Mechanisms of Oxidation with Oxygen

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ABSTRACT   Several topics are dealt with in discussing the reactions of molecular oxygen, but a common goal is pursued in each: to try to understand the reactions in terms of the fundamental properties of the oxygen molecule, and of the other reactants. The paper first describes the electronic structure of oxygen and of two low-lying electronically excited states. Concern with the low-lying electronically excited states is no longer the sole property of spectroscopists; recently, evidence has been presented for the participation of such activated molecules in chemical reactions. The chemistry of oxygen is dominated by the fact that the molecule in the ground state has two unpaired electrons, whereas the products of oxidation in many important reactions have zero spin. In its reactions with transition metal ions the restrictions imposed by the spin state of the oxygen molecule are easily circumvented. A number of reactions of oxygen with metal ions have been studied in considerable detail; conclusions on basic aspects of the reaction mechanism are outlined. Among the most interesting reactions of oxygen are those in which it is reversibly absorbed by reducing agents. Reversible absorption to form a peroxide in the bound state is possible; some of the conditions which must be fulfilled by a reducing system to qualify as storing oxygen in this way are reasonably well understood and are here enunciated. Little has been done on the formation of oxygen from water; some factors involved in this process are discussed.

INTRODUCTION

It would be quite impossible to compress into the scope of this paper even a superficial discussion of every aspect of the chemistry of an element as individual and important as oxygen. I have chosen therefore to treat only certain aspects, selected because they especially interest me and/or because I feel I have some special competence to deal with them. The topics I have chosen are: the chemistry of the electronically excited states of the element; the effect of the spin state of the molecule on the mechanism of reaction; the mechanisms of reactions with simple transition metal complexes; comments on oxygen-carrying complexes; comments on the formation of oxygen in aqueous solution. These sections will be prefaced by a brief discussion of the electronic structure of the element in its ground state and the excited states whose chemistry in condensed phases has been somewhat explored.

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The Electronic Structure of Oxygen and of Its Excited States

Molecular orbital theory provides a simple explanation of the fact that the
molecule of oxygen in its ground state has two unpaired electrons and a means
of understanding the electronic structure of the excited states. The chemistry
of molecular oxygen is dominated by the fact that it is a biradical; the chem-
istry of the excited states of oxygen is currently receiving considerable attention
and will be outlined in this paper. Since we will attempt throughout to under-
stand the observations in terms of fundamental properties of the systems, it
seems appropriate to begin this paper by presenting a description of the
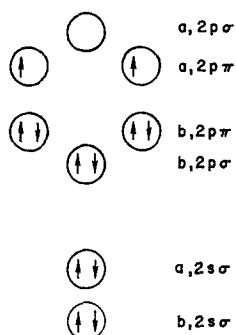electronic structure of the various forms of oxygen.

ELECTRONIC STRUCTURE OF O_2

FIGURE 1. Molecular orbital scheme.

The energy levels which arise from the interactions of s and p orbitals for
atoms of the same kind are shown in Fig. 1. The two lowest lying orbitals re-
sult from the interaction of the $2s$ orbitals at the two centers. The $2p\sigma(b)$ and
$2p\sigma(a)$ orbitals arise from the interaction of the two p orbitals, one at each
center, directed along the internuclear axis. The resulting molecular orbitals
have cylindrical symmetry about the internuclear axis (just as do those arising
from the interaction of the s orbitals), and are thus classified as of the σ type.
The four remaining orbitals arise from overlap of the p orbitals, two at each
center, which are perpendicular to the internuclear axis. Since the two p
orbitals at each center have equal energies, doubly degenerate bonding and
antibonding molecular orbitals arise from the interactions between the orbitals
at the two centers. The orbitals are perpendicular to the internuclear axis and
therefore are classified as of the π type.

Each oxygen atom contributes 6 valence electrons, and when the total of 12
is fitted into the orbital scheme, the electronic arrangement shown in Fig. 1
results. The fact that oxygen has two unpaired electrons is thus seen to be a
natural consequence of the fact that the molecule has 12 valence electrons, so

that each of the doubly degenerate $2p\pi(a)$ orbitals is only half-filled. The alternative ways of arranging the two electrons in the $2p\pi(a)$ orbitals will be considered later. They lead to higher energies because electron-electron repulsions are greater for them, and they correspond to excited states of the oxygen molecule.

The excess of bonding over antibonding electrons for the electronic structure depicted in Fig. 1 is 4 and thus the bond energy for the oxygen molecule is much greater than that corresponding to a single bond. The heat of dissociation for O_2 is 118 kcal per mole; for breaking the O—O bond in H_2O_2, it is *ca.* 35 kcal per mole. When O_2 is reduced to O_2^-, the excess of bonding over antibonding electrons decreases to 3. Corresponding to this change, the O-O distance increases when O_2 changes to O_2^-, from 1.21 A in the former species to 1.28 A in the latter. When a second electron is added, the excess of bonding over antibonding is only two; in $O_2^=$, only a single bond is left and the O-O distance is now ~1.49 A. Further reduction by a $1e^-$ change would still leave one bonding electron in excess of the antibonding. It is not known, however, whether or how long the species $H_2O_2^-$ exists. In solution it may well be unstable to OH^- and OH because the solvation energy for OH^- is greater than that of $H_2O_2^-$. When one more electron is added, the excess of bonding over antibonding electrons is zero, and the O-O bonding interactions are completely dissolved by the $4e^-$ reduction of O_2.

The configurations

$$\textcircled{\uparrow\downarrow} \quad \bigcirc \qquad\qquad \textcircled{\uparrow} \quad \textcircled{\downarrow}$$
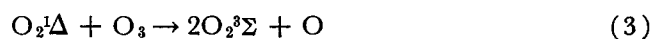
$$\textit{1} \qquad\qquad\qquad \textit{2}$$

for the electrons in the $2p\pi(a)$ orbitals correspond to excited states of the molecule. The spins are opposed for each and thus the arrangements (1) and (2) represent singlet states. The quantum number measuring the component of orbital angular momentum along the internuclear axis has a magnitude of one for each π orbital, but has opposite signs for the members of each degenerate pair. Thus for configuration (1), the total orbital angular momentum quantum number is 2, and the signature for the state is $^1\Delta$; for configuration (2), the total orbital angular momentum quantum number is zero and the signature for the state is $^1\Sigma$. The $^1\Delta$ state lies 23.4 kcal above the ground state $(^3\Sigma)$, and the $^1\Sigma$ lies 37.5 kcal above it (1).
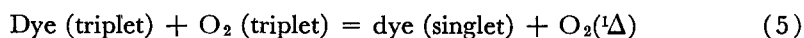
Reactions of Electronically Excited Oxygen

A spin change takes place in the transition from the $^1\Sigma$ or $^1\Delta$ level to the $^3\Sigma$ ground state, and the decay from either of these levels by emitting radiation is delayed. The life time of the excited molecules in solution, and even in the gas

phase at ordinary pressures is mainly determined not by processes involving the emission of radiation but rather by those brought about by collisions. In such collisions there is then the possibility that the active species will undergo reaction.

