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CATALYSIS IN INORGANIC REDOX REACTIONS AND MECHANISM*

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Catalysis in inorganic redox reactions operates through a redox cycle or through complex formation between the catalyst and one of the reactants. Reactions occurring with inner sphere mechanism, appear to be catalyzed, but in reality they are not. Induced reactions too do not fall in the category of catalysed reactions. Some reactions are made faster by an optimum concentration of a substance, ensuing a chain mechanism. Such reactions too cannot be regarded as catalyzed. Trace metal ions present as impurities in the reagents and the distilled water are often the source or catalysis in redox reactions.

Key Words : Catalysis; Mechanism; Redox Reactions

INTRODUCTION

CATALYSIS is a phenomenon of wide coverage involving homogeneous and heterogeneous systems, but studies in the former systems are more defined and governed by rigorous chemical laws. Homogeneous systems involve gas phase reactions and more commonly aqueous systems. The latter comprise acid-base reactions, substitution reactions and redox reactions involving chemical change and isotopic exchange reactions with no net chemical change. I wish to describe in my lecture the catalytic role of substances in redox reactions involving chemical change. However, whatever be the description of catalytic role for redox systems, it may also be partly or wholly true for other systems.

Kinetics has been one of the strong tools to know the mechanism of reactions. Kinetics involves the effect of several parameters on the rate, and catalysis by substances has a significant role in elucidating the mechanism. It is therefore pertinent to categorize the various ways in which the mechanistic role of catalyst can be described. In redox reactions which by and large, are inorganic in nature, catalysis by metal ions is a general feature. These metal ions are present in traces in the reagents and even in the distilled water. More common of them are copper (II), iron(III), manganese(II), osmium(VIII) etc. In addition to these, salts and complexes of silver(I), gold(III), ruthenium(II), palladium(II), platium(II) etc. have often been employed to study catalysis in a kinetics study.

Before describing the role of a catalyst in redox reactions let us see what a catalyst is. The commonly known definition that it is a substance which participates

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in the reaction in such a way that it is the product also, is a thermodynamic one. The definition from the viewpoint of kinetics is that it is one of the reactants which appears in the rate law, but not in the stoichiometric equation. The stoichiometry and the rate law for the Ag(I) catalysed oxidation of Mn(II) with peroxydisulphate[1] are given as follows :

Stoichiometry

$$S_2O_8^{2-} + 2Mn(II) \xrightarrow{Ag(I)} 2SO_4^{2-} + 2Mn(III) \quad ...(1)$$

Rate Law

$$-\, d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}]\,[Ag(I)] \quad ...(2)$$

—consistent with the following mechanism

$$S_2O_8^{2-} + Ag(I) \xrightarrow{k} SO_4^{-} + SO_4^{2-} + Ag(II) \quad ...(3)$$

$$Ag(II) + Mn(II) \xrightarrow{fast} Ag(I) + Mn(III) \quad ...(4)$$

$$SO_4^{-} + Mn(II) \xrightarrow{fast} Ag(I) + Mn(II) \quad ...(5)$$

The catalyst functions by opening new paths for the reaction which have increased rates. The above reaction provides an example for such a new path.

Examples

The main role of a catalyst in all such reactions is through a redox cycle involving two oxidation states of the metal, one of which is highly reactive. In the above example Ag(I) is the normal oxidation state and Ag(II) is the reactive state, and it is the Ag(I)/Ag(II) cycle that operates in the redox reaction. Ag(I)/Ag(II) is not the unique redox cycle for Ag(I) and the other redox cycle for the same metal is Ag(I)/Ag(O) as round in the oxidation[2] of H_3PO_2 with vanadium(V). Following are the stoichiometry, rate law and mechanism.

Stoichiometry

$$H_3PO_2 + 2V(V) + H_2O \longrightarrow H_3PO_3 + 2V(IV) + 2H^+ \quad ...(6)$$

Rate Law

$$-\, d[V(V)]/dt = k\,[Ag(II)]\,[H_3PO_2] \quad ...(7)$$

Mechanism

$$Ag(I) + H_3PO_2 \xrightarrow{k} Ag(O) + H_3PO_2^+ \quad ...(8)$$

$$H_3PO_2^+ + H_2O \xrightarrow{fast} H_3PO_3 + 2H^+ \quad ...(9)$$

$$Ag(O) + V(V) \xrightarrow{fast} Ag(I) + V(IV) \quad ...(10)$$

Thus we find that in the first example the rate is independent of the reducing substance and in the other one, rate is independent of the concentration of the oxidant. This is usually what is found in case of redox cycles involving silver (I).

