] $[OH^-] = 0.1\,M$, $[Fe(CN)_6^{3-}] = 5.0 \times 10^{-4}\,M$, $[OsO_4] = 3.90 \times 10^{-6}\,M$ and $[lysine] = 4.0 \times 10^{-3}\,M$.
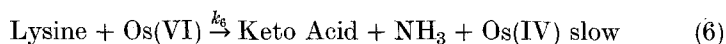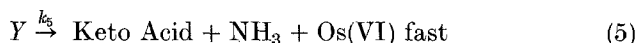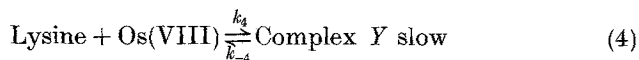
Discussion

A zero order dependence in ferricyanide clearly suggests its involvement in the fast step. The strong catalytic incluence of low ferrocyanide ion also suggests the possible interaction between lysine and ferrocyanide to give a complex. As the oxidation does not proceed in absence of osmium(VIII) (even in presence of ferrocyanide), the lysine—ferrocyanide complex formed is oxidised by osmium(VIII) in a slow step. The following mechanism may be proposed.

$$\text{Lysine} + Fe(CN)_6^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex } X \text{ fast} \tag{1}$$

$$X + \text{Os(VIII)} \overset{k_2}{\rightarrow} \text{Os(VI)} + Fe(CN)_6^{4-} + \text{Oxidation products slow} \tag{2}$$

$$\text{Os(VI)} + 2\,Fe(CN)_6^{3-} \overset{k_3}{\rightarrow} \text{Os(VIII)} + 2\,Fe(CN)_6^{4-} \text{ fast} \tag{3}$$

The amino acid—ferrocyanide complex has already been characterised spectrophotometrically in our earlier studies[1]. Similar results were obtained for the lysine—ferrocyanide complex. Iron(II) complexes of aminoacids[4] and in some cases $Fe(CN)_6^{4-}$ complexes[5] are also reported in literature.

It is mentioned[3,6] that amino acids form complexes with osmium(VIII) which are subsequently degraded to keto acids, ammonia and osmium(VI). The liberation of ammonia has been a function of the rate of oxidation. It is also mentioned that at high

amino acid concentration, osmium(VI) is further reduced to osmium(IV) by a fresh molecule of amino acid via a slow step. In the case of lysine the reactions may be represented as,

$$\text{Lysine} + \text{Os(VIII)} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{Complex } Y \text{ slow} \tag{4}$$

$$Y \overset{k_5}{\rightarrow} \text{Keto Acid} + NH_3 + \text{Os(VI)} \text{ fast} \tag{5}$$

$$\text{Lysine} + \text{Os(VI)} \overset{k_6}{\rightarrow} \text{Keto Acid} + NH_3 + \text{Os(IV)} \text{ slow} \tag{6}$$

However in the presence of ferricyanide a fast interaction between
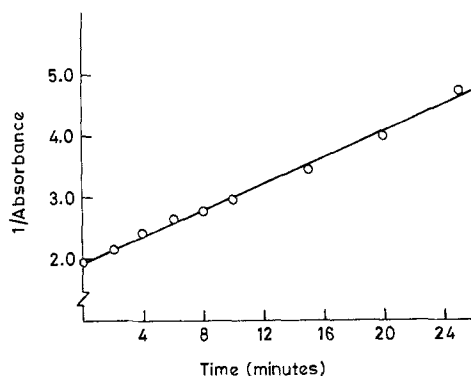
Fig. 3. $[Fe(CN)_6^{3-}]^{-1}$—time plot at $35°$; $[OH^-] = 0.1\,M$, $[\text{Os(VIII)}] = 3.90 \times 10^{-6}\,M$, $[Fe(CN)_6^{3-}] = 5.0 \times 10^{-4}\,M$, $[Fe(CN)_6^{4-}] = 5.0 \times 10^{-3}\,M$ and [lysine] $= 4.0 \times 10^{-2}\,M$

osmium(VI) species and $Fe(CN)_6^{3-}$ takes place to regenerate osmium-(VIII)[7].

Applying the steady state condition with respect to X, Y and osmium(VI) in the steps (1)—(6), the rate law equation for the disappearance of ferricyanide is obtained as,

$$-\frac{d}{dt}[Fe(CN)_6^{3-}] = \frac{k_3[\text{lysine}][\text{Osmium(VIII)}][Fe(CN)_6^{3-}]^2}{k_6[\text{lysine}] + k_3[Fe(CN)_6^{3-}]^2}$$

$$\{\frac{k_4 k_5}{k_{-4} + k_5} + \frac{k_1 k_2}{k_{-1}}[Fe(CN)_6^{4-}]\} \tag{7}$$

where $k_1 \gg k_2\,[\text{Os(VIII)}]$ has been taken as suitable approximation.

According to rate law equation (7) the rate would be proportional to $[\text{Os(VIII)}]$ and $\{Const. + [\text{Fe(CN)}_6^{4-}]\}$ as obtained experimentally. The order in lysine and ferricyanide would be variable. At low lysine concentration where $k_3 [\text{Fe(CN)}_6^{3-}]^2$ would be large in comparison to k_6 [lysine] (k_6 being small) and the rate would be of first order in lysine and zero order in ferricyanide. However, at large lysine concentrations, the above approximation is not valid and eventually the rate would be proportional to

$$\frac{[\text{Lysine}]}{k_6 [\text{lysine}] + k_3 [\text{Fe(CN)}_6^{3-}]^2}$$

suggesting a straight plot of $1/k_0$ vs. $1/[\text{lysine}]$. Further at extremely large concentrations where the rate would become nearly independent to [lysine] the order in Fe(CN)_6^{3-} would be nearly two. Our experimental results in Fig. 1 C and Fig. 3 show a good agreement to this fact.

The slight decrease in rate constants at large ferrocyanide concentration could be due to little conversion of osmium(VIII) to Os(VI) by the reverse of step (3) resulting in a decrease in the concentration of catalyst osmium(VIII).

Acknowledgement

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