From time to time, various chemical reactions have been attributed to electronically activated oxygen. For example, one explanation (2) of the fact that the quantum yield of the decomposition of ozone brought about by ultra-violet light can exceed 2 is that O_2 $^1\Delta$ acts as a chain carrier. A mechanism featuring O_2 $^1\Delta$ as an intermediate is the following:

$$O_3 + h\nu \rightarrow O_2 + O \tag{1}$$

$$O + O_3 \rightarrow O_2{}^1\Delta + O_2 \tag{2}$$

$$O_2{}^1\Delta + O_3 \rightarrow 2O_2{}^3\Sigma + O \tag{3}$$

$$2O + M \rightarrow O_2 + M \tag{4}$$

The dye-sensitized photoreaction of certain organic substrates with oxygen was explained by Kautsky (3) as resulting from the attack on the substrate by electronically excited oxygen. The active oxygen is believed to be formed in a reaction such as (5) below.

$$\text{Dye (triplet)} + O_2 \text{ (triplet)} = \text{dye (singlet)} + O_2(^1\Delta) \tag{5}$$

Only recently, however, has fairly convincing evidence been obtained for the participation of electronically activated oxygen in chemical reactions.

A variety (4–6) of studies have shown that when oxygen at pressures in the range of 0.1 to 4 mm is subjected to an electric discharge, as much as 10 per cent of the oxygen is converted to the $^1\Delta$ state. Corey and Taylor (7) have reported that endoperoxides form when a stream of oxygen is passed first through a discharge and then through a solution containing an aromatic hydrocarbon. In the cases studied, the products are identical to those which form in the photochemical reaction of the hydroperoxides with oxygen. The reaction of $O_2(^1\Delta)$ is not particularly efficient. Moreover the rate of peroxide formation is found to be markedly sensitive to the nature of the solvent, being only one-twentieth as great in decalin as in benzene. There is a possibility that $O_2(^1\Delta)$ associates fairly strongly with bases. A low lying orbital which can accept electrons from a base is formally vacant (configuration (1) above) but it must be remembered that this orbital cannot be taken up by the pair of electrons donated by the base without cost. When the bond to a base is formed, the pair of oxygen electrons in the $2p\pi(a)$ level becomes concentrated on a single nucleus and this gives a positive contribution to the total energy balance.
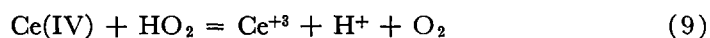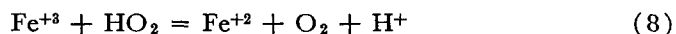
Recently, direct evidence has been offered for the formation of $^1\Delta$ (and $^1\Sigma$) oxygen in at least one chemical reaction. It has been known for many years (8) that red light is emitted when chlorine reacts with hydrogen peroxide in alkaline solution and this phenomenon has become the subject of renewed intensive investigation (9). In one (10) of the recent papers on this subject, eight different lines were reported as was the observation that the light is emitted from gas bubbles rather than from the body of the solution itself. A very intense line of 12,700 A can be attributed to the $^1\Delta$-$^3\Sigma$ transition and the weaker line at 10,700 A to the same transition but starting with the $^1\Delta$ oxygen molecule in the first excited vibrational levels. Lines at 7619 A and 8645 A are ascribable to the $^1\Sigma$-$^3\Sigma$ transition. The origin of the lines at 6350 A and 7030 A is more mysterious. It should be noted that a quantum at 6350 A has precisely twice the energy of one at 12,700 A and it has been suggested that the line at 6350 A is emitted by the transitions of dimers of $^1\Delta$ oxygen

$$(O_2(^1\Delta))_2 \rightarrow (O_2(^3\Sigma))_2 + h\nu \tag{6}$$

and that at 7030 A has the same origin but involves also a change in vibrational state. In any event, the spectroscopic work makes it certain that electronically excited molecules are produced in the reaction although the yield has not yet been specified.

Recently also, evidence has been presented for the conclusion that the excited molecules which are formed in the ClO^-—HO_2^- can take part in chemical reactions. Foote and Wexler (11) have shown that when certain hydrocarbons are added to the reaction mixture endoperoxides are formed, or products suggesting the formation of endoperoxides as intermediates. The products in question do not result from the interaction of OCl^- or HO_2^- with the hydrocarbon. According to Connick (12), the reaction of hypochlorite and hydrogen peroxide proceeds through $HOOCl$ as an intermediate. If this intermediate breaks spontaneously into H^+, Cl^-, and O_2, to conserve spin the oxygen must be formed in a singlet state. The reaction is sufficiently exothermic to form electronically excited oxygen, even without borrowing from the activation energy.

Stauff and Lohmann (13) have noted that many reactions in which oxygen is evolved (or consumed) emit light. These include the reactions in aqueous solution with H_2O_2 of Fe^{+2}, Ti(III), or Ce(IV). The reactions:

$$2HO_2 = H_2O_2 + O_2 \tag{7}$$

$$Fe^{+3} + HO_2 = Fe^{+2} + O_2 + H^+ \tag{8}$$

$$Ce(IV) + HO_2 = Ce^{+3} + H^+ + O_2 \tag{9}$$

as well as the reactions of H_2O_2 with a variety of $2e^-$ oxidizing agents are sufficiently exothermic so that when account is taken of a small contribution from the energy of activation, sufficient energy is at hand to generate electronically excited O_2.

There is a class of reactions among those which O_3 undergoes in which it seems reasonable that O_2 in a singlet state is formed. Thus when O_3 reacts with Cl^- in acidic solution, the products are Cl_2, O_2, and H_2O. The rate-determining step involves the encounter of one Cl^- with one O_3 molecule, and it can reasonably be formulated as

$$Cl^- + O_3 \rightarrow ClO^- + O_2; \quad \Delta H = 3.5 \tag{10}$$

Because the reaction does not have chain character and because the frequency factor for it is normal, the suggestion (14) has been made that the primary product of the reaction is oxygen in a singlet state (the activation energy, 17.6 kcal, is ample to accommodate this assumption). Systems in which ozone is a reactant are not well suited to a search for singlet oxygen by chemical means because ozone is itself so reactive. However, a spectroscopic investigation would seem to be of interest in this system and others like it; *i.e.*, those in which a diamagnetic species reacts with ozone by a non-chain path.

The Spin State of Oxygen and Reaction Mechanisms

For many reactions of oxygen with strongly nucleophilic $2e^-$ reducing agents reasonable mechanisms can be written in which a peroxy intermediate is formed by a simple bimolecular process. Thus for the reaction of $SO_3^=$ with O_2, which forms $SO_4^=$ as end product, we are obliged to investigate reaction (11) as a possible intermediate step:

$$\begin{array}{c} O \\ SO_3^- + O_2 = [OSOO]^{-2} \quad \Delta H < -30 \text{ kcal} \\ O \end{array} \tag{11}$$
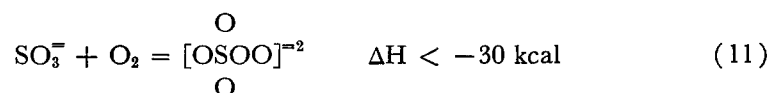
Reaction (11) is strongly exothermic, but has not been observed, even when the chain path for the reaction is strongly inhibited (15).

