

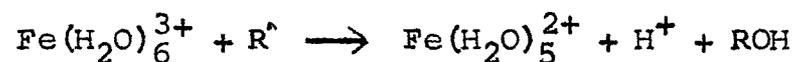
INTRODUCTION

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 has 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 transfer of electrons is a book keeping device for effecting the changes in oxidation states and for balancing the equations.

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



Iron(III) ion may act as an oxidizing agent by transferring hydroxyl radical to a substrate :



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 up of electrons.

The problem, then, in studying the mechanism of an oxidation - reduction reaction, is to find out whether atom transfer or electron transfer occurs, which atoms are transferred or how many electrons are transferred, and what intermediates, stable or unstable, are formed. A complete study would include a detailed picture of the transition state for all steps involved. Not only the composition but also the geometry of the transition state is desired.

Oxidation - reduction in inorganic reactions :

Two general classes of transition states emerge for redox reactions involving metal complexes, the so-called "Outer - sphere" and "inner-sphere" types¹. In the first of these, the inner coordination shells of both metal ions are intact in the transition state. In the second case, the two metal ions are connected through a bridging ligand common to both coordination shells. In both cases, either atom or electron transfer can occur. It is also possible that outer sphere reactions can have weak bridging groups connecting the two coordination shells.

Oxidation - reduction in organic reactions :

The oxidation - reduction concepts, however, are not so clearly applicable in organic chemistry, for when carbon compounds are oxidized their component atoms are very seldom

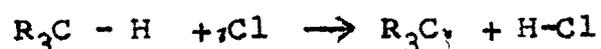
deprived of their surrounding complete electron shells. Again, few oxidations of organic compounds are reversible reactions and formulation of a reaction scheme that would lead to an overall free energy decrease gives no warranty that such a reaction can be effected.

Classification of oxidation processes :

The study of oxidation is essentially an examination of ways by which electrons can be removed from organic compounds. Now organic compounds are essentially covalent and have their valency electrons associated together in pairs. Moreover they are mainly composed of a carbon skeleton surrounded by a skin of hydrogen and consequently have few superficial electrons accessible for direct attack by colliding reagents. Covalent bond fission is an essential feature of organic reactions and it can be effected by two different pathways, viz., "homolytic reactions" in which electron pairs are symmetrically disrupted and "heterolytic reactions" in which electron pairs are transferred from one particle to another as an undivided entity. Electron removals by these two pathways have clearly distinguishable characteristics.

In homolytic oxidations electrons are removed singly from organic molecules by active atoms, such as chlorine, or by active free radicals. Though molecules containing unshared electrons can be oxidized in this way, homolytic oxidations

usually involve the removal from an organic molecule of one electron together with a hydrogen nucleus, e.g.,



The initial organic product necessarily has an unpaired electron and so must perforce undergo a reaction of similar type, e.g.,



or must combine with another free radical before stable entities alone result. Thus chain reactions, dimerizations or disproportionations, e.g.,



are typical of homolytic oxidation.

All homolytic electron transfer reactions, such as above, require very much less activation energy than that needed for the direct breakage of a covalence. Hence homolytic oxidations, when once started, proceed very rapidly indeed. The traces of free radicals required for the initiation of homolytic oxidation may be formed by the thermal dissociation of molecules which have weak covalences, by disruption of molecules by exposure to radiant energy, high-energy particles (eg., α -rays) or electrons (β -rays), or by single electron transfer from ions of transition elements which can have

incomplete inner (d, . . .) electron shells. Consequently oxidations which are demonstrably prone to catalysis in these ways are homolytic in type.

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents which can, by a single process, gain control of a further electron pair. Heterolytic oxidants therefore attack the exposed electron pairs of atoms such as oxygen, nitrogen or sulphur, or the loosely held π -electrons of olefins, rather than the buried electron pairs of C-H, O-H or N-H bonds. Again, heterolytic reactions yield stable molecular, or ionic, products in one, or at most two consecutive stages and very seldom lead on to chain reactions. On the other hand they usually require more activation energy than homolytic reactions and so tend to be slower processes. They do not necessarily require catalysis, but even if this is so then the catalysts - bases, acids or lewis acids - are quite different from those concerned in promoting homolytic reactions.

Electron transfer reactions :

Oxidation-reduction reactions may involve one or more electron transfer. Depending upon the number of electrons transferred between the oxidant and 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"². This hypothesis involves the principle that an oxidation-reduction reaction takes place in one or more successive single electron transfer steps. 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., $\text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^-$)^{3,4}.
- ii) Shaffer's principle of "equivalence change"^{5,6} 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+} .