Copper(II) catalysis in the oxidation[3] of V(III) by Fe(III) in acid solutions is operated through Cu(II)/Cu(I) cycle and thus the rate is independent of the concentration of oxidant. The stoichiometry, rate law and the mechanism are given below :

Stoichiometry

$$V(III) + Fe(III) \longrightarrow V(IV) + Fe(II) \qquad ...(11)$$

Rate Law

$$-\, d[Fe(III)]/dt = k\,[V(III)]\,[Cu(II)] \qquad ...(12)$$

Mechanism

$$V(III) + Cu(II) \xrightarrow{k} V(IV) + Cu(I) \qquad ...(13)$$

$$Cu(I) + Fe(III) \xrightarrow{\text{fast}} Cu(II) + Fe(II) \qquad ...(14)$$

Oxidation[4] of phosphite with $Fe(CN)_6^{3-}$ is catalyzed by osmium(VIII) and the rate is independent of the concentration of $Fe(CN)_6^{3-}$. The redox cycle Os(VIII)/Os(VI) operates. Osmium(VIII) is reduced with phosphite in a slow step to osmium(VI) and the latter is oxidized to osmium(VIII) in a fast step with $Fe(CN)_6^{3-}$.

Stoichiometry

$$2Fe(CN)_6^{3-} + HPO_3^{2-} + 2OH^- \longrightarrow 2Fe(CN)_6^{4-} + HPO_4^{2-} + H_2O \qquad ...(15)$$

Rate Law

$$-\, d[Fe(CN)_6^{3-}]/dt = \frac{2kK\,[Os(VIII)]\,[OH^-]\,[HPO_3^{2-}]}{(1 + K\,[OH^-])} \qquad ...(16)$$

Mechanism

$$Os^{VIII}O_3(OH)_3^- + OH^- \overset{K}{\rightleftharpoons} OsO_4^{VIII}(OH)_2^{2-} + H_2O \qquad ...(17)$$

$$Os^{VIII}O_4(OH)_2^{2-} + HPO_3^{2-} + H_2O \xrightarrow{k} Os^{VI}O_2(OH)_4^{2-} + HPO_4^{2-} \qquad ...(18)$$

$$Os^{VI}O_2(OH)_4^{2-} + 2Fe(CN)_6^{3-} \xrightarrow{\text{fast}} Os^{VIII}O_2(OH)_4 + 2Fe(CN)_6^{4-} \qquad ...(19)$$

$$Os^{VIII}O_2(OH)_4 + OH^- \xrightarrow{\text{fast}} Os^{VIII}O_3(OH)_3^- + H_2O \qquad ...(20)$$

Thus we can have numerous such examples in which the transition metal ions operate the catalysis through a redox cycle. It is obvious from the above examples that the rate is independent of the concentration of one of the reactants. However, there are examples where the redox cycle operates but the rate is not independent of the concentration of any one of the reactants. I shall return to this point later.

From the kinetics point of view a general case of catalysis involving a redox cycle is given by the following mechanism where R_1 and R_2 are the reactants, P_1 and P_2 are the products, and C is a catalyst. C^* is the reactive intermediate of an oxidation state different than that of C.

Mechanism

$$R_1 + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_1 + C^* \qquad \ldots(21)$$

$$C^* + R_2 \xrightarrow{k_3} P_2 + C \qquad \ldots(22)$$

Rate Law

$$-\mathrm{d}[R_2]/\mathrm{d}t = \frac{k_1 k_3 [R_1][C][R_2]}{(k_2[P_1] + k_3[R_2])} \qquad \ldots(23)$$

If in the rate law (23), $k_3[R_2] \gg k_2[P_1]$, it reduces to (24).