The fact that reaction (11) is so slow can at least in part be attributed to the spin change which accompanies it. The restrictions imposed by the spin change must be considered in two aspects. The restriction comes about because angular momentum must be conserved, and the coupling of electron spins with the environment is so weak that spin angular momentum is not readily exchanged with the environment. Just what the half-time for a change in spin state in a particular molecule is may be difficult to say, but for some polyatomic molecules it is known to be as short as 10^{-7} sec. (the singlet-triplet conversion for many organic molecules excited by radiation competes with

the allowed transition to the ground state). A delay of 10^{-7} sec. to allow for the spin change would of itself not be a severe limitation on the reaction rate except for the fact that for reaction to be consummated, the spin change must take place during the life time of the O_2-substrate collision complex. Unless the O_2-substrate system has a low-lying triplet state, the interaction between the partners will be one of repulsion at all separations and thus the spin change must take place during a time of the order of 10^{-12}; *i.e.*, the life time of a collision complex. If the electron pair of the reducing agent is to occupy one of the lower lying orbitals of O_2 without spin change for the system, an electron must be promoted to a higher level, and as we have seen, in the oxygen molecule this will take an energy in excess of 100 kcal, much greater than the binding energy we can reasonably invoke. Among the ways of relaxing the restrictions imposed by the spin change are these: (*a*) to arrange for the collision complex to last a long time (but it is not at all clear that the oxygen molecule has a "handle" which a reducing agent such as SO_3^- c⁻ take advantage of); (*b*) to choose a substrate which has a low-lying triplet state for the O_2-substrate complex, *i.e.* for which the triplet state does not reside solely in the O—O bond system, but involves the substrate as well.

It is interesting that even in the reaction of oxygen with carbanions, a free radical path appears to be chosen (16) rather than one involving simple addition of the oxygen molecule to the organic base. The ideas which were presented above, however, do suggest that if the reducing molecule has a low-lying triplet state, the simple addition of oxygen might be observed. The reaction of oxygen with a carbanion is exothermic to the extent of about 30 kcal. The singlet-triplet conversion should therefore not demand an energy in excess of this by more than some reasonable amount (made up from the activation energy) if the process is to be facile enough to be observed. Such a transfer of spin may in fact take place in the reaction of hexaphenylethane with oxygen. Methoff and Branch (17) concluded that one of the rate-determining processes in the reaction is the dissociation of the organic molecule to triphenylmethyl radicals, but that there is another path the rate of which depends directly on the reaction of oxygen with hexaphenylethane. The reaction by the second path may circumvent the spin restriction by the simple device of forming $\phi_3C\cdot$ and $\phi_3COO\cdot$ as products; on the other hand, it is possible that for a molecule as complicated as $\phi_3COOC\phi_3$ there exists a triplet state of lower energy than the radical products. It will be suggested later that the rather facile reaction of oxygen with complexes of Ru(II) may meet the spin requirement by transferring spin to the ruthenium product.

In view of the cleanness of the products (18, 19) in the reaction of some metal- and metalloid-organic compounds with oxygen, there is a temptation to ascribe simple bimolecular paths to them. However, good evidence has been presented in a number of individual cases that the reactions actually take

place by chain mechanisms. On the basis of Bamford and Nevitt's (20) results for the reaction of oxygen with boron trimethyl the conclusion seems to follow directly. It is less direct in the oxidation of the zinc alkyls. The reaction of $Zn(C_2H_5)_2$ with O_2 is reported to be smooth with $Zn(C_2H_5)_2O_2$ as product. But it is likely on the basis of the kinetics which have been gone into in considerable detail that the reaction in this case has chain character. Also with $Zn(CH_3)_2$ (21) at sufficiently low pressure of the reactants, a rather clean reaction to form solid intermediate products can be isolated. However, the kinetic behavior again suggests that the reaction takes place on the surface, and may in addition be a chain reaction. The possibility of a simple non-chain bimolecular reaction between oxygen and the class of molecules under present consideration does, however, not seem far-fetched. In evaluating this possibility an interaction with oxygen in which the reducing agent acts as an acid would need to be considered, i.e. with the O_2-substrate complex being stabilized by O_2 acting as donor, in contrast to the interactions exemplified by sulfite ion as a reducing agent. Davies et al. (22) have presented evidence that the reaction in solutions of tri-n-butylboron with O_2 ion can be strongly inhibited, and it seems likely that here also the reactions have chain character.

Though it is obvious that by a free radical path the reactions of a biradical such as O_2 can avoid the spin restriction, the point seems worth making for the sake of completeness. The reaction of O_2 with a free radical can always take place as indicated in equation (12) with the spin restriction reducing the rate by only a factor of 2.

$$A \cdot\ +\ O_2 \rightarrow AO_2 \qquad\qquad (12)$$

While meeting the spin restriction seems to be a necessary condition for facile reaction of O_2, it is by no means a sufficient one even for reactions with free radicals. The reaction of oxygen with a large number of radicals is extremely rapid: with CH_3 (23) or H (24) for example reaction takes place on virtually every collision if a third body is present to remove the energy liberated in bond formation. But even carbon radicals, when they are highly oxidized, may discriminate against reaction with oxygen in favor of reacting with a halogen for example. This appears to be the case for the radical derived from oxalate (be it CO_2^- or $C_2O_4^-$) which reacts (25) much more rapidly with Cl_2 than with O_2. Nitric oxide is a familiar example of low reactivity toward O_2 of a radical. The reaction of NO with O_2 does not take place in the presence of a neutral third body, but only when the third body is another molecule of NO. Apparently not enough energy is gained in forming the NO—O_2 bond to make up for the loss sustained in localizing one electron from each of the reactants in the bond.
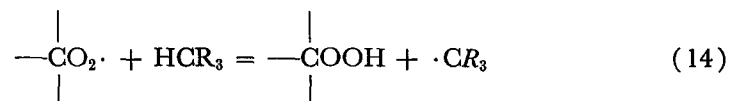
The radical which results when atomic hydrogen or a simple carbon radical adds to O_2 is itself a powerful oxidizing agent. Evidence (26) has been advanced in support of the conclusion that reaction (12) is reversible:

$$Ce(IV) + H_2O_2 \rightleftarrows Ce^{+3} + HO_2 + H^+ \qquad (13)$$

i.e. HO_2 in acid solution can oxidize a reducing agent as unreactive as Ce^{+3} (aq.). This conclusion is consistent with the value of $E°$ estimated (27) for the H_2O_2-HO_2 couple and which has been measured for the Ce^{+3}-$Ce(IV)$ couple in sulfuric acid solution (28).

$$H_2O_2 = HO_2 + H^+ + e^- \qquad E° = -1.4$$
$$Ce^{+3} = Ce^{+4} + e^- \qquad E° = -1.41 \text{ in } 1 \text{ M } H_2SO_4$$
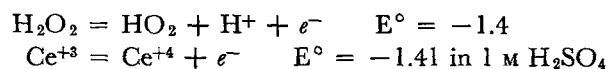
Reactions of the type

$$-\overset{|}{\underset{|}{C}}O_2\cdot + HCR_3 = -\overset{|}{\underset{|}{C}}OOH + \cdot CR_3 \qquad (14)$$

are somewhat endothermic for some C—H bonds but often occur with great facility so that together with the rapid reaction of $R_3C\cdot$ with O_2, a chain path for the autoxidation of R_3CH is developed. Though these chain reactions are important and show many interesting and individual features which depend on the choice of the substrate, they will not be discussed further here.