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 $\text{Tl(I)}-\text{Tl(III)}$ exchange⁷.

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 possibility⁸. Another expected feature of these reactions will be the frequent occurrence of catalysis since the normal paths will be slow.

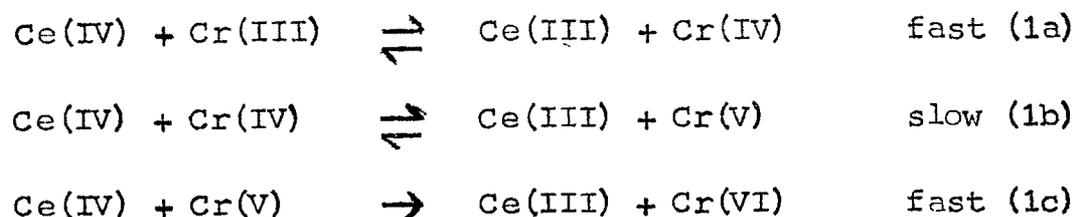
Unstable oxidation states :

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)⁹, V(III) or V(IV)¹⁰ can only be explained through the formation of unstable Tl(II) species.

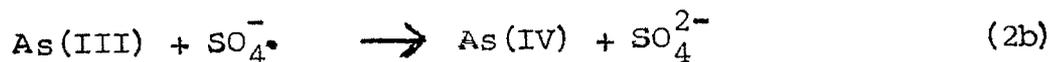
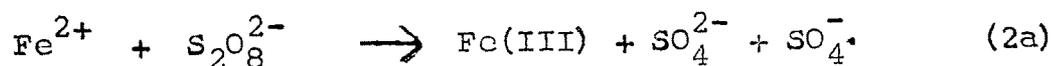
The interconversions between Cr(III) and Cr(VI) always appear to involve the unstable states Cr(IV) and Cr(V). In a classic study, King and Tong¹¹ have worked out the details of the redox reaction between Ce(IV) and Cr(III) in aqueous sulphuric acid. The rate law was found to be as in (1) which is very reasonably explained by the mechanism,

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

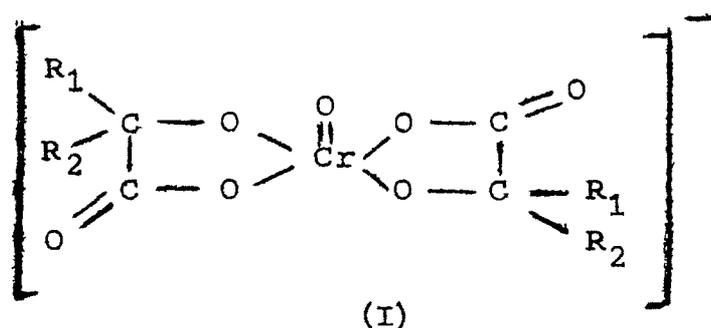
involving steps of 1(a) to 1(c). The first step is a rapid



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^-)¹² and the analytically important oxidation of ferrous ion by acid chromate ion¹³. 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 occurs¹¹. 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 iodide¹⁴. 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)¹⁵.



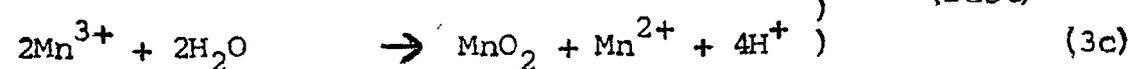
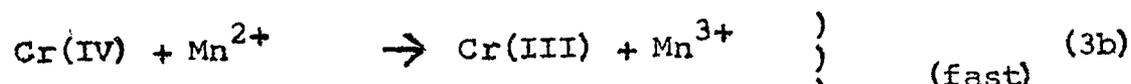
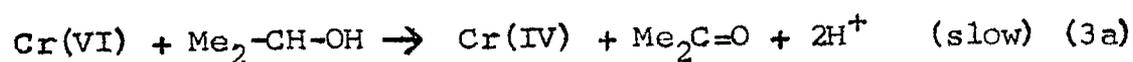
While the chromium(V) formed during chromium(VI) oxidations is unstable, water soluble stable carboxylate chromium(V) complexes have been synthesised (I)¹⁶. The redox



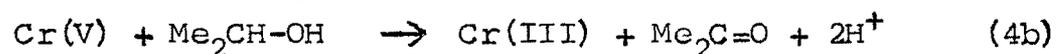
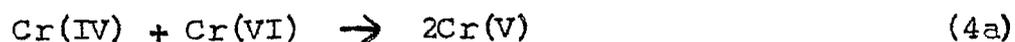
reactions and mechanisms involving (I) with various organic and metal reductants have been reported¹⁷. The formation of oxochromate(IV) complexes of various porphyrin ligands and some alkoxide complexes of Cr(IV) in non-aqueous solvents have been reported¹⁸. The rapid decomposition in contact with moisture complicates further studies on these systems.

