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STUDIORUM PROGRESSUS

Atom Transfer Mechanisms in Oxidation Processes*

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Abstract

The emphasis placed on electron transfer in connection with oxidation reactions has often resulted in these processes being considered as a group apart from the main class of chemical reactions. Although some oxidations, for example certain exchange reactions between ions in solution, can be reasonably described as electron transfer processes, there are very many other oxidations, whose mechanisms are much better described in the familiar terms of modern organic chemistry.

The use of isotopes as tracers has shown, that many oxidations proceed with transfer of atoms or groups from oxidant to reductant and *vice versa*; the use of the kinetic isotope effect has shown that such transfer is seldom an incidental process, but is almost always a part of the slow step of the reaction. In this paper, oxidations involving the transfer of such species as oxygen atoms, hydride ions, hydrogen atoms, chlorine atoms, and hydroxyl radicals are discussed in terms of mechanism. An attempt is made to show that a graded series of mechanisms is possible ranging from what appear to be pure electron transfer processes at one end to certain atom transfer processes at the other. The latter group belong, in fact, in the familiar realm of ordinary chemical raactions, in which strong bonds are being broken and formed in the activated complex.

The concept of oxidation-reduction as an electron transfer process has been strongly emphasized for some time with the result that oxidation processes have come to be considered as a group apart from the main class of chemical reactions. An enormous amount of information has accumulated in the last two or three decades regarding the mechanisms of non-oxidative processes particularly in organic chemistry but only recently have oxidation reactions come under close scrutiny. The use of isotopes has shown that many oxidations of both organic and inorganic substrates proceed with transfer of atoms or groups from oxidant to reductant and *vice versa*. One way to distinguish oxidations from all other chemical reactions except electron excitation processes is to visualize them as occurring by purely electronic transitions not involving bond making or bond breaking except, in some cases, as mere adjuncts to the electron transfer. Just as the use of isotopes has demonstrated that transfer of atoms often occurs between oxidant and reductant, so the use of the kinetic isotope effect has demonstrated that the bond breaking which often accompanies an oxidation is seldom an incidental process to the electron transfer but is rather almost always a part of the slow step of the reaction.

A recent suggestion that 'the true mechanism of organic oxidation may well be identical with the well-recognized fundamental *definition* of oxidation, i.e., *a loss of electrons*'[1] seems unfortunate. It appears in fact that many oxidations of both organic and inorganic substrates have mechanisms which are readily explicable in the terms used to describe the well known reactions of organic chemistry[2]. For example ANBAR and TAUBE using O^{18} have shown that the oxidation of nitrite by hypochlorite in aqueous solution takes place with substantially complete transfer of oxygen to nitrite[3]. The mechanism appears to be a displacement on the oxygen of the hypochlorite, the nitrite ion displacing chloride in the manner of an SN_2 reaction,

$$NO_2^- + OCl^- \longrightarrow [O_2N \cdots O \cdots Cl] \longrightarrow NO_3^- + Cl^-$$

The orbitals which are used to bind the atoms in the activated complex are not known with any certainty but it appears reasonable that the use of *p* orbitals on oxygen would provide a convenient path for the reaction.

Certain reactions, of course, appear to be well described as electron transfers, in particular the exchange reactions in solution between ions of the same metal but of different valence. There is a possible difficulty in the way of an arbitrary distinction between electron and atom transfer mechanisms. The exchange which occurs between $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ can be followed radiochemically and is rapid as it is for the similar systems MnO_4^-–MnO_4^{-2}, $IrCl_6^{-3}$–$IrCl_6^{-2}$, and $W(CN)_6^{-3}$–$W(CN)_6^{-2}$, $Os(dipy)_3^{+2}$–$Os(dipy)_3^{+3}$ [4–6]. Electron transfer is the obvious path for these reactions yet even here it is easy to show that some mass transfer probably accompanies the electron transfer. Taking the ferricyanide-ferrocyanide case as an example it is clear that in aqueous solution the more highly charged ferrocyanide ion will be more highly solvated than will the ferricyanide ion. When the electron transfer occurs, however, the positions are reversed and undoubtedly some water molecules which had been solvating the ferrocyanide ion before reaction and solvating both ions in the activated complex will change their allegiance to the newly formed ferricyanide ion when the activated complex splits. Such a transfer of molecules from the second coordination sphere of one metal ion to the second coordination sphere of the other may seem a trivial affair considering that exchange of solvating molecules with bulk solvent occurs readily and considering that the forces involved must be small for ions of such size. Yet one can imagine a graded series of reactions in which the coordinated groups which are transferred vary from being loosely bound to the central atoms to being tightly bound. The case of oxygen atom transfer from hypochlorite to nitrite is in the latter category.

