

I N T R O D U C T I O N

There has been considerable interest in recent years in oxidation-reduction reactions. The classical definition of oxidation and reduction in terms of gain or loss of oxygen have in modern times been abandoned in favour of the concept of electron loss (oxidation) and electron gain (reduction). Oxidation-reduction reactions are also defined as involving changes in oxidation states or oxidation numbers. The assignment of oxidation numbers is based on the following rules : (i) the oxidation number of an atom in an element is zero; (ii) the oxidation number of monoatomic ion is its charge; (iii) the oxidation number of each atom in a covalent compound of known structure is the charge remaining on the atom when each shared electron pair is assigned completely to the more electronegative of the two atoms sharing it. An electron pair shared by like atoms is split between them and (iv) the oxidation number of an element in a compound of uncertain structure is usually obtained by assigning reasonable oxidation numbers to the other elements in the compound. Generalisations are also made depending on the position of an element in the periodic table.

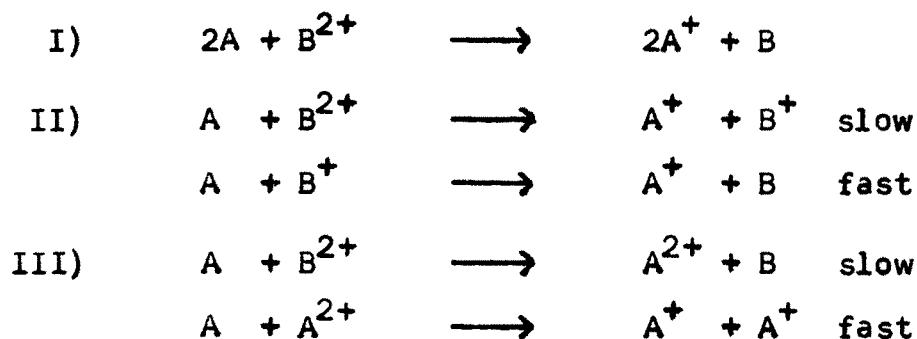
Oxidation-reduction reactions may involve one or more electron transfer. Depending upon the number of electrons transferred between the oxidant and the reductant, the reaction may proceed in one or more steps.

Such electron transfers are governed by two classical principles :

i) The first of these is the Michaelis principle of "Compulsory univalent oxidation steps"¹. This hypothesis involves the principle that an oxidation-reduction reaction takes place in one or more successive, single electron transfer steps. This principle evolved from a consideration of a restricted field of redox reactions, of which the oxidation of hydroquinones to quinones through semiquinone intermediate is typical and is now generally recognized as being without universal validity. Apart from reactions involving metal ions, many 2-equivalent redox reactions are now known which proceed in one step through the transfer of a hydride ion or an oxygen atom (e.g. $\text{NO}_2^- + \text{OCl}^- \longrightarrow \text{NO}_3^- + \text{Cl}^-$)^{2,3}.

ii) Shaffer's principle of "equivalence change"^{4,5} refers to the observation that non-complementary reactions (i.e., those between 1-equivalent oxidants and 2-equivalent reductants or vice versa) are often slow compared with complementary ones (those between 1-equivalent oxidants and 1-equivalent reductants or 2-equivalent oxidants and 2-equivalent reductants). Examples are the slow reduction of Tl^{3+} by Fe^{2+} or Ce^{4+} by Tl^+ compared with the rapid reduction of Tl^{3+} by Sn^{2+} and of Ce^{4+} by Fe^{2+} . This can be interpreted in terms of the following types of

mechanism for a typical non-complementary reaction in which 'A' is oxidised to 'A⁺' and 'B²⁺' is reduced to 'B' :



The first of these mechanisms is expected to be slow because it involves a termolecular step and the last two because they involve the formation of unstable intermediates (B⁺ or A²⁺).

One of the implications of the comparison on which the principle of equivalence change is based is that reactions between 2-equivalent oxidants and 2-equivalent reductants occur by a concerted 2-equivalent step. This may well be the case for reactions such as the Tl(I) - Tl(III) exchange.⁶

The observation expressed by Shaffer, for non-complementary reactions, is based on the low probability of termolecular mechanisms as one possibility or the formation of the unstable valence states as the other possibility.⁷ Another expected feature of these reactions will be the frequent occurrence of catalysis since the normal paths will be slow.

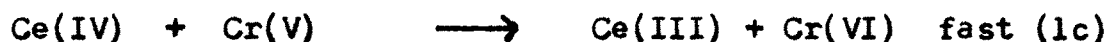
Unstable oxidation states :

The formation of unstable oxidation states during the course of non-complementary reactions has been now anticipated in a number of such reactions with sufficient proofs. The reductions, for example, of Tl(III) by Fe(II)⁸, V(III) or V(IV)⁹ can only be explained through the formation of unstable Tl(II) species.