The reduction of chromic acid to a chromic salt by an organic compound¹⁹ must necessarily occur in stages since the overall valency change from Cr(VI) to Cr(III) involves the transfer of three valency electrons, i.e., more than can be provided by the rupture of any covalence. In the oxidation of isopropanol the rate-determining reaction undoubtedly involves the reduction of Cr(VI) to an unstable ion of Cr(IV). This is

so since the oxidation carried out in presence of a manganese(II) salt leads to manganese dioxide formation. The amount of manganese dioxide formed accounts for one-third of the oxidising power of the initial chromate, although chromic acid itself does not oxidise manganous ions. Hence one may write as in (3a,3b,3c) :



If manganese or cerous salts are present in excess, then the initial rate of oxidation of isopropanol by chromic acid is reduced by about 50% and hence Westheimer concluded that, in the absence of manganous ions, the following fast reactions (4a,4b) occur, the oxidation of the isopropanol being regarded entirely as a two-electron transfer.



Even yet very little is known about the nature and chemical properties of the ions formed in aqueous acid from either Cr(V) or Cr(IV), for their lifetimes are too short for their study by spectroscopic methods. A further complication concerning chromic acid oxidations is the fact that many

different ionic species of Cr(VI) can exist in solution.

In the thallium(III) oxidation of organic compounds²⁰ thallium(II) is found to be an intermediate species.

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 made²¹. The catalysis by Ag(I)¹⁰, Cu(II), Mn(II) and Cr(III) in oxidation-reduction reactions are also found to occur through formation of unstable oxidation states²²⁻²⁴.

Catalysis :

In catalysis, an outside substance added to a reaction influences the rate of the reaction without itself undergoing any change chemically. Such outside substances, called catalysts, influence reactions by changing the reaction path. Such catalytic influence arises as a consequence of lowering the energy of activation. For all practical purposes, the catalyst can : 1) increase the velocity of a reaction, (2) direct the reaction towards a specific product and (3) eliminate undesired side reactions. In short, by means of catalysis, higher yields of a purer product in shorter reaction time become possible. In solution reactions involving inorganic oxidations, the catalysts are ions having unstable oxidation states. This case is a particular example of

homogeneous catalysis where the catalyst is in the same phase as the reactants.

Chromium(III) is a case in point as it has been utilized as a catalyst for cerimetric analysis of organic²⁴ and inorganic²⁵ **substrates**. The catalysis is understood to be due to the intermediate oxidation states of chromium. A detailed study of the chromium(III) catalysis of cerium(IV)-arsenic(III) reaction emphasized the role of chromium(IV)²⁵. Among others, osmium(VIII) has been frequently used as a catalyst for many organic and inorganic reactions both in alkali and acid media²⁶.

Recently another concept was introduced into the literature of catalysis, namely, 'complex action' catalysts, i.e., mixed catalysts which are comprised of two or more catalytic substances each capable of catalyzing a particular reaction^{27,28}.

Induced reactions :

In some cases in which an intermediate valence state is produced from a catalyst species the original state may not be regenerated fast enough compared to continued reaction of the intermediate state. In such cases the 'catalyst' is consumed and the system is referred to as an 'induced' or 'coupled redox system'. An example of such a system is the oxidation of I^- by $HCrO_4^-$ induced by Fe^{++} ²⁹. Here I^- or Fe^{++}

and HCrO_4^- react to form an intermediate state, presumably Cr(V) and I (or Fe^{3+}). In presence of excess Fe^{++} or I^- the Cr(V) state is further reduced to Cr(IV) or Cr(III) . The Cr(IV) goes on to react with another equivalent of I^- to give Cr(III) and I . Depending on the relative concentrations, it is found that about two equivalents of I^- and one of Fe^{++} are oxidized for each Cr(VI) reduced to Cr(III) . The study of induced reactions is very valuable in giving information on the reactivity and presence of intermediate valence states.

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 complexes³⁰ 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.