When we come as far along the graded series as the nitrite-hypochlorite reaction we find ourselves in the familiar realm of ordinary chemical reactions in which strong bonds are being broken and formed in the activated complex. Thus the nitrite ion as it approaches the hypochlorite ion begins to alter its bond lengths and bond angles so that in the activated complex its geometry resembles more that of the trigonal nitrate ion. The changes in geometry are quite small in this case which doubtless is a factor favouring the reaction.

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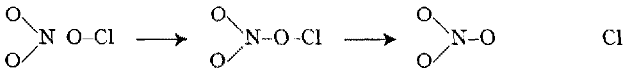

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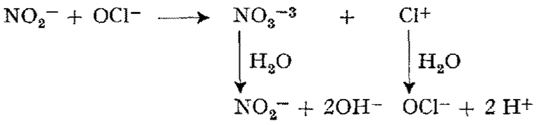
Let us consider the following hypothetical reaction which is merely exchange of oxygen between nitrite and hypochlorite i.e., oxide ion transfer without attendant oxidation or reduction.

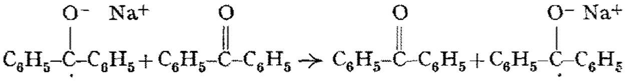


$$NO_2^- + OCl^- \longrightarrow \underset{\displaystyle NO_2^- + 2OH^-}{\overset{\displaystyle NO_3^{-3}}{\Big\downarrow H_2O}} + \underset{\displaystyle OCl^- + 2\,H^+}{\overset{\displaystyle Cl^+}{\Big\downarrow H_2O}}$$

The arrangement of atoms in the activated complex should be much the same as in I but a different electron distribution is required, an impossible situation since the electrons will automatically take up positions of minimum energy. In all chemical reactions the atoms in the reacting molecules take up different relative positions to one another when they form the activated complex and oxidation occurs when the electron distribution of minimum energy is such that the products formed on scission of the complex are in different oxidation states than they were before reaction.

MARCUS[7] has pointed out that unlike most chemical reactions the so-called electron transfer processes, typified by the $Fe(CN)_6^{-4}$–$Fe(CN)_6^{-3}$ exchange, require only a weak electronic interaction of the reactants to couple them electronically and so permit electron transfer to occur. The formal similarity between photochemical excitation on the one hand and these electron transfer processes on the other has led to the application of the Franck-Condon principle to the study of these reactions, in particular the restrictions placed by this principle, which states that atomic motions are slow compared to the speed of an electron jump, on electron transfer between solvated ions[8]. If the ferrous-ferric ion exchange in aqueous solution occurs by electron transfer it has been shown that considerable reorganization of the solvation spheres is required prior to the electron transfer to keep the overall free energy change zero. This is because the two cations have different charges and hence have their solvation spheres at different distances. If a direct electron transfer occurred between normally solvated Fe^{+2} and Fe^{+3} the products would be formed in excited states and hence the overall free energy change would not be zero as required. This and other aspects of inorganic oxidation are discussed by BASOLO and PEARSON[9].

Much attention has recently been devoted to these reactions, which can be fairly labelled electron transfer processes, and considerable success has been achieved in their quantitative treatment[10, 11]. It should be pointed out however that recent work by ADAM and WEISSMAN[12] indicates that atom transfer is a better way to describe at least one case of exchange in solution. They studied the exchange between benzophenone and its sodium ketyl by means of electron spin resonance.



$$C_6H_5\text{–}\underset{\cdot}{\overset{O^-\ Na^+}{\overset{|}{C}}}\text{–}C_6H_5 + C_6H_5\text{–}\overset{O}{\overset{\|}{C}}\text{–}C_6H_5 \rightarrow C_6H_5\text{–}\overset{O}{\overset{\|}{C}}\text{–}C_6H_5 + C_6H_5\text{–}\underset{\cdot}{\overset{O^-\ Na^+}{\overset{|}{C}}}\text{–}C_6H_5$$

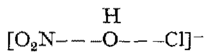
They showed that the spin resonance spectrum of the ketyl which is split by the nuclear spin of the nearby Na^{23} nucleus is greatly altered in the presence of excess benzophenone. It is altered in such a way that the exchange which occurs must result from each electron which is transferred from ketyl to ketone being accompanied by a sodium nucleus, in other words, sodium atom transfer from ketyl to ketone.