Reactions with Transition Metal Ions

In contrast to the reactions of oxygen with organic molecules which often proceed by chain mechanisms, many of the reactions with transition metal ions take place by paths involving single rate-determining steps of simple order in reducing and oxidizing agents. One transition metal ion can differ from another quite dramatically in chemistry so that the reaction of each transition metal ion reducing agent with oxygen has some distinctive and unusual feature. However, because I cannot hope to be complete in describing what has been done in studying these reactions, I shall select systems which provide evidence on the two basic questions we will consider: (*a*) Is a direct bond between oxygen and the metal ion necessary, or can the reduction occur by an outer-sphere mechanism? (*b*) Are both $1e^-$ and $2e^-$ (conceivably even $4e^-$) single-step reductions of oxygen possible? If they are, what factors determine the particular reaction path the system chooses? As for the systems considered in the previous section, spin conservation is an important requirement in these also, but it is usually met without difficulty because the transition metal ions have unpaired electrons in either the reduced or oxidized form. Difficulty on this

score would be encountered only for a couple which is spin-paired in both oxidized and reduced states (for example Pt(II)-Pt(IV)) and which undergoes a $2e^-$ oxidation in the rate-determining step.

The driving force of each reaction will be of importance to us and it is convenient at the outset to summarize the information on the states of equilibrium of the different systems. The values of E° for the various oxidation-reduction couples shown below are taken from Latimer's Oxidation Potentials (29), except for those involving HO_2 and O_2^-.

Couple	E°
$O_2^- = O_2 + e^-$	$+0.40$*
$Cr^{+2} = Cr^{+3} + e^-$	$+0.41$
$V^{+2} = V^{+3} + e^-$	$+0.26$
$HO_2 = O_2 + H^+ + e^-$	0.1*
$V^{+2} + H_2O = VO^{+2} + 2H^+ + 2e^-$	-0.10
$H_2O_2 = O_2 + 2H^+ + 2e^-$	-0.67
$Fe^{+2} = Fe^{+3} + e^-$	-0.77
$Pu^{+3} = Pu^{+4} + e^-$	-0.97
$2H_2O = O_2 + 4H^+ + 4e^-$	-1.23
$2H_2O = H_2O_2 + 2H^+ + 2e^-$	-1.77

* Estimated from the value of E° for HO_2—O_2 given by Tsao and Wilmarth (27), using 10^{-5} for the dissociation constant (30) of HO_2.

The difference in E° for the O_2^--O_2 and O_2^--HO_2 couples should be noted. It reflects the affinity of O_2^- for H^+; though K_{diss} for HO_2 is not known with complete certainty the value given is probably correct to within two orders of magnitude.
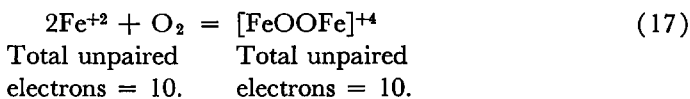
According to the values of E° tabulated,

$$Fe^{+2} + O_2 = Fe^{+3} + O_2^- \tag{15}$$
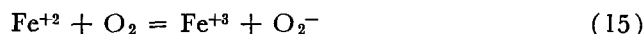
involves a standard free energy increase of about 28 kcal and the value of ΔH° cannot be expected to be much different. With the energetics for reaction (15) so unfavorable, it is clear that the outer-sphere reduction of O_2 by Fe^{+2} will be very slow. Unless some unusual interaction of Fe^{+3} with O_2^- is invoked, the energies will not be much more favorable even if the product ions are assumed to associate. The affinity of Fe^{+3} with an ion such as O_2^- which has an average of $\frac{1}{2}$ unit of negative charge per oxygen atom is not expected to be great, probably not as great as Fe^{+3} with SO_4^{-2}, and an interaction like this (31) would reduce ΔF° by only 4 to 5 kcal. In view of these considerations it is not surprising that the system finds a path more favorable than that expressed by equation (15). The rate law in perchlorate (32) and sulfate media (33) takes the form:

$$Rate = k(Fe^{+2})^2(O_2) \tag{16}$$

i.e., two rather than one Fe^{+2} are required in the rate-determining step to reduce O_2.

The rate law expressed by equation (16) can be taken to imply a rate-determining step in which O_2 is directly reduced to O_2^- by two Fe^{+2} ions. Since H^+ is not involved in the activated complex, the peroxide ion is presumably stabilized by interaction with the Fe^{+3} produced. If we use for each of the Fe^{+3}-O_2^- interactions the value of the association constant reported (34) for $Fe^{+3} + HO_2^-$, $\Delta F°$ for reaction (17) is calculated as 11 kcal, and this is

$$2Fe^{+2} + O_2 = [FeOOFe]^{+4} \qquad (17)$$
$$\text{Total unpaired} \qquad \text{Total unpaired}$$
$$\text{electrons} = 10. \qquad \text{electrons} = 10.$$

probably not far from the value of $\Delta H°$ for the reaction. The enthalpy of activation for the reaction is 17 kcal. It should be noted that reaction (17) can take place without net spin change.

When $H_2PO_4^-$ is present in the reaction medium, the rate law for the reaction of ferrous ion with oxygen becomes (35)

$$\text{Rate} = k(Fe^{+2})(O_2)(H_2PO_4^-)^2 \qquad (18)$$

The ion $H_2PO_4^-$ associates much more strongly with ferric than with ferrous ion, thus the reducing strength of ferrous ion is increased, and apparently the reduction of O_2 to O_2^- becomes possible.

The ion Pu^{+3} is an even weaker reducing agent than is Fe^{+2} and in view of the analysis of the energetics of the $1e^-$ reduction process made above, the reduction of O_2 by a process first order in (Pu^{+3}) is expected to be extremely slow. The reaction is in fact observed (36) to be second order in (Pu^{+3}) and to be assisted by SO_4^- which stabilizes Pu^{+4} over Pu^{+3}. An important result of the study of the Pu^{+3}-O_2 reaction is that hydrogen peroxide was identified as a reaction product. This possibility does not exist for many of the transition metal ion reactions with O_2, because hydrogen peroxide reacts with the reducing agent too rapidly. The rate of the reaction of Pu^{+3} was measured also in D_2O as solvent and the rate was found to decrease by only 20 to 30 per cent as compared to H_2O. This result makes it unlikely that a proton shift from H_2O to (incipient) peroxide is involved in the rate-determining act.