Present work :

The work undertaken in the present thesis entitled "A study of kinetics and mechanism of some catalysed and uncatalysed oxidation reactions", comprises the following :

IA Chromium(III) catalysed cerium(IV) oxidation of dimethyl sulfoxide (DMSO) :

The chromium(III) catalysis of cerium(IV) oxidation of DMSO in an acid medium is studied. A chromium(IV) species is involved in the catalysed path. $H_3Ce(SO_4)_4^-$ is understood to be the active oxidant in both the uncatalysed and catalysed reactions in the presence of sulphuric acid. Chromium(III) was unchanged after the reaction. It is found that no

catalyst - substrate complex formation is involved in the reaction. A mechanism is proposed to explain the experimental results.

IB Chromium(VI) oxidation of DMSO in aqueous acetic acid :

The oxidation of DMSO by chromium(VI) in aqueous acetic acid is fourth order, first order each in oxidant, substrate and second order in acid. Chromium(III) and dimethyl sulfone are the only products found and the reaction is not affected by initial addition of the products. Intervention of chromium(IV) in the mechanism is indicated in experiments in presence of manganese(II) and free radicals shown by polymerisation in presence of acrylamide. Added chloride ions inhibit the oxidation. A mechanism in agreement with experimental data has been proposed.

II Osmium(VIII) catalysed cerium(IV) oxidation of antimony(III) :

The oxidation - reduction reaction between cerium(IV) and antimony(III) catalyzed by osmium(VIII) has been studied in sulphuric acid and perchloric acid media. The reaction is first order in osmium(VIII) over a wide concentration range. The cerium(IV) and arsenic(III) dependencies are complex and depend upon the relative ratios of these two species. A reaction mechanism and resulting rate law which satisfy the experimental results are reported. Antimony(III) reduces osmium(VIII) to osmium(VI) and osmium(IV) by two-electron

steps. The resulting osmium(IV) and osmium(VI) are reoxidized to osmium(VIII) by cerium(IV) in one-electron steps. The main active species is found to be $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$.

IIIA Manganese(III) oxidation of arsenic(III) in aqueous sulphuric acid :

The noncomplementary manganese(III) oxidation of arsenic(III) follows an approximately second order rate law in aqueous sulphuric acid. The initially added product manganese(II) decreases the rate while arsenic(V) has no effect. The order in H^+ is found to be -0.8 and the main active species is understood to be $\text{Mn}(\text{OH})_2^+$. A mechanism in agreement with experimental data has been proposed and rate law verified. Some rate constants are obtained. Calculated rates using these constants are in reasonable agreement with the experimental rates.

IIIB Chloride catalysed manganese(III) oxidation of arsenic(III) in aqueous sulphuric acid :

The reaction is first order in manganese(III), fractional order in arsenic(III) and chloride and is found to be independent of H^+ concentration. The initially added products, arsenic(V) and manganese(II) have no effect on the reaction. A mechanism in agreement with the experimental results has been proposed and the rate law verified. Some reaction constants are obtained. Calculated rates using these

derived constants are in reasonable agreement with the experimental rates.

IIIC Osmium(VIII) catalysed manganese(III) oxidation of arsenic(III) in aqueous sulphuric acid :

The oxidation-reduction reaction between manganese(III) and arsenic(III) catalysed by osmium(VIII) has been studied in 5M sulphuric acid. The order in osmium(VIII) is around unity. The manganese(III) and arsenic(III) dependencies are complex and depend upon the relative ratios of these two species. A reaction mechanism and resulting rate law which satisfy the experimental results are reported. Arsenic(III) reduces osmium(VIII) to osmium(VI) and osmium(IV) by two-electron steps. The resulting osmium(IV) and osmium(VI) are reoxidized to osmium(VIII) by manganese(III) in one-electron steps. The active species of manganese(III) is found to be Mn(OH)^{2+} .

References

- 1 H. Taube,
Adv. Inorg. Chem. Radiochem, 1, 1 (1959).
- 2 L. Michaelis,
Trans. Electrochem. Soc, 71, 107 (1937);
Cold Spring Harbor Symp. Quant. Biol, 7, 33 (1939).
- 3 M. Anbar and H. Taube,
J. Am. Chem. Soc., 80, 1073 (1958).
- 4 Stewart,
Experimentia, 15, 401 (1959).
- 5 P.A. Shaffer,
J. Am. Chem. Soc., 55, 2169 (1933);
P.A. Shaffer,
J. Phys. Chem., 40, 1021 (1936);
P.A. Shaffer,
Cold Spring Harbor Symp. Quant. Biol, 1, 50 (1939).
- 6 J. Halpern,
Can. J. Chem., 37, 148 (1959).
- 7 R.J. Prestwood and A.C. Wahl,
J. Am. Chem. Soc., 71, 3137 (1949);
G. Harbottle and R.W. Dodson,
J. Am. Chem. Soc., 73, 2442 (1951) and
S.W. Gilks and G. Nord-Waind,
Disc. Faraday Soc., 29, 102 (1960).