The purpose of this article then is to consider some oxidations which are not adequately described as electron transfer processes and to emphasize the similarity which exists between the mechanisms of these reactions and those of ordinary non-oxidative chemical processes.

1- and 2-Equivalent Oxidations. As early as 1929 KIRK and BROWNE distinguished between reagents which could oxidize in 1- and 2-equivalent steps by a study of the products formed when hydrazine is oxidized[13].

KIRK and BROWNE used the terms mono de-electronator and di-de-electronator and others have called them 1- and 2-electron transfer reagents but as HIGGINSON and MARSHALL[14] point out these terms imply that the reaction necessarily occurs via electron transfer; they therefore prefer the designations 1- and 2-equivalent oxidants or reductants. Some reagents can function as either 1- or 2-equivalent reagents and subsequent work supports KIRK and BROWNE's concept[15, 16]. WESTHEIMER[17] has made the following distinction between 1- and 2-equivalent reactions. If a molecule with an even number of electrons is oxidized or reduced to another molecule with an even number of electrons the process is considered to be a 2-equivalent oxidation unless a species is produced which contains an odd number of electrons and has a half life of $> 10^{-11}$ s. The simultaneous transfer of two electrons is considered improbable on quantum mechanical grounds but since atomic motion is slow compared to electronic motion any oxidation which proceeds by way of atom transfer can also involve a 2-electron transfer without the latter being considered 'simultaneous'. The question then arises must all 2-equivalent reactions proceed with atom transfer. It appears that most if not all of them do. One equivalent oxidation reactions on the other hand might proceed with or without atom transfer.

Oxygen Atom Transfer to Reductant. TAUBE's work with O^{18} has demonstrated that oxygen transfer is an important mode of oxidation in solution. The nitrite-hypochlorite reaction referred to earlier is catalyzed by acid and it seems reasonable to locate the proton in the activated complex on the oxygen atom being transferred[3].



$$[O_2N\text{---}\overset{H}{O}\text{---}Cl]^-$$

The resulting decrease in coulombic repulsion between the anions is doubtless an important factor but there are several oxidation reactions between anions which proceed with oxygen transfer and are inhibited by acid. The oxidation of cyanide ion by permanganate ion in basic solution results in transfer of oxygen from the permanganate to cyanide. Below pH 8 where the cyanide exists almost completely as HCN the reaction is very slow[18].

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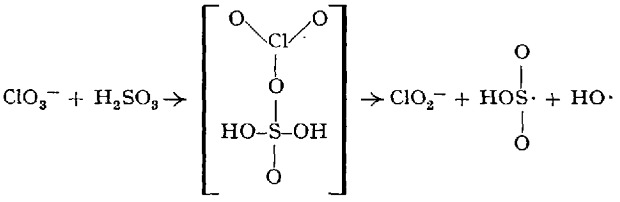
Similarly formate ion is oxidized by permanganate ion faster than is formic acid. Some oxygen transfer also occurs in this reaction[19].

In basic solution hypochlorite oxidizes sulfite with oxygen transfer being the principal reaction path. In acid solution however displacement on the chlorine atom of the hypochlorite appears to be favoured[20].

$$SO_3^{-2} + ClO^- \xrightarrow{H^+} [O_3S{-}{-}{-}Cl{-}{-}{-}O\cdot H]^{-2} \rightarrow SO_3Cl^- + OH^-$$
$$SO_3Cl^- + OH^- \longrightarrow SO_4^{-2} + H^+ + Cl^-$$

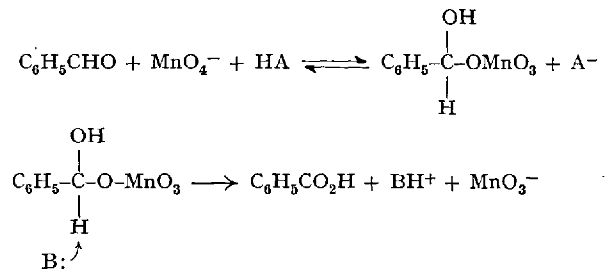
TAUBE *et al.* have also demonstrated transfer of oxygen to sulfite from BrO_3^-, ClO_2^-, ClO_3^-, and H_2O_2. In acid solution the latter reagent transfers both its oxygen atoms to the substrate[21]. It has been suggested that the sulfite-chlorate system for one involves more than a simple oxygen transfer since in the pH range of 1–3·5 it can initiate polymerization[22,23] a diagnostic test for the presence of free radical intermediates. To accommodate the known oxygen transfer with the presence of radical intermediates the following mechanism has been proposed[24].