The reaction of U^{+4} with O_2 proceeds (37) in accordance with a simple rate law:

$$\text{Rate} = \frac{k(U^{+4})(O_2)}{(H^+)} \qquad (19)$$

but apparently involves a complex mechanism. The evidence which supports this conclusion is that the reaction is markedly inhibited by Cl^- or by Ag^+.

The effect of Ag^+ on the rate is quite striking. At low concentration metallic silver is deposited and the consumption of U^{+4} is suppressed completely for a time, following which the reaction recovers at a normal rate. The reaction clearly deserves more study. The rates on the whole are so reproducible that it seems unlikely that a chain reaction in the usual sense is involved. The inhibiting effects reported may be a consequence of the formation of an intermediate which in the normal course of events leads to a high induction factor in terms of additional molecules of O_2 brought into reaction, this succession of events being interrupted by the inhibitors. It is tempting to try to construct a sequence based on the rate-determining formation of an intermediate such as $U(VI) \cdot O_2^-$, and subsequent reactions of this species with U^{+4}, Cl^-, or Ag^+.

If indeed the intermediate $U(VI) \cdot O_2$ is formed, the reaction represents a $2e^-$ reduction of O_2. There is no difficulty with spin conservation in the formation reaction:

$$U(IV) + O_2 \rightarrow U(VI) \cdot O_2^- \tag{20}$$
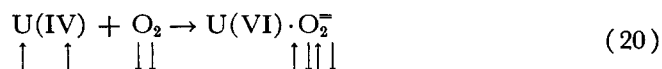
However, the reaction of $U(IV)$ with the intermediate would present difficulty with respect to spin change so that the obvious consummation of the reaction by the process:

$$U(VI) \cdot O_2^- + U(IV) \rightarrow 2U(VI) \tag{21}$$
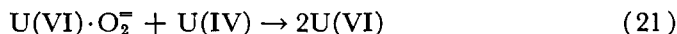
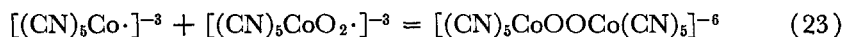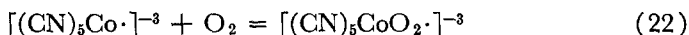would be hampered by the necessity for spin change.

The reaction of V^{+2} with O_2 (38) is a well defined example of a $2e^-$ rate-determining reduction of the molecule. The evidence for this conclusion is of the most dependable kind, based as it is on identification of immediate products. The reaction of V^{+2} with O_2 is very rapid[1] and the immediate product is at least 80 per cent VO^{+2}. This observation is significant because the reaction of O_2 with V^{+3} is slow; further, it is extremely unlikely that any O_2^- formed by $1e^-$ reduction of O_2 would show a marked preference for reaction with V^{+3} over V^{+2}, particularly because the latter is present in great abundance. The conclusions based on product identification are, of course, possible only because the reaction of V^{+2} with VO^{+2} is not extremely rapid (40). The analysis described depends on correcting for the contribution to the immediate stoichiometry made by the reaction of the peroxide which it is assumed is formed in the rate-determining step. Hydrogen peroxide reacts rapidly with V^{+2} to raise 25 per cent of the reducing agent to the $+4$ state and the remainder to the $+3$ state.

[1] Of the order of milliseconds with V^{+2} at 0.01 M (reference 39).

In the systems discussed thus far, the observations have supported rather definite conclusions on one of the general questions posed earlier: does reaction take place by one-electron or two-electron transfer? Experiments with systems in which the oxidized metal complexes are substitution-inert have led to conclusions on the second of the general questions: in a particular instance, is a direct bond between oxygen and the reducing metal ion established in the reduction process, or can reduction take place without taking advantage of a metal ion-oxygen bond? The observations most pertinent to the second question raised have been made by Wilmarth and coworkers. Thus Haim and Wilmarth (41) have shown that when Cr^{+2} in the presence of CN^- reacts with O_2, $Cr(CN)_6^{-3}$ is the major product. Most complexes of $Cr(III)$ are slow to undergo substitution, and it is expected that if a Cr—O bond were established in the course of the oxidation (*cf*. the reaction of O_2 with $Cr(II)$ in the presence of NH_3 as described below), $Cr(CN)_5OH_2^-$ would be observed as product. It seems certain therefore that in reacting with $Cr(CN)_6^{-4}$, O_2 does not displace CN^- from a normal coordination position and reaction rather takes place by an outer-sphere activated complex. Attack of this kind is possible here (*a*) because $Cr(CN)_6^{-4}$ is a very powerful reducing agent and there is no large energy barrier to a $1e^-$ reduction process. (*b*) Since $Cr(II)$ is spin-paired in the cyanide complex, the electron which is given up leaves a t_{2g} orbital and thus attack at the face of an octahedron is favored. Whether a $Cr(III)$-oxygen bond is formed in the products, or whether such attack takes place over larger distances is not known. It is worth noting, however, that the former mechanism is not likely in this case, because each of the three t_{2g} orbitals is occupied in $Cr(III)$ and an extra ligand could only be accommodated by pairing electrons in these orbitals, and this would correspond to a state of high energy. The question raised here about the details of so called outer-sphere activated complexes is general. No direct experimental means of distinguishing the case of actual bond formation in an abnormal coordination position and no bond formation have been suggested. It seems likely, however, that this distinction will be possible when the qualitative argument advanced above is made more quantitative.

In contrast with the case discussed for $Cr(CN)_6^{-4}$, when Co^{+2} in the presence of CN^- reacts with O_2, metal-oxygen bonds are formed. Conditions can be found under which $[(CN)_5CoOOCo(CN)_5]^{-6}$ is the major product (41). The reducing agent in this system differs in an important respect from that discussed in the previous paragraph. When combined with CN^-, Co^{+2} adopts a spin-paired state, but this leaves an electron in excess of those needed to complete the t_{2g} orbital set. As a result, the Co^{+2}-CN^- complex does not have a regular octahedral structure. The species $Co(CN)_5^{-3}$ is the dominant form in the solutions; in this ion the sixth coordination position is at the very least labile, and may in fact be occupied only by the extra electron. The species
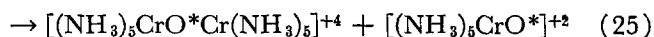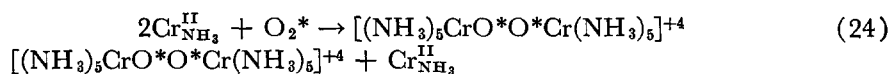
$Co(CN)_5^{-3}$ can be regarded as a radical, and the reaction with oxygen as taking place as follows:—

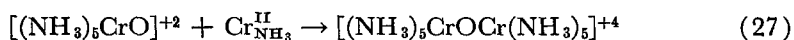$$[(CN)_5Co \cdot]^{-3} + O_2 = [(CN)_5CoO_2 \cdot]^{-3} \tag{22}$$

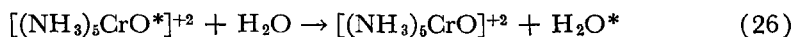$$[(CN)_5Co \cdot]^{-3} + [(CN)_5CoO_2 \cdot]^{-3} = [(CN)_5CoOOCo(CN)_5]^{-6} \tag{23}$$

When the concentration of CN^- is made high enough, some $Co(CN)_6^{-3}$ does form. It should be noted that Co^{++} in the presence of CN^- is a very powerful reducing agent, so that there is no serious energy barrier to the $1e^-$ reduction of O_2 in the system.