$$-\mathrm{d}[R_2]/\mathrm{d}t = k_1[R_1][C] \qquad \ldots(24)$$

and thus the rate is independent of the concentration of R_2. The examples of Ag(I) and Os(VIII) catalyses given above just refer to this special situation. If, however, $k_2[P_1] \gg k_3[R_2]$, rate law (23) reduces to (25)

$$-\mathrm{d}[R_2]/\mathrm{d}t = k_1 \frac{k_3}{k_2} \frac{[R_1][C][R_2]}{[P_1]} \qquad \ldots(25)$$

Oxidation[5] of $Fe(CN)_6^{4-}$ with $H_4P_2O_8$ in the presence of $Cu(EDTA)^{2-}$ complex is an example which has a general rate law of the type (23) which can be reduced to the type (24) or (25) under the two extreme conditions. The simplified mechanism and and the rate law are the following:

Stoichiometry

$$H_4P_2^{VI}O_8 + 2Fe(CN)_6^{4-} + 2H^+ \longrightarrow 2H_3P^{V}O_4 + 2Fe(CN)_6^{3-} \qquad \ldots(26)$$

Mechanism

$$Cu^{II}(EDTA)^{2-} + Fe(CN)_6^{4-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cu^{I}(EDTA)^{3-} + Fe(CN)_6^{3-} \qquad \ldots(27)$$

$$Cu(EDTA)^{3-} + H_4P_2O_8 \xrightarrow{k_3} \text{products} \qquad \ldots(28)$$

Rate Law

$$+ d[Fe(CN)_6^{3-}]/dt = \frac{k_1k_3\,[Cu^{II}\,EDTA]\,[Fe(CN)_6^{4-}]\,[H_4P_2O_8]}{(k_2\,[Fe(CN)_6^{3-}] + k_3\,[H_4P_2O_8])} \quad ...(29)$$

If one takes into account the hydrogen ion dependence and the various species of Fe(II) and $H_4P_2O_8$, the complete rate law is (30) which is very complicated. Nevertheless, it has been verified under various situations of concentrations.

Rate Law

$$+ d[Fe(III)]/dt = \frac{k_1k_3\,[Cu^{II}\,edta]\,[PDP]\,[Fe(CN)_6^{4-}]\,[H^+]^2}{(k_2k_5\,[Fe(III)] + k_3k_1k_2\,[PDP]\,[H^+])\,(1 + K_3)\,[H^+] + K_3K_4\,[H^+]^2)} \quad ...(30)$$

Mechanism

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^- \quad ...(31)$$

$$HP_2O_8^- + H^+ \overset{K_2}{\rightleftharpoons} H_4P_2O_8 \quad ...(32)$$

$$Fe(CN)_6^{4-} + H^+ \overset{K_3}{\rightleftharpoons} HFe(CN)_6^{3-} \quad ...(33)$$

$$HFe(CN)_6^{3-} + H^+ \overset{K_4}{\rightleftharpoons} H_2Fe(CN)_6^{2-} \quad ...(34)$$

$$Cu(EDTA)^{2-} + HFe(CN)_6^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cu(EDTA)^{3-} + HFe(CN)_6^{2-} \quad ...(35)$$

$$Cu(EDTA)^{3-} + H_4P_2O_8 \xrightarrow{k_3} \text{products} \quad ...(36)$$

TABLE I

Effect of Fe(III) and Cu(II) on the initial rate (v_0) in the $Fe(CN)_6^{4-}$ — $H_4P_2O_8$ reaction in the absence and presence of EDTA

[PDP] = 1×10^{-3}M; $[Fe(CN)_6^{4-}] = 1.0 \times 10^{-2}$M; $[HClO_4]$ = 0.05M; 35° [EDTA] = 0

10^3[Fe(III)]/M	0.1	1.0	10.0	100.0	
$10^6(v_0)/Ms^{-1}$	5.0	11	13	24	
	[EDTA] = 2×10^{-3}M				
10^3[Fe(III)]/M	0.0	0.1	1.0	10.0	100.0
$10^6(v_0)/Ms^{-1}$	1.9	1.9	1.7	1.8	1.7
	[EDTA] = 0				
10^3[Cu(II)]/M	1.0	10.0	20.0	40.0	
$10^6(v_0)/Ms^{-1}$	18	8	5.0	2.0	
	[EDTA] = 2×10^{-4}M				
10^3[Cu(II)]/M	1.0	10.0	20.0	40.0	
$10^6(v_0)/Ms^{-1}$	2.7	5.3	8.7	13	