$$HSO_3\cdot + HO\cdot \longrightarrow 2H^+ + SO_4^{-2}$$
$$HSO_3\cdot \text{ or } HO\cdot + \text{monomer} \longrightarrow \text{polymer.}$$

The scission of the above activated complex to give ClO_2^-, $HSO_3\cdot$ and $HO\cdot$ rather than ClO_2^-, $2\,H^+$ and SO_4^{-2} seems surprising. The radicals which initiate polymerization may be formed in small amount by a competing side reaction rather than by the principal, oxygen transfer, route.

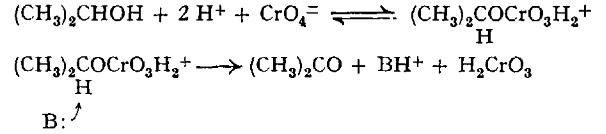
Turning to an organic substrate, benzaldehyde, which is oxidized by permanganate to benzoic acid, we find that a somewhat different mechanism is required. The mechanism must be in accord with the fact that O^{18} from MnO_4^{18-} is found in the benzoic acid formed in the reaction and also with the fact that a large isotope effect (7:1) is observed when C_6H_5CDO is oxidized by permanganate. The following mechanism which is also in accord with the reaction kinetics has been suggested[25].



$$C_6H_5CHO + MnO_4^- + HA \rightleftharpoons C_6H_5\text{-}\overset{OH}{\underset{H}{C}}\text{-}OMnO_3 + A^-$$
$$C_6H_5\text{-}\overset{OH}{\underset{H}{C}}\text{-}O\text{-}MnO_3 \longrightarrow C_6H_5CO_2H + BH^+ + MnO_3^-$$
$$B\!:$$

Oxygen atom transfer occurs in this process but the rate controlling step of the reaction is a series of electron pair shifts, to use the common terminology of organic chemistry, which is initiated by proton removal by the base B:. The kinetic isotope effect shows that the latter operation is a part of the rate controlling step.

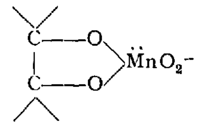
The above mechanism is similar to that elucidated by the important work of WESTHEIMER on the chromate oxidation of isopropyl alcohol, the mechanism of which is[26]:



$$(CH_3)_2CHOH + 2\,H^+ + CrO_4^= \rightleftharpoons (CH_3)_2\underset{H}{C}OCrO_3H_2^+$$
$$(CH_3)_2\underset{H}{C}OCrO_3H_2^+ \longrightarrow (CH_3)_2CO + BH^+ + H_2CrO_3$$
$$B\!:$$

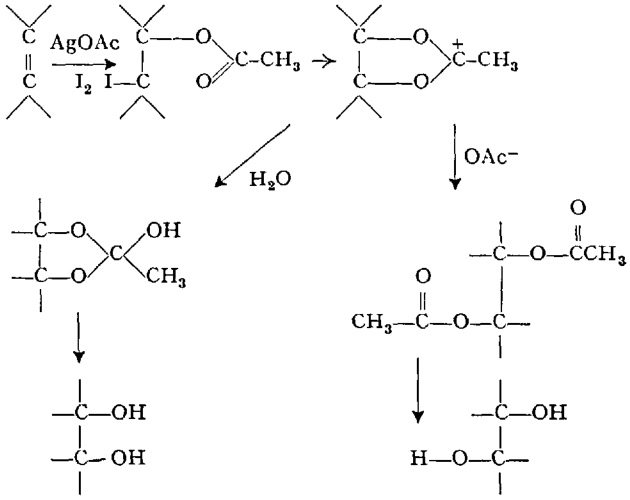
The proof of formation of the intermediate chromate ester, the existence of a large kinetic isotope effect, the existence of base catalysis and the form of the reaction kinetics all give strong support to this mechanism[27–29]. It is clear however that here any introduction of oxygen is merely a consequence of the mode of formation of the chromate ester. The rate controlling step of the oxidation involves proton removal and a shift of electrons. (See however ROCEK[30].)