When NH_3 rather than CN^- is the ligand, the chemistry of the $Cr(II)-O_2$ reaction alters dramatically. The change probably has less to do with differences between CN^- and NH_3 as conducting ligands than it does with the differences in the symmetry of the donor orbitals as they are affected by the ligands. The complex of Cr^{+2} with NH_3 is spin-free and as a result the donor orbital has e_g symmetry—that is, it is directed toward the normal coordination positions, rather than toward the octahedron faces as with t_{2g} orbitals, so that attack by the reducing agent at a normal coordination position is expected. The observations in fact show $[(NH_3)_5CrOCr(NH_3)_5]^{+4}$ rather than $Cr(NH_3)_6^{+3}$ as the major product.

Oxygen tracer experiments have further illuminated the mechanism of reaction of Cr^{+2} in the presence of NH_3 with O_2. Joyner and Wilmarth (42) have shown that between 40 and 70 per cent of the oxygen in the binuclear $Cr(III)$ product originates in O_2. Variable transfer in excess of 50 per cent has the following plausible explanation (42).

$$2Cr_{NH_3}^{II} + O_2^* \rightarrow [(NH_3)_5CrO^*O^*Cr(NH_3)_5]^{+4} \tag{24}$$
$$[(NH_3)_5CrO^*O^*Cr(NH_3)_5]^{+4} + Cr_{NH_3}^{II}$$

$$\rightarrow [(NH_3)_5CrO^*Cr(NH_3)_5]^{+4} + [(NH_3)_5CrO^*]^{+2} \tag{25}$$

Now in $[(NH_3)_5CrO^*]^{+2}$, chromium is formally in the $+4$ oxidation state, and complexes of $Cr(IV)$ in all likelihood are substitution-labile (43), so that it is reasonable to expect some exchange with the solvent (reaction 26) before the species is reduced by $Cr(II)$ (reaction 27).

$$[(NH_3)_5CrO^*]^{+2} + H_2O \rightarrow [(NH_3)_5CrO]^{+2} + H_2O^* \tag{26}$$

$$[(NH_3)_5CrO]^{+2} + Cr_{NH_3}^{II} \rightarrow [(NH_3)_5CrOCr(NH_3)_5]^{+4} \tag{27}$$

If oxygen exchange in the $Cr(IV)$ complex is complete before reduction by $Cr(II)$ takes place, precisely 50 per cent of the oxygen in the binuclear product will be derived from the gaseous oxidizing agent. Labeling in excess of this is readily understood by competition between reactions (26) and (27). The

mechanism does not explain how only 40 per cent of the binuclear product can come to be labeled, but it is so reasonable that it almost certainly describes the bulk of the reaction. A contribution by some other path must be invoked to account for the defect in the extent of labeling and Joyner and Wilmarth in fact offer a plausible suggestion for this path (42).

Tracer experiments have also been done on the reaction of Cr_{aq}^{2+} with oxygen (42 a). The main product of the reaction is $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{+4}$. In this system, all the O atoms of the oxidizing agent appear in the $Cr(III)$ product.

Work is in progress (44) on the reaction of oxygen with the substitution-inert reducing agent $Ru(NH_3)_6^{+2}$. Although the normal coordination positions are firmly occupied, and the reducing power of the ion is not very great (E° for $Ru(NH_3)_6^{+2}$–$Ru(NH_3)_6^{+3} + e^-$ is ca. -0.2) (45), the reaction is rapid and first order in the reducing agent. The dominant $Ru(III)$ product is $Ru(NH_3)_6^{+3}$, but it seems likely that a portion of the reaction yields a different product, because the product solution behaves quite differently on aging than does one containing $Ru(NH_3)_6^{+3}$ formed in another way. It will be important, though difficult, to learn whether the primary reaction involves a $1e^-$ transfer or a $2e^-$ transfer. The spin restriction can be cirvumvented even if a $2e^-$ transfer takes place because $Ru(IV)$ can absorb the unpaired spins:

$$Ru(II) + O_2 \rightarrow Ru(IV) + O_2^- \qquad (28)$$
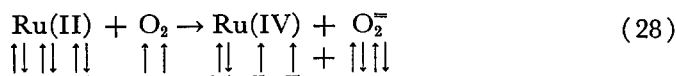
Let us turn now to a system which involves the general issues we have been concerned with, but is of more direct biochemical interest than those we have thus far discussed. Wang and coworkers (46) have studied the reaction with oxygen of the dimethyl ester of ferrohemochrome in ethanol-benzene solution containing pyridine. Ferrohemochrome in aqueous solution is much more powerfully reducing than is Fe^{+2} (aq.). The rate of the reaction is given by the kinetic expression:

$$\frac{-d(\text{heme})}{dt} = \left(k + \frac{k'}{\text{Py}}\right)(\text{heme})(O_2) \qquad (29)$$

The ferroheme is apparently a powerful enough reducing agent to react with oxygen by a process first order in the concentration of the reducing agent. If the dominant form of the $Fe(II)$ is assumed to be the dipyridine-ferrohemochrome, the first term of the rate law implies reaction of O_2 with the intact dipyridine complex and the second with the form in equilibrium with it which contains one less pyridine. It is not unreasonable to suppose that by the second path, O_2 makes a bond to the $Fe(II)$ in the activated complex using the coordination position vacated by the pyridine. But does the first

path imply that O_2^- is formed by electron transfer apart from the reducing agent, or is an intermediate formed in which the coordination number of Fe is increased to 7?

A Class of Oxygen Carriers

One of the most fascinating subjects in transition metal ion–oxygen chemistry is the reversible absorption of oxygen by certain metal complexes. In principle several different types of oxygen carriers can be distinguished: those which hold oxygen as the molecule, as O_2^-, as a peroxide, or with the oxidizing capacity completely transferred to the metal complex (i.e., the oxygen molecule is completely reduced). The distinction between the first two categories may not be at all sharp, since it may be concerned only with the question of electron distribution in the oxygen-containing complex. Presumably, in each of the first two types, a single metal ion binds one oxygen molecule. If we take the third category to comprise those for which two metal ions react for each O_2, it is clearly distinguishable from the others. The fourth is again clearly distinguishable because we define it as that in which the bond in O_2 has been completely broken.

