STUDIES ON THE AUTOXIDATION OF SOME IRON II COMPOUNDS

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STUDIES ON THE AUTOXIDATION OF SOME IRON(II) COMPOUNDS

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SUMMARY

The effect of hydroxyl ion and citrate ion concentrations on the rate of autoxidation of Fe II has been investigated in the present study. Different mixtures of constant final volume, different initial hydroxyl ion concentrations and variable citrate ion concentrations at fixed temperatures were prepared. The rate of autoxidation was followed by analysing aliquots of the reaction mixture for Fe II. This was done by titration against standard potassium dichromate using diphenyl benzidine as indicator.

The hydroxyl ion was found to enhance the autoxidation process. This was reflected on the increase in the initial rate of reaction and on the increase in the specific rate constant of the reaction. The citrate ion had a similar effect and the temperature was found to increase the specific reaction rates.

The results were explained on the basis of the oxidisability of the different iron II species present in the reaction mixture. These species are $\left[Fe(H_2O)_6\right]^{++}$, $\left[Fe(OH)_n\right]^{-n+2}$ and $\left[Fe(cit)_n\right]^{-3n+2}$.

The oxidation potentials of the aquo and hydroxo complexes are -0.77 and +0.56 volts respectively. The corresponding oxidation potential of the citrato complex has a value which lies between those of the aquo and hydroxo complexes. Thus, both the hydroxo and citrato complexes are oxidisable with dissolved oxygen while the aquo complex is not.

All the plots relating log(a-x) versus (t) obeyed the first order rate law with respect to Fe II giving a straight line relation with a distinct break. This was explained by assuming that in the early stages of the reaction both the hydroxo and citrato complexes are oxidised. As the oxidation process goes on the pH of the reaction mixture drops and the concentration of the hydroxo complex becomes negligibly small. Thus, the part of the curve after the break point represents the oxidation of the citrato complex only. A mechanism for the reaction is suggested.

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INTRODUCTION

INTRODUCTION

Oxidation and reduction

The term oxidation is applied to any process which involves the passage of a compound representing a lower stage of combination with oxygen to a substance equivalent to a higher stage of combination with oxygen, by the addition of oxygen or of an electronegative atom or radical, or by the removal of hydrogen or an electropositive atom or radical. Reduction is the converse of oxidation.

In terms of the ionic theory, oxidation is defined as a process ~~accompanied~~ by loss of electrons. For example the oxidation of ferrous salts to ferric salts can be simply represented as the change of the ferrous to the ferric ion by the loss of an electron, i.e.

$$Fe^{++} \longrightarrow Fe^{+++} + e$$

Reduction, on the other hand, can be considered as a process accompanied by gain of electrons, e.g. reduction of a chlorine atom to chloride ion:

$$Cl + e \longrightarrow Cl^{-}$$

Thus, in the oxidation of ferrous chloride by chlorine, the over all reaction can be represented as:

$$2\ Fe^{++} + Cl_2 \longrightarrow 2\ Fe^{+++} + 2\ Cl^-$$

In the case of gaseous systems the evidence is clear that direct electron transfer between molecules does occur. In a number of cases the probability of electron transfer, expressed as a collision diameter, is known.

Electron transfer which would go readily in gas phase between two particles will be hindered by the presence of solvent molecules. This is because such molecules prevent the extension into space of the orbitals on the exchanging particles.

In particular the ligands of a complex ion will act as good insulating groups for electrons and orbitals of the central metal ion.

In aqueous solution it is usually possible to imagine atom or group transfer, rather than electron transfer, as occurring in redox reaction. For example iron II ion may act as reducing agent by transferring a hydrogen atom from its hydration shell to a substrate.

$$Fe(H_2O)_6^{2+} + R' \longrightarrow Fe(H_2O)_5(OH)^{2+} + RH$$

Iron III ion may act as oxidising agent by transferring hydroxyl radical to a substrate.

$$Fe(H_2O)_6^{3+} + R' \longrightarrow Fe(H_2O)_6^{2+} + H^+ + ROH$$

In general transfer of a positive group or atom is equivalent to the transfer of electrons, and transfer of a negative group or atom is equivalent to the taking of electrons.

Oxidation-Reduction Processes :

The rates of redox processes are of considerable chemical interest and many detailed kinetic studies have involved complex ions, including the aquo cations of the transitional elements. Especially useful, are rate studies of isotopic exchange reactions between two valency states of an element. Since these reactions can proceed, on a formal basis at least, by the transfer of an electron from the reduced to the oxidized form of an element they are termed "electron exchange reactions".

e.g.

$$Fe^{2+}_{aq} + \overset{*}{Fe}{}^{3+}_{aq} \rightleftharpoons \left[Fe^{2+}_{aq} \xrightarrow{e} \overset{*}{Fe}{}^{3+}_{aq} \right] \neq \rightleftharpoons Fe^{3+}_{aq} + \overset{*}{Fe}{}^{2+}_{aq}$$

No exchange reactions so far reported have involved oppositely charged ionic reactants.