Permanganate ion behaves as an oxygen donor when it oxidizes olefins to glycols. It was early postulated[31,32] that a cyclic ester is the intermediate, and recent work has shown that the



oxygen in the glycol comes from the permanganate, not from the solvent[33].

The mechanism of a similar reaction, the Prevost oxidation of olefins to glycols using silver acetate and iodine has been confirmed recently by the use of O^{18} as



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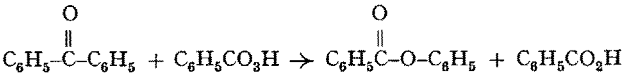
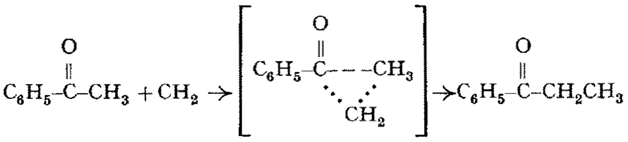
tracer. The use of 'wet' or 'dry' conditions determines the stereochemistry of, and the source of oxygen in, the product[34].

The perbenzoic acid oxidation of benzophenone to phenyl benzoate has been shown to take place with the carbonyl oxygen in the ketone becoming the carbonyl oxygen in the ester[35].



$$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + C_6H_5CO_3H \rightarrow C_6H_5\overset{O}{\overset{\|}{C}}{-}O{-}C_6H_5 + C_6H_5CO_2H$$

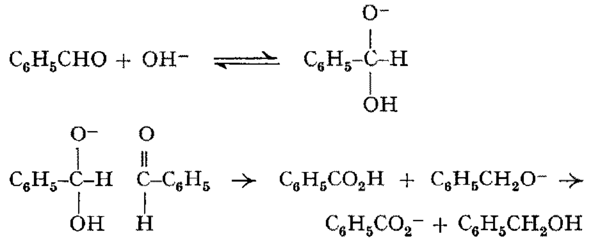
This insertion of an oxygen atom between two bonded carbon atoms is similar to the behaviour of the carbene, CH_2, produced by the irradiation of diazomethane[36].



$$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + CH_2 \rightarrow \left[\underset{CH_2}{C_6H_5{-}\overset{O}{\overset{\|}{C}}\text{- - -}CH_3} \right] \rightarrow C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_3$$

It is of interest that O and CH_2 are isoelectronic.

Hydride Transfer to Oxidant. A hydride reaction is the transfer in a single step of a proton and two electrons from reducing agent to oxidizing agent. Reactions believed to take place by this mechanism are very common in organic chemistry. They include the Cannizzaro reaction[37], the Meerwein-Pondorff reduction and its analog the Oppenauer oxidation[38], the Sommelet reaction[39], the Leuckart reaction[40], the base catalyzed carbinol-carbonyl equilibrium[41], the reduction by Grignard reagents of hindered ketones[42], and others[43–45]. The Cannizzaro reaction is often written as proceeding through a hydride transfer to benzaldehyde from the conjugate base of benzaldehyde hydrate[37,46]. The low deuterium isotope effect, $k_{\mathrm{H}}k_{\mathrm{D}} = 1{\cdot}8$[47], found for



$$C_6H_5CHO + OH^- \rightleftharpoons C_6H_5{-}\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}{-}H$$

$$C_6H_5{-}\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}{-}H \quad \underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}}{-}C_6H_5 \rightarrow C_6H_5CO_2H + C_6H_5CH_2O^- \rightarrow C_6H_5CO_2^- + C_6H_5CH_2OH$$

this reaction when C_6H_5CDO is used is surprising but may still be in accord with this mechanism (see later section). Doering and Aschner showed that the base catalyzed carbinol-carbonyl equilibrium is a 2-equivalent reaction by demonstrating the indifference of the reacting centers to the presence of a radical, Bindschedler's Green. Either a 1-electron transfer or a hydrogen atom transfer should involve this reactive species[41].

$$\begin{array}{lcll} R_2CHOH + OH^- & \rightleftharpoons & R_2CHO^- + H_2O & \text{fast} \\ R_2CHO^- + R'_2C{=}O & \rightleftharpoons & R_2C{=}O + R'_2CHO^- & \text{slow} \\ R'_2CHO^- + H_2O & \rightleftharpoons & R'_2CHOH + OH^- & \text{fast} \end{array}$$

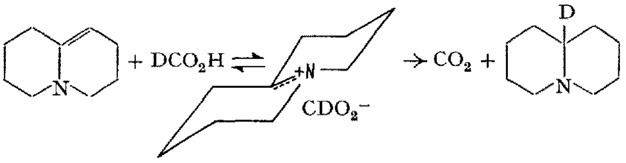
An interesting intramolecular reaction of this type has recently been reported by Dvornik and Edwards[48].