The trace amounts of copper(II) and iron(II) present in the reagents or distilled water greatly influence the rate of reaction. Aqueous Fe(II)/Fe(III) and EDTA complexes of Cu(II) accelerate the rate whereas aquo-Cu(II) ions inhibit the rate EDTA complexes of Fe(III) have no effect on the rate. These results presented in Table I clearly bring out these facts. Although kinetics of Fe(II) catalyzed reaction have not been studied, perhaps the catalysis can be explained on the same lines as for Cu^{II} EDTA complex. However, the inhibition by aquo Cu(II) is still a mystery.

Another way in which the catalysis operates, is through modification of the reacting species and the path of the reaction essentially does not change. In this process the catalyst forms an intermediate complex which is more reactive. A general case with R_1 and R_2 as reactants and 'C' as a catalyst is given below:

Mechanism

$$R_1 + C \overset{K}{\rightleftharpoons} R_1C \qquad \ldots(37)$$

$$R_1C + R_2 \overset{k}{\longrightarrow} \text{products} \qquad \ldots(38)$$

Rate Law

$$-\,\mathrm{d}\,[R_2]/\mathrm{d}t = \frac{kK\,[R_1]\,[C]\,[R_2]}{(1 + K\,[R_1])} \qquad \ldots(39)$$

Cu(II) catalyzed oxidation[6] of NH_3OH^+ with $S_2O_8^{2-}$ is one such example.

$$Cu^{2+} + S_2O_8^{2-} \overset{K}{\rightleftharpoons} CuS_2O_8 \qquad \ldots(40)$$

$$CuS_2O_8 + NH_3OH^+ \overset{k}{\longrightarrow} \text{products} \qquad \ldots(41)$$

There is spectrophotometric evidence too for the complex formation in addition to the kinetics one. There is absolutely no evidence for Cu(II)/Cu(I) or Cu(II)/Cu(III) redox cycle. Similarly, in the Fe(III) catalyzed oxidation[7] of hydrazine with peroxydisulphate, there is strong kinetics evidence for the complex formation between Fe^{3+} and $S_2O_8^{2-}$. The reaction, however, is quite complicated since the complex $FeS_2O_8^+$ undergoes further complexing with hydrazine and that they form at least three such complexes. Two of them are kinetically reactive.

Mechanism

$$Fe^{3+} + S_2O_8^{2-} \overset{K}{\rightleftharpoons} FeS_2O_8^+ \qquad \ldots(42)$$

$$FeS_2O_8^+ + N_2H_5^+ \overset{K_1}{\rightleftharpoons} FeS_2O_8.N_2H_4^+ + H^+ \qquad \ldots(43)$$

$$\Big\downarrow k_1$$

$$\text{products}$$

$$FeS_2O_8 \cdot N_2H_4^+ + N_2H_5^+ \overset{K_2}{\rightleftharpoons} FeS_2O_8 \cdot N_2H_4 \cdot N_2H_5^{2+} \qquad \ldots(44)$$

$$FeS_2O_8 \cdot N_2H_4 \cdot N_2H_5^+ \overset{K_3}{\rightleftharpoons} FeS_2O_8(N_2H_4)_2^+ + H^+ \qquad \ldots(45)$$
$$\Big\downarrow k_2$$
$$\rightarrow \text{products}$$

The limiting rate laws under the two conditions, $[N_2H_5^+] < 5.0 \times 10^{-3}M$ and $[N_2H_5^+] > 15 \times 10^{-3}M$, are

$$-\,d\,[S_2O_8^{2-}]/dt = \frac{kK_1\,[N_2H_5^+]\,[Fe(III)]/[H^+]}{1 + (K_1\,[N_2H_5^+]/[H^+])} \qquad \ldots(46)$$

and

$$-\,d\,[S_2O_8^{2-}]/dt = \frac{k_2K_3\,[Fe(III)]}{[H^+] + K_3} \qquad \ldots(47)$$

Thus one can see that the rate is independent of $[S_2O_8^{2-}]$ under all conditions and it is also independent of the concentration of hydrazine when the excess of latter is present.