The interactions giving rise to the first class are still imperfectly understood. In some important cases, the arrangement of O_2 with respect to the metal ion is still in doubt. Griffith (47) has offered the interesting suggestion that the O_2 molecule in the complex with hemoglobin is arranged with its two atoms equidistant from the iron atom. Ibers and LaPlaca (48) have shown that this kind of geometry is featured in the reversible oxygen carrier, Ir[P(C₆H₅)₃]₂ClCO, discovered by Vaska (49). No oxygen carriers of the fourth class have been characterized. Numerous examples of the peroxide class exist and since they appear to involve rather orthodox chemistry[2] (50), this is the class which we shall consider, attempting to define the conditions which must be fulfilled for a metal complex system to qualify as an oxygen carrier of this class.

To make the discussion as concrete as possible, we shall take the reduced state of the metal ion to be +2, and the oxidized form +3. The reaction we are interested in then takes the form expressed in equation (30).

$$2M^{II}L_6 + O_2 = L_5M^{III}OOM^{III}L_5 + 2L \qquad (30)$$
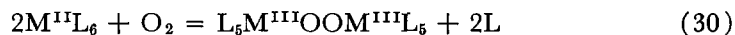
One obvious condition that the system must satisfy for reversible oxygen absorption is that the equilibrium constant for reaction 30 be close to unity. To learn what this means in terms of the value of $E°$ for the half-reaction

$$L + M^{II}L_5H_2O = M^{III}L_6 + H_2O + e^- \qquad (31)$$
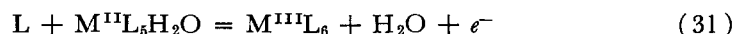
the affinity of $O_2^=$ for the metal ions must be known. If it is assumed that for

[2] But note that in [(NH₃)₅CoO₂Co(NH₃)₅]⁺⁵ the axis of the O—O group is reported as being perpendicular to the Co-Co line.

each of the M(III)-peroxide bonds the association quotient is 10^{-10}, *i.e.* very nearly that of Fe^{+3} for HO_2^-, then to have the equilibrium quotient for reaction (30) equal to unity, $E°$ for the half-reaction 31 must be *ca.* -0.5.

A second important condition is that as O_2 is being introduced to $M^{II}L_6$, the reaction of $M^{II}L_6$ with $[L_5MOOML_5]$ be not too rapid (see reactions 25 and 27). Reduction of the O—O bond in this manner, of course, leads to loss of oxygen-carrying capacity. Among the ways in which the rate of this undesirable side reaction may be reduced are: restricting the motion of the metal ion complexes (as by incorporating them into a high polymer or the solid phase), restricting the rate by making the groups L bulky, and possibly also providing a hydrophobic environment along the lines suggested by Wang (51) as the means whereby the oxidation by O_2 of Fe(II) in hemoglobin to Fe(III) is inhibited.

Unless unusual circumstances prevail, the M^{+3}—O_2^-—M^{+3} bonds will not be thermodynamically stable with respect to $2MOH^{+2} + H_2O_2$. The rate of this dissociation reaction must be made small; among the ways to accomplish this is for the $+3$ state of the complex ion system to be substitution-inert (although this may not be the only way to satisfy the condition imposed).

A fourth condition is that an oxidation state of the metal higher than $+3$ be not readily accessible. If a $+4$ oxidation state were easily reached, then complete reduction of the O—O bond could ensue.

Finally, it is required that the equilibrium expressed by equation 30 be established rapidly enough. Ideally, this would be achieved if the complex having the metal in the $+2$ oxidation state were pentacoordinated with a square pyramidal arrangement, but in the $+3$ state it were hexacoordinated. Under these ideal conditions no ligand association stabilization energy is sacrificed on reduction; *i.e.*, if the $+2$ state is pentacoordinated it is not formed in a coordinatively unsaturated condition when the O_2^- leaves as O_2. Even though this ideal state may not always be achieved, it will assist in lowering the activation energy for reaction (30) if a configuration of lower coordination number for the $+2$ oxidation state be not too high in energy, compared to the usual.

Complexes (52) of Co(II) with amino acids and with salicylaldehyde-thylenediimines and related substances (53) are notable among those which show a considerable capacity in absorbing oxygen reversibly. Criterion 1 is actually closely met in these complexes as are criteria 3 and 4. Criterion 2 is met particularly if the reactions occur in the solid state (though other possibilities for meeting this condition should be explored for these complexes). In regard to criterion 5, it should be noted that a change in coordination number for complexes of Co(II) is not difficult to achieve, and specifically in the salicylaldehydethylenediimine series, a coordination of 4 or 5 is probably not unusually high in energy.

Even with NH_3 as ligand, Co(II) shows some capacity as an oxygen carrier (54), but this system would be weak on the score of criteria 2 and 5. The system with CN^- satisfies criterion 5 nicely, fails to some extent in 2, and fails most completely in 1.

These considerations provide a fairly satisfying rationalization of the behavior of some selected systems; however, the influence of ligands in their great variety on such properties of complexes as the stability of various oxidation states, inertia to substitution, and stability of states of different coordination number is not understood thoroughly enough or quantitatively enough to answer with confidence even a simple question such as this: are peroxide carriers possible with Fe complexes? My confidence in the variety offered by transition metal complexes is such that I am inclined to think that they are, but I am much less confident of being able to suggest a successful recipe.

Formation of the O—O Bond

Little is known of the detailed mechanism by which molecular oxygen is formed from species containing the element in the completely reduced state. Some idea of what is possible can be gained by applying the principle of microscopic reversibility to what is known about or has reasonably been proposed for the reduction of H_2O_2.

Based on the assumed $1e^-$ reduction of H_2O_2 by Fe^{+2}, the reaction by which the O—O bond is formed in the reverse reaction becomes:

$$FeOH^{+2} + OH \rightarrow Fe^{+2} + H_2O_2 \qquad (32)$$
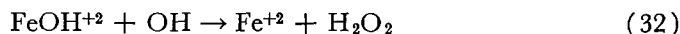
Here the hydroxyl radical reduces Fe(III) to Fe(II), and although this kind of reaction has not been demonstrated for the hydroxyl radical, the analogous reaction is known for other strongly electronegative radicals. For example, the reaction:

$$(NH_3)_5CoI^{+2} + I \rightarrow Co(II) + I_2 \qquad (33)$$
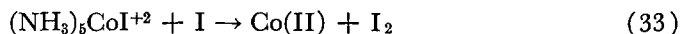
takes place with high efficiency (55). The slow step in the over-all formation of O_2 by this mechanism would be the formation of HO. In acidic solution HO is a very powerful oxidizing agent:

$$H_2O = H^+ + OH + e^- \qquad -2.7 \qquad (34)$$
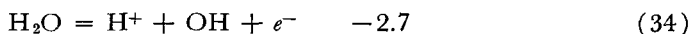
Even a couple as strongly oxidizing as Co^{+2} (aq.)-Co^{+3} (aq.) ($E^\circ = -1.8$) is not known with certainty to form HO at a rate which is competitive with other processes for the destruction of Co^{+3} (aq.). At pH 7, E° for the H_2O-OH couple would be increased to -2.3 volt, but the oxidizing agents that liberate OH from water at this pH are also rare indeed.