Although a hydride transfer is a most reasonable mechanism to write for the organic reactions listed earlier, there is some difficulty in obtaining proof that this is indeed the reaction path. In all cases equilibria prior to the rate controlling step hinder a thorough study of the reaction. Recently kinetic and isotopic evidence in support of the hydride transfer mechanism has been obtained by a study of the reduction of the triphenylmethyl cation by alcohols in strongly acid solution[49] and by formate ion[50] in formic acid.

$$\begin{array}{lcl} (C_6H_5)_3C^+ + R_2CHOH & \rightarrow & (C_6H_5)_3CH + R_2C{=}O + H^+ \\ (C_6H_5)_3C^+ + H{-}CO_2^- & \rightarrow & (C_6H_5)_3CH + CO_2 \end{array}$$

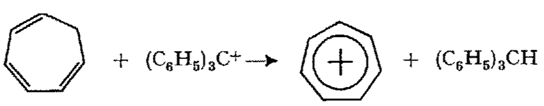
The use of R_2CDOH and DCO_2H resulted in the production of $(C_6H_5)_3CD$ thus fixing the position of the hydrogen transferred in the reduction.

Leonard and Sauers[51] have shown that the formic acid reduction of enamines proceeds by a similar mechanism and it seems likely that the Leuckart reaction also goes by this path.



The reduction of diazonium salts by alcohols appears to take place by both a hydride transfer mechanism analogous to the carbonium ion reductions above and by a free radical chain process[52].

Hydride abstraction by carbonium ions has been used to prepare tropylium ions from cycloheptatriene[53].



An interesting oxidation which bears a marked formal resemblance to hydride transfer is the reaction of hydrazoic acid with nitrous acid in acid solution.

$$HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O$$

Tracer work with N^{15} has shown that the reaction path is probably the following[54].

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$$N_3^- + NO^+ \longrightarrow [NNNNO] \longrightarrow N_2 + N_2O$$

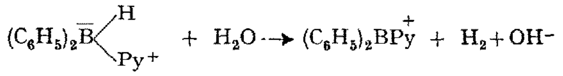
This reaction is effectively a nitride transfer, N^-, from azide ion to the oxidizing agent, NO^+. Like the hydride ion the nitride ion despite its being isoelectronic with atomic oxygen causes a 2-equivalent reduction. Transfer of nitrogen of any charge other than -3 will result in an oxidation or reduction. This applies also to transfer of oxygen, halogen, and hydrogen of charge other than -2, -1, and $+1$ respectively and results from our quite artificial concept of oxidation-reduction.

Molecular hydrogen in solution can bring about reduction by a homogeneous process. Cupric ion is not only reduced itself by hydrogen in aqueous solution but catalyzes the reduction of such substrates as $Cr_2O_7^{-2}$, IO_3^- and Ce^{+4}. The mechanism appears to be the following, the first step being a hydride transfer[55].

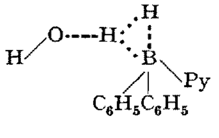
$$Cu^{+2} + H_2 \rightleftharpoons CuH^+ + H^+$$
$$CuH^+ + Cu^{+2} \rightarrow 2\,Cu^+ + H^+$$
$$2\,Cu^+ + \text{substrate} \longrightarrow \text{products} + 2\,Cu^{+2}$$

Although the evidence for the formation of CuH^+ is indirect, that is, the ion CuH^+ has not been isolated, the above mechanism fits the kinetic data very nicely.

It has recently been pointed out that small deuterium kinetic isotope effects seem to be the rule for hydride transfer reactions[56] (see however Ref. [43]). The hydrolysis of pyridine diphenylborane is assumed to go by the following mechanism:



Hawthorne and Lewis explain the small kinetic isotope effect observed when B–H is replaced by B–D, $\frac{k_{\text{B-H}}}{k_{\text{B-D}}} = 1{\cdot}52$, as being due to a non linear transition state in which the B–H stretching frequency is only partly lost in the transition state. When D_2O is used as reagent in the above reaction a much larger isotope effect, $\frac{k_{H_2O}}{k_{D_2O}} = 6{\cdot}90$, results indicating loss of most of the O–H stretching vibration in the water molecule involved in the transition state.