In general, K of equation (37) is small and there is no kinetic evidence for complex formation. It is from structural properties and other methods that one can know of the complex formation. Silver(I) catalyzed oxidation[8] of As(III) and Sb(III) with peroxodiphosphate is an example for this and the rate law is (48)

$$-\,d\,[As(III)]/dt = k\,[PDP]\,[As(III)]\,[Ag(I)] \qquad \ldots(48)$$

at constant hydrogen-ion concentration. k is quite complex if one considers the complete rate law for the hydrogen ion dependence.

Reactions of relatively unreactive molecules such as hydrogen have been shown to be catalyzed by a variety of metal ions and complexes. An example of such a reaction is the oxidation[9] of H_2 in aqueous solutions by oxidants such as Cr(VI), Fe(III) etc. catalyzed by Cu(II). The mechanism and the rate law are the following :

Mechanism

$$Cu^{2+} + H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+ \qquad \ldots(49)$$

$$CuH^+ + Cu^{2+} \overset{k_3}{\rightarrow} 2Cu^+ + H^+ \qquad \ldots(50)$$

$$2Cu^+ + 2/3Cr(VI) \overset{\text{fast}}{\longrightarrow} 2Cu^{2+} + 2/3Cr(III) \qquad \ldots(51)$$

Rate Law

$$-\,d\,[H_2]/dt = \frac{k_1k_3[Cu^{2+}]^2\,[H_2]}{k_2[H^+] + k_3[Cu^{2+}]} \qquad \ldots(52)$$

The order in Cu(II) varies between one and two and the rate has inverse hydrogen-ion dependence. In a rather loose sense, the role of Cu(II) catalyst can be regarded as stabilising H^- ion released by heterolytic splitting of H_2 into H^- and

H^+. The ability to stabilize otherwise unstable reaction intermediates such as hydride ion, alkyl group etc. by coordination as ligands is one of the factors that explains the versatile ability of transition metal ions in a great variety of reactions.

There are instances where one may have direct evidence for a redox cycle to operate, but there is no kinetic evidence. One such instance is the Ag(I) catalyzed oxidation[10] of water with peroxodiphosphate. Silver(I) and PDP are likely to form a weak complex. Under proper *p*H conditions, Ag(I) and pdp yield a chocolate coloured solution which can be regarded a complex of Ag(II)/Ag(III) with PDP. Thus, higher valent silver is definitely formed on mixing Ag(I) and pdp, and water is oxidized presumably with Ag(II)/Ag(III). However, there is no kinetic evidence for a redox cycle like Ag(I)/Ag(II) or Ag(I)/Ag(III). Since in other oxidation of peroxodiphosphate (As(III), Sb(III), $N_2H_5^+$, NH_3OH^+ etc.) the rate is not independent of the reducing substance though there is evidence for higher valent silver, it appears that highervalent silver has no existence as an intermediate. but that it is formed transiently in the activated complex itself.

Reactions between negatively charged ions such as MnO_4^- and MnO_4^{2-} are catalyzed by cations such as Cs^+ and $Co(NH_3)_6^{3+}$, and the catalysis has been attributed to the formation of ion pairs. Most reactions involving $Fe(CN)_6^{4+}$ and $Fe(CN)_6^{3-}$ are catalyzed by alkali metal cations.[11]

Similarly, the reaction between two metal ions is catalyzed in the presence of anions which form ion pairs. The reduced charge on the reactants brings about greater overlap of the orbitals and facilitates the electron transfer.

It may be mentioned that most of the electron exchange reactions or redox reactions between two different metal ions seem to be catalyzed by anions or neutral molecules. However, these are not true cases of catalysis according to the definition of the catalysis. The anions or groups from complexes with one of the metal ions and the two ions react by an inner sphere mechanism. The anions or groups never exist in the free state. The reactions[12] of $Cr(H_2O)_6^{2+}$ with different $Co(NH_3)_5X^{3+}$ complex ions show increased rate if X is H_2O and is replaced by OH^-, and Cl^-. It is not a case of catalysis by OH^- or Cl^- since they become part of the product $CrOH^{2+}$ or $CrCl^{2-}$ after the reaction. A reaction worth reporting in this connection is the oxidation[13] of Cr(II) with Fe(III) in presence of chloride ions. The reaction is catalyzed by chloride ions only partially. Part of the reaction occurs as $FeCl^{2+}$ and Cr^{2+} which is not truly catalytic. The complete rate law is