The interconversions between Cr(III) and Cr(VI) always appear to involve the unstable states Cr(IV) and Cr(V). In a classic study, King and Tong¹⁰ have worked out the details of the redox reaction between Ce(IV) and Cr(III) in aqueous sulphuric acid. The rate law was found to be as in (1) which is very reasonably explained by the mechanism

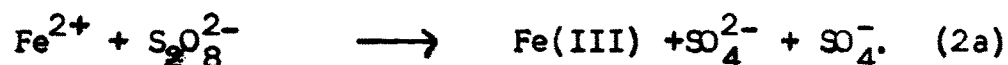
$$\text{Rate} = \frac{k[\text{Ce(IV)}]^2 [\text{Cr(III)}]}{[\text{Ce(III)}]} \quad \dots \quad (1)$$

involving steps of 1(a) to 1(c). The first step is a rapid



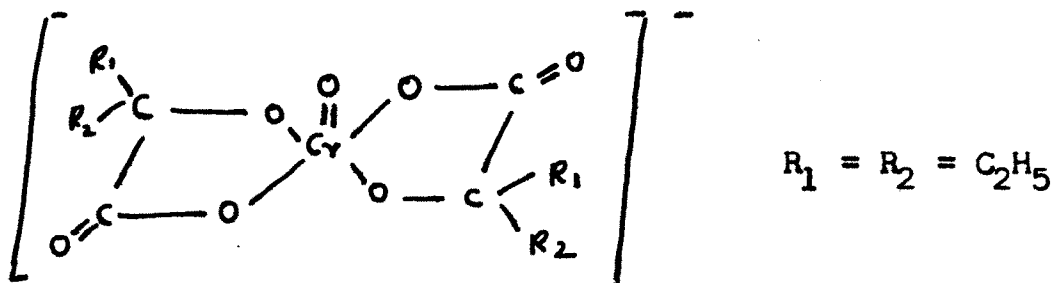
equilibrium, and the second step, the interconversion of Cr(IV) and Cr(V), is rate determining. Excellent support

comes from the studies of related reactions such as the oxidation of vanadyl ion by acid chromate ion (HCrO_4^-)¹¹ and the analytically important oxidation of ferrous ion by acid chromate ion¹². It is significant that in the above example, the changeover from Cr(V) to Cr(IV) or vice versa, is rate determining. This may be related to the likelihood that, at this stage, a change in coordination number from 4 to 6 occurs¹⁰. The existence of the intermediates, Cr(IV) and Cr(V), is sustained by the observation of induced oxidations. The direct reaction of acid chromate and iodide ion is slow, but the addition of Fe^{2+} or VO^{2+} will cause rapid oxidation of iodide¹³. The stoichiometric examination of the reaction between acid chromate and Fe^{2+} or VO^{2+} in presence of iodide leads to the conclusion that the rapid oxidation of iodide is because of its reaction with Cr(V). A related phenomenon is seen in the oxidation of As(III) by persulphate ion. This slow reaction is accelerated or oxidation is induced by adding Fe(II) and the reaction is postulated to go by the formation of As(IV) from the reaction (2a,2b)¹⁴.



While the chromium(V) formed during chromium(VI) oxidation is unstable, water soluble stable carboxylate

chromium(V) complexes have been synthesised (I)¹⁵. The redox reactions and mechanisms involving I with various organic and metal reductants have been reported¹⁶. The formation of oxochromate(IV) complexes of various



porphyrin ligands and some alkoxide complexes of Cr(IV) in non-aqueous solvents have been reported¹⁷. The rapid decomposition in contact with moisture complicates further studies on these systems.

As mentioned earlier, another feature of these unstable oxidation states is the frequent occurrence of catalysis. A number of studies of the catalysis by platinum metals of oxidation reactions have been made¹⁸. The catalysis by Ag(I)⁹, Cu(II), Mn(II) and Cr(III) in oxidation-reduction reactions are also found to occur through formation of unstable oxidation states¹⁹⁻²¹.

The predominant species :

The rate equation that can be interpreted in terms of mechanistic proposals expresses the rate as a function of the concentrations of species in their predominant forms. The experimental data, however, are originally formulated

in terms of laboratory concentrations, variously referred to as stoichiometric or total concentrations. One case to be considered is when a reactant is converted to an entirely different species by reaction with the solvent or with other substrates. In many instances this is almost a trivial situation : the addition of a small concentration of NH_3 to aqueous mineral acid converts it almost entirely to NH_4^+ , and the real laboratory variables are $[\text{NH}_4^+]$ and $[\text{H}^+]$. The concentration of NH_3 , being quite small, is controlled only indirectly. Similarly, when VCl_4 is dissolved in water, VO^{2+} is formed, and when cyanogen is dissolved in base, it undergoes complete conversion to CN^- and CNO^- .