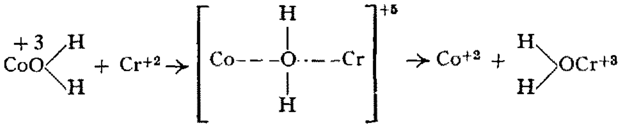


Hawthorne and Lewis point out that the most reasonable point of attack of an electrophile on a bond to hydrogen will be at the point of high electron density, that is, the bond itself[56,57]. A non linear transition state as above with consequent partial retention of the hydrogen stretching vibration in the transition state is not unexpected.

Cl. HO. etc. Transfer to Reductant. Taube *et al.* utilizing the fact that complex ions of Cr (III) are stable in aqueous solution, i.e., do not exchange their coordinated groups, have shown that atom transfer accompanies the oxidation of Cr (II) by certain oxidizing agents. Thus the oxidation of chromous ion by ferric ion which is catalyzed by chloride ions proceeds with transfer of coordinated chlorine from iron to chromium[58]; the activated complex being:

$$[Cr - Cl - Fe]^{+4}$$

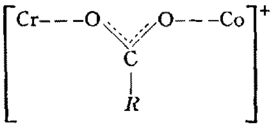
Similarly the chlorine atoms of $CoCl^{++}$, $AuCl_4^-$, and $Co(NH_3)_5Cl^{++}$ become incorporated in the coordination sphere of the Cr (III) formed when these reagents oxidize Cr (II). Indeed the oxidation of Cr (II) by Co (III) $(NH_3)_5X$ where $X = N_3^-$, Br^-, CNS^-, $CH_3CO_2^-$, $PO_4^{\equiv}$, and $SO_4^=$, results in the transfer of X in every case[59]. Since these ligands are joined to both oxidizing and reducing agent in the activated complex they are called bridging groups. Hydroxyl ion and probably water can also serve as a bridging group in this reaction and on examining the oxygen–18 kinetic isotope effect when these groups are transferred, it is clear that the cobalt-oxygen bond is partially broken in the activated complex[60].



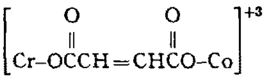
An interesting aspect of the Cr(II)–Co(III) oxidation is that if the bridging group is fumarate ion the rate is considerably faster than if it is either acetate or succinate[61].

	rate
$HO_2CCH{=}CHCO_2^-$	1·13
$CH_3CO_2^-$	0·15
$HO_2C\text{-}CH_2CH_2\text{-}CO_2^-$	0·19

Presumably the carboxylate groups in acetate, succinate (and isophthalate) function as bridges in the activated complex by bonding to both cobalt and chromium as follows:



With fumarate ion (or terephthalate ion), a bridge of much lower energy can be formed using both carboxylate groups as follows:



$$\left[Cr\text{-}O\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}O\text{-}Co\right]^{+3}$$

The chromium and cobalt are now connected electronically through the π electron system of the bridging group allowing immediate electron reorganization to occur. Succinate ion can bond to both chromium and cobalt just as fumarate ion can but the bridging is ineffective because of the lack of electronic coupling.

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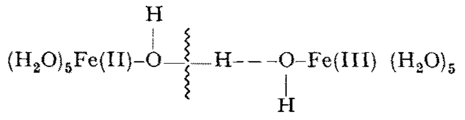
Since chromium undergoes a unit valence change in the above reactions it is apparent that the transferred group is effectively a radical. Now presumably these radical reactions proceed with homolytic bond rupture whereas the oxidations in which an oxygen atom or a hydride ion are transferred proceed with heterolytic bond rupture. Yet both kinds of reaction proceed in aqueous solution and do not show marked differences in character. There is not, in fact, the sharp dichotomy to which we have become accustomed in organic chemistry between radical reactions (homolytic bond cleavage) and the so-called ionic reactions (heterolytic bond cleavage)[62]. The former reactions, because of the production of neutral reactive radicals, often proceed by chain mechanisms and the rates are often largely independent of solvent whereas the inorganic species, like Cr (III) which are produced by radical transfer are stable ions. In this connection it is interesting that HALPERN has shown that the homogeneous reaction of hydrogen with Ag^+ proceeds by two paths probably involving homolytic and heterolytic bond splitting respectively[55].