$$-\mathrm{d}[\mathrm{Fe(III)}]/\mathrm{d}t = k_1[\mathrm{Cr^{2+}}][\mathrm{Fe^{3+}}] + k_2[\mathrm{Cr^{2+}}][\mathrm{FeOH^{2+}}] + k_3[\mathrm{Cr^{2+}}][\mathrm{FeCl^{2+}}] + k_4[\mathrm{Cr^{2+}}][\mathrm{Fe^{3+}}][\mathrm{Cl^-}] \quad \ldots(53)$$

The first two terms refer to the uncatalyzed reactions and the fourth term refers to the catalyzed reaction. The mechanism of the catalyzed path (4th) may be the following :

$$Cr(H_2O)_6^{2+} + Fe(H_2O)_6^{3+}, Cl^- \longrightarrow [(H_2O)_5\, Cr^{II}\text{–}Cl\text{–}H_2O - Fe^{III}(H_2O)_5]^{4+}$$
$$\longrightarrow Cr(H_2O)_5\, Cl^{2+} + Fe(H_2O)_6^{2+}$$

and

$$Cr(H_2O)_5\, Cl^{+} + Fe(H_2O)_6^{3+} \longrightarrow [(H_2O)_5\, Cr^{II}\text{–}Cl\text{–}H_2O - Fe^{III}(H_2O)_5]^{4+}$$
$$\longrightarrow Cr(H_2O)_5\, Cl^{2+} + Fe(H_2O)_6^{2+}$$

The point to be stressed is that bridge-activated inner sphere mechanism should not be confused with the process of catalysis.

Although induction period may be one of the characteristics of the catalyzed reactions, Induced reactions are not to be regarded as catalyzed reactions. The classical induced oxidation of arsenite with oxygen in the presence of sulphite is too well known.

Since then several induced reactions, mostly involving Cr(VI) have been discovered. Induced oxidations involving permanganate have been recently reported.[14] The reaction[15] of peroxodiphosphate with hypophosphite or phosphite in acidic solutions, is slow, but both these reactions are induced by iron(II). The details for H_3PO_2 are given below.

$$H_4P_2O_8 + Fe(II) \longrightarrow H_3PO_4 + HPO_4 + Fe(III) \quad ...(54)$$

$$HPO_4^{-} + Fe(II) \longrightarrow HPO_4^{\cdot 2-} + Fe(III) \quad ...(55)$$

$$2HPO_4^{-} + H_3PO_2 + H_2O \longrightarrow 2HPO_4^{2-} + H_3PO_3 \quad ...(56)$$

There is yet another class of reactions which does not fall in the category of catalyzed reactions, but appears to be one. The oxidation[16] of H_2O_2 with Tl(III) is very slow, but in the presence of 1×10^{-7}M or more of Fe(II), the reaction is over within seconds. Following is the mechanism :

Fe(II) present ($1 \times 10^{-7}M$) *as pre-reductor in the oxidation of* H_2O_2 *with Thallium(III) in Aqueous* $HClO_4$ *Solutions*

$$Tl(III) + H_2O_2 \xrightarrow{\text{slow}} Tl(I) + O_2 + 2H^+ \quad ...(57)$$

$$Tl(III) + Fe(II) \xrightarrow{\text{fast}} Tl(II) + Fe(III) \quad ...(58)$$

$$Tl(II) + H_2O_2 \xrightarrow{\text{fast}} Tl(I) + H_2O_2^{+} \quad ...(59)$$

$$Tl(III) + H_2O_2 \xrightarrow{\text{fast}} Tl(II) + O_2 + 2H^+ \quad ...(60)$$

An optimum concentration of Fe(II) to start the reaction to a chain process in 10^{-7}M. The chain involves Tl(II) and $H_2O_2^{+}$ as the intermediates. Fe(II) is not a catalyst. Fe(II)/Fe(III) redox cycle does not operate since Fe(III) has no effect on the reaction. It is not an induced reaction either. Fe(II) can be regarded as a pre-reductor.