The species involved in many overall chemical reactions may be subject to other equilibria, which are maintained rapidly relative to the main reaction. These equilibria serve to reduce the concentration of a reacting species from the value of the formal concentration. For example, the concentration of Fe^{3+} in a solution is lowered appreciably by the addition of even small quantities of HF owing to the formation of the rather stable complex FeF^{2+} , and the partial ionization of H_3PO_2 lowers the concentration of this species below the added quantity.

To formulate the reaction rate as a function of species concentrations, therefore, requires a knowledge of the existence of such equilibria and, generally speaking, the knowledge or determination of one or more

equilibrium constants. The distinction between the species and laboratory concentrations is particularly critical in the cases of partially displaced equilibria, because the rate equations, if cast in the form of reaction rate as a function of laboratory concentrations, quite often resemble the equations applicable to entirely different mechanisms.

A familiar and frequent incident where preequilibria are important has to do with the pH dependence of a reaction rate. The case where an acid-base reaction converts a significant fraction of a reactant into a different form (which may be more reactive than the original) and the case where only a very small fraction is converted to a highly reactive form often lead to rate laws of the same algebraic form. In general, one must be able to evaluate the appropriate equilibrium constants to distinguish the alternatives.

Effect of ions on the rate :

The rates of redox reactions of complex ions are very sensitive to the presence of other ions in the solution. Usually, added anions have the greatest influence on the reaction of two cations with each other, and added cations influence the rate of two anions with each other. Large effects of anions on the rate are usually attributed to the formation of bridged species if labile complexes are involved.

In the redox reactions between two cations, if the reducing agent is complexed first, it will be more stabilized in the oxidised form and hence the reaction is speeded up in presence of anion. Also a negative ion should enable two positive ions to approach each other more easily. This will be most effective if the negative ion is between the two cations in the transition state.

If the oxidising agent is complexed first, the anion may stabilise it and slow down its rate of reaction. For example, the rate of reactions of Ce^{4+} oxidations are reduced strongly by forming sulphate complexes²² in presence of sulphate. This shows, in agreement with theory, that coulombic repulsions between the reactants do not play a dominant role. The conclusion to be drawn is not that electrostatic factors do not exist, but that other factors (reorganisation energies) are of greater importance. Some significant effects of chloride ion are particularly noticeable in redox reactions. The redox reactions, in which the reductant is able to form complexes with chloride, are found to be accelerated by chloride ion. Among the reductants that can form complexes with chloride are Tl(I) , Sn(II) and Sb(III) . Presumably because of the complex formation, the oxidation potentials of such redox systems are changed. The oxidation potentials of the complexes Hg(II)/Hg(I) , Fe(III)/Fe(II) and Tl(III)/Tl(I) are decreased considerably in presence of chloride ion²³⁻²⁵.

Present work :

The work undertaken in the present dissertation entitled "Study of Kinetics and Mechanism of Some Inorganic Reactions in Presence of Salts" comprises the following:

- (I) Vanadium(V) oxidation of thallium(I) in hydrochloric acid.

The vanadium(V) oxidation of thallium(I) is facile in concentrated hydrochloric acid only. The reaction was studied in 4 m hydrochloric acid and was found to follow the second order rate law. The detailed study led to a mechanism involving intervention of reactive thallium(II) species and the reaction is understood to occur between VO^{2+} of the oxidant species and TlCl_3^{2-} of the reductant.

- (II) Analysis of thallium(I) by vanadium(V)

The reaction between vanadium(V) and thallium(I) studied in chapter (I) it is found that 50% of the reaction is complete within 30 minutes at room temperature. Therefore this reaction is utilised to determine thallium(I) by vanadium(V) at a slight higher temperature of 40°C . The determination was carried out at the ranges of concentrations i.e. 1×10^{-4} to $4 \times 10^{-4} \text{ mol dm}^{-3}$ and 1×10^{-3} to $5 \times 10^{-3} \text{ mol dm}^{-3}$.

(III) Effect of sulphate ions on the thallium(III)-
Uranium(IV) reaction : Analysis of the reported
data.

The reaction between Tl(III) and U(IV) has been studied²⁶ by A.C. Harkness and J. Halpern perchloric acid. The reaction was found to be accelerated by the addition of sulphate ion which was explained due to the complex formation of thallium(III) with sulphate. But they have not analysed the data in order to know which of the thallium(III) sulphate species is active.

Therefore, in this chapter an attempt is made to analyse the reported data for a probable mechanism in presence of sulphate.

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