$$2\,Ag^+ + H_2 \rightarrow [Ag^+---H---H---Ag^+] \rightarrow 2\,AgH^+$$
$$Ag^+ + H_2 \rightarrow [Ag^{\delta+}---H---H^{\delta+}] \rightarrow AgH + H^+$$

Hydrogen Atom Transfer to Oxidant.—The reaction of silver ion with hydrogen just referred to is an example of this process. In addition there are many well substantiated examples of oxidations proceeding by way of hydrogen atom transfer from organic compounds to free radicals[63].

HUDIS and DODSON have suggested that hydrogen atom transfer may be involved in the exchange between Fe^{+2} and Fe^{+3} in aqueous solution[64]. One might have expected some similarity to the $Fe(CN)_6^{-3}$–$Fe(CN)_6^{-4}$ exchange which proceeds by way of an electron jump through the firmly bound but polarizible coordination spheres of the central ions. However the exchange between Fe^{+2} and Fe^{+3} proceeds at only one half the rate in D_2O as in H_2O. The viscosity difference would account for only 20–30% of this effect and there seems to be little doubt that the solvent molecules play an important part in the reaction. Hydrogen atom transfer from hydrated ferrous ion, Fe(II) $(H_2O)_6$, to hydrolyzed ferric ion, Fe(III), $(H_2O)_5OH$ would account for these results, these two ions being involved, in the light of the kinetics, in the major reaction path[64].



$$(H_2O)_5Fe(II)\text{–}\overset{H}{O}\text{—}H\text{---}\underset{H}{O}\text{–}Fe(III)\ (H_2O)_5$$

The required zero free energy change is accomodated by this mechanism since reactants and products are identical. However the isotope effect may be due, not to hydrogen-oxygen bond breaking in the activated complex, but rather to a large solvent effect. It has been shown[65] that an isotope effect of some magnitude exists even for the reaction of $Cr(NH_3)_5Cl^{+2}$ with Cr (II), a reaction which was shown to take place by chlorine atom transfer[59]. It appears that more information on the solvating characteristics of H_2O and D_2O is required before the solvent isotope effect can be safely applied to the reactions of ions in solution.

Conclusions

The purpose of this article has not been to discredit in any way the commonly used definitions of oxidation in terms of electron transfer. Nor is it by any means intended to imply that oxidations do not occur in some cases by what could be called an electron transfer process. However sufficient evidence exists, some of which has been cited herein, to show that the mechanisms of a great many other oxidation reactions would be grossly oversimplified if they were considered as electron transfer processes. Most of these reactions are, in fact, represented quite satisfactorily by the familiar mechanisms of modern organic chemistry.

Acknowledgment.—The author is grateful to Drs. J. HALPERN and K. B. WIBERG for helpful discussions.

Résumé

L'emploi des isotopes a prouvé que beaucoup d'oxydations procèdent d'échanges d'atomes ou de groupes d'atomes de l'oxydant au réducteur ou vice versa. Ici, le mécanisme des oxydations comportant l'échange de telles matières en tant qu'atomes d'oxygène, ions hydrides, atomes d'hydrogène et atomes de chlor sont étudiées et discutées.

CONGRESSUS

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The Finson Memorial Congress

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The 3rd International Congress on Photobiology will be held in Copenhagen July 31–August 5, 1960. President of the Finson Memorial Congress is BØRGE CHR. CHRISTENSEN, M.D., Dr. Sc., The Finson Memorial Hospital, Strand boulevard, Copenhagen. The Secretary General of the Congress is Dr. techn. B. BUCHMANN, Biofysisk Laboratorium, Juliane Mariesvej 30, Copenhagen. The program of the Congress will consist of contributed papers and of a series of symposia on the following topics:

Biological action spectra;
Initial mechanisms involved in radiation effects;
Phototherapy;
Photoreceptors in aquatic organisms;
The results of the 3rd International Geophysical Year in regard to radiation;
Plant Cell response to visible light excluding photosynthesis;
Biological clocks;
The effects of long visible and near infrared radiation;
Photoreactivation–invited papers for a session.

Inquiries may be sent to the President or to the Secretary General of the Congress.

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