Trace Metal Ions

In the beginning a reference was made to the presence of trace metal ions present in the reagents and the distilled water and their influence on the rates of chemical reactions. This effect is so significant and of such a magnitude that it requires a special mention.

It is well known that oxidations of As(III) are catalyzed by Os(VIII), iodide, Cu(II) and perhaps other metal ions which are still to be discovered. The system of As(III) is peculiar in so far that one does not obtain reproducible results in redox reaction particularly in oxidations with Ce(IV),[17] peroxydisulphate[18] and hexacyanoferrate(III).[19] Limited reproducibility is obtained only when the same stock solution of As(III) is employed. Perhaps one or more trace metal ions are present in As(III) samples which make the kinetic results irreproducible. Cobalt(II) has the same role in the decomposition of peroxymonosulphuric acid.[20] 1×10^{-9} molar concentrations of Co(II) increases the rate of decomposition. Similarly, a quantity of Cu(II) of the order of 1×10^{-6}M present in reagents or distilled water is responsible for the irreproducible results in redox reactions involving peroxydisulphate. All such systems can be made to yield reproducible results by complexing these trace metal ions with EDTA. However, while doing so, one must ensure that EDTA itself does not participate in any type of redox reaction.

Catalysis by trace metal ions is more obvious in reactions involving hexacyanoferrate(III) and hexacyanoferrate(II). The catalysis by Cu(II) is so significant in the cysteine oxidation[21] with $Fe(CN)_6^{3-}$ that one can determine the quantity of Cu(II) in samples by studying the kinetics of this reaction. This quantity is of the order of 10^{-8}M. Similarly, oxidations[22] of hydroxylamine with $Fe(CN)_6^{3-}$ are catalyzed by Cu(II) and Fe(II)/Fe(III). Catalysis by Cu(II) and Fe(III) in peroxodiphosphate oxidation of $Fe(CN)_6^{4-}$ has already been talked of, and 1×10^{-9}M Fe(II) is effective as a catalyst. The following chart clearly shows the difference in the catalytic behaviours of Cu(II) and Fe(III) in the presence of EDTA. Role of Cu^{II} (aquo) and Fe^{III} (aquo) and their EDTA complexes in $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ systems.

1. Cu^{II}(aquo) inhibits
2. Cu^{II}(EDTA) catalyzes

$$Fe(CN)_6^{4-} \underset{\text{reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} Fe(CN)_6^{3-}$$

1. Cu^{II}(aquo) catalyzes
2. Fe^{III}(aquo) catalyzes

$$Fe(CN)_6^{4-} \underset{\text{reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} Fe(CN)_6^{3-}$$

1. Fe^{III}(EDTA) catalyzes
2. Fe^{III}(aquo) inhibits

In the end it is necessary to mention one of our recent observations highlighting the same point, i.e., the significant role of trace metal ion impurities in the redox reactions. It is the oxidation of pyridine with hexacyanoferrate(III) in alkaline solutions. The rate is independent of the concentrations of both the reactants, C_6H_5N and $Fe(CN)_6^{3-}$. This is impossible and the rate should depend on the concentration of something under all situations. A careful analysis by atomic absorption spectroscopy revealed that 10^{-8}M impurity of Os^{VIII} monitors the rate of reaction. Os(VIII) forms complexes with pyridine. The rate is 1st order in Os^{VIII} or in such Os(VIII) complexes and thus the rate is independent of C_6H_5N. These complexes undergo redox reaction yielding Os(VI) and C_5H_5NO. Os(VI) is oxidized in a fast step with $Fe(CN)_6^{3-}$ and thus the rate is independent of $Fe(CN)_6^{3-}$.

Based on these observations of catalysis by trace metal ions and also the fact that perhaps most reactions in our body are catalyzed by trace metal ions, one wonders whether the catalysis by metal ions is a universal feature in inorganic redox reactions. Such a sweeping statement is incapable of a proof at moment since there is a limit to the purity of the obtainable chemicals and the distilled water and we really cannot have the reagents free of trace metal ions. It would therefore be premature to make a sweeping statement that all redox reactions are metal-ion catalyzed ones.

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