- 8 F. Basolo and R.G. Pearson,
"Mechanisms of Inorganic Reactions",
John Wiley, New York, 2nd edition (1967) p. 474.
- 9 C.E. Johnson Jr.,
J. Am. Chem. Soc., 74, 959 (1952);
K.G. Ashurst and W.C.E. Higginson,
J. Chem. Soc., 3044 (1953) and
S.A. Chimatadar and J.R. Raju,
J. Inorg. Nucl. Chem., 43, 1947 (1981).
- 10 W.C.E. Higginson, D.R. Rosseinsky, J.B. Stead
and A.G. Sykes,
Disc. Faraday Soc, 29, 49 (1960).
- 11 J.Y. Tong and E.L. King,
J. Am. Chem. Soc., 82, 3805 (1960).
- 12 J.H. Espenson,
J. Am. Chem. Soc., 85, 5101 (1964).
- 13 J.H. Espenson and E.L. King,
J. Am. Chem. Soc., 85, 3328 (1963).
- 14 F.H. Westheimer,
Chem. Rev., 45, 419 (1949).
- 15 R. Woods, I.M. Kolthoff and E.J. Meehan,
J. Am. Chem. Soc., 85, 2385, 3334 (1963).
- 16 R.N. Bose, V.D. Neff and E.S. Gould,
Inorg. Chem., 25, 165 (1986).

- 17 V.S. Srinivasan and E.S. Gould,
Inorg. Chem., 20, 3176 (1981);
N. Rajasekar, R. Subramanian and E.S. Gould,
Inorg. Chem., 22, 971 (1983);
R.N. Bose and E.S. Gould,
Inorg. Chem., 24, 2832 (1985) and
R.N. Bose and E.S. Gould,
Inorg. Chem., 25, 94 (1986).
- 18 D.J. Liston and O.B. West,
Inorg. Chem., 24, 1568 (1985);
Y. Lung-Chi and T.C. Bruice,
J. Am. Chem. Soc., 107, 512 (1985);
M. Hagihara and H. Yamasaki,
J. Am. Chem. Soc., 81, 3160 (1959) and
E.C. Alyea, J.S. Basi, D.C. Bradley and M. Chisholm,
J. Chem. Soc., A, 772 (1971).
- 19 W.A. Waters,
"Mechanisms of oxidation of organic compounds"
John Wiley and Sons Inc, New York (1964) p. 49.
- 20 S.A. Chimatadar and J.R. Raju,
The J. Of Karnatak Univ. Science 27, 39 (1982).
- 21 U.S. Mehrotra and S.P. Mushran,
Can. J. Chem., 48, 1148 (1970);
U.S. Mehrotra, M.C. Agarwal and S.P. Mushran,
J. Inorg. Nucl. Chem., 32, 2325 (1970);
S.P. Mushran, M.C. Agarwal and H.C. Gupta,
Ind. J. Chem., 10, 642 (1972).
- 22 J. Halpern and J.G. Smith,
Can. J. Chem., 34, 1419 (1956).

- 23 S.K. Mishra and Y.K. Gupta,
J. Inorg. Nucl. Chem., 30(11), 2991 (1968).
- 24 W.H. Richardson,
in "Oxidations in Organic Chemistry", Edited by
K.B. Wiberg, Academic Press, New York (1965) p. 272,
and references therein.
- 25 S.A.Chimatadar, S.T.Nandibewoor, M.I.Sambrani and
J.R. Raju,
J. Chem. Soc., Dalton Trans, 573 (1987).
- 26 S.K. Upadyay and M.C. Agarwal,
J. Scient. Ind. Res, 42, 508 (1983);
P. Veerasomaiah, K. Balreddy, B.Sethuram
and T. Navaneethrao,
Ind. J. Chem., 26A, 402 (1987).
- 27 V.I. Komarewsky, C.H. Riesz and G. Thodos,
J. Am. Chem. Soc., 61, 2525 (1939).
- 28 N. Swarnalakshmi, V.Uma, B.Sethuram and T.Navaneethrao,
Indian J. Chem., 26A, 592 (1987).
- 29 C. Benson,
J. Phys. Chem., 7, 1 (1903);
F.H. Westheimer,
Chem. Revs., 45, 419 (1949).
- 30 P. George and D.H. Irvine,
J. Chem. Soc., 587 (1954).