In considering the reverse of a $2e^-$ reduction of H_2O_2, we consider the reaction (let us take the change in oxidation number for the oxidizing atom

M to be from $+4$ to $+2$)

$$M^{IV}OH + OH^- \rightarrow M(II) + H_2O_2 \qquad (35)$$

or

$$M^{IV}(OH)_2 \rightarrow M(II) + H_2O_2. \qquad (36)$$
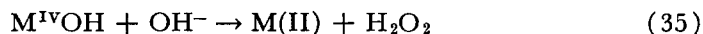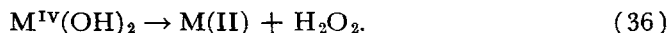
The two formulations differ in an important detail. In the first, one of the OH groups incorporated into the H_2O_2 molecule is external to the oxidizing complex; in the second, both OH groups originate in the oxidizing complex and H_2O_2 is formed by a rearrangement within this complex. The reduction of H_2O_2 by a process corresponding to the second mechanism is in fact known. Thus it has been shown (56) that when SO_2 (aq.) reacts with H_2O_2 to form $SO_4^=$, each molecule of this product contains two oxygen atoms which are derived from the H_2O_2.

When the reverse of the mechanism portrayed in equations (24), (25), and (27) is considered, some rather remarkable reactions are implied. Here we take the oxidizing atom to undergo a net change in oxidation number from $+3$ to $+2$, but the $+4$ state is involved as an intermediate. The first step is the disproportionation:

$$M^{III}OM^{III} \rightarrow M(II) + M(IV) \qquad (37)$$
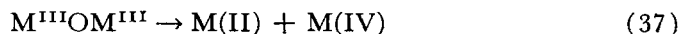
This is followed by formation of the O—O bond, the oxidation being brought about by the change $M(IV)$ to $M(III)$ and $M(III)$ to $M(II)$ (with in all likelihood the atom which was originally $M(IV)$ remaining as part of the binuclear product).

$$M(IV) + M^{III}OM^{III} \rightarrow M^{III}OOM^{III} + M(II) \qquad (38)$$

None of these mechanisms has been proven for reactions in which oxygen is formed. A system which may involve a variation of reaction (32), and a variation which should much facilitate reaction, is the oxidation of H_2O by Co^{+3} (aq.). An important term in the rate law has the form:[a] (57–60)

$$\frac{-d(Co^{+3})}{dt} = \frac{k(Co^{+3})^2}{(H^+)^2}$$

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[a] The agreement between different workers who have investigated this system is by no means complete, but all agree that the rate law features more than one term. A term in the rate law first order in (Co^{+3}) has been reported by Noyes and Dahl (57) and by Bawn and White (58). It was observed also by Weiser (59), but Weiser found the term to be unreproducible and dependent on the past history of the Co^{+3} solution. Bawn and White report a second path having the form $(Co^{+3})^2/(H^+)^n$ where n lies between 1 and 2, and a term corresponding to this but with $n = 2$ was found also by Weiser. Baxendale and Wells (60) report a single term featuring $(Co^{+3})^{3/2}$ (likely a composite of a first order and second term) and inverse in $(H^+)^2$. The discussion in the body of the paper is based on the assumption that the only intrinsic path which has been demonstrated is described by a rate law of the form $k(Co^{+3})^2/(H^+)^2$.

Here we can consider the reaction to take place by:

$$CoOH^{+2} + HOCo^{+2} \rightarrow 2Co^{+2} + H_2O_2$$
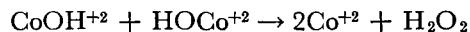
Instead of HO attacking $CoOH^{+2}$, in analogy to reaction 32, another $CoOH^{+2}$, which can be regarded as a source of HO, attacks; by this device, the necessity of forming free HO is avoided and in principle at least, the high energy barrier that formation of OH calls for need not be surmounted. The formation of O_2 from coordinated oxygen has in fact been demonstrated (61) in a somewhat related system. When $S_2O_8^-$ in the presence of Ag^+ acts on $(NH_3)_5CoOH_2^{+3}$, Co^{+2} is produced. Tracer experiments have shown that much of the oxygen in the original aquo ion appears in the O_2 which is formed. While the general nature of the process is established by the tracer experiments, the identity of the external oxidizing agent is not known. It may be HO, SO_4^-, or Ag^{+2}, or some species that we have not even considered.

It must be emphasized that although the mechanism suggested for the reduction of Co^{+3} (aq.) by H_2O is plausible in the light of various lines of evidence it is by no means proven. The rate-determining step may in fact be

$$2Co(III) \rightarrow Co(IV) + Co(II)$$
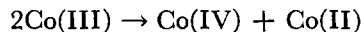
with Co(IV) reacting to form H_2O_2 by a mechanism similar to reaction (35) or (36).

The reactions in which O_2 is formed by oxidation of water are clearly important and as they are so little understood, they call for intensive, systematic investigation.

REFERENCES

1. HERZBERG, G., The Spectra of Diatomic Molecules, New York, D. Van Nostrand Co., Inc., 1950.
2. SCHUMACHER, H. J., J. Am. Chem. Soc., 1930, 52, 2377.
3. KAUTSKY, H., and DE BRUIJN, H., Naturwissenschaften, 1931, 19, 1043.
4. FONER, S. N., and HUDSON, R. L., J. Chem. Physics, 1956, 25, 601.
5. HERRON, J. T., and SCHIFF, H. I., Canad. J. Chem., 1958, 36, 1159.
6. ELIAS, E., OGRYZLO, E. A., AND SCHIFF, H. I., Canad. J. Chem., 1959, 37, 1680.
7. COREY, E. J., and TAYLOR, W. C., J. Am. Chem. Soc., 1964, 86, 3881.
8. MALLET, L., Compt. rend. Soc. biol., 1927, 185, 352. Groh, P., Bull. Soc. chim. France, 1938, 5, series 5, 12.
9. GATLOW, G., and SCHNEIDER, A., Naturwissenschaften, 1954, 41, 116. SELIGER, H. H., Anal. Biochem., 1960, 1, 60. STAUFF, J., and SCHMIDKING, H., Z. physikal. Chem., 1962, 35, 295. KHAN, A. U., and KASHA, M., J. Chem. Physics, 1963, 39, 2105.
10. BROWN, R. J., and OGRYZLO, E. A., Proc. Chem. Soc., 1964, 117.

11. FOOTE, C. S., and WEXLER, S., *J. Am. Chem. Soc.*, 1964, **86**, 3879.
12. CONNICK, R. E., *J. Am. Chem. Soc.* 1947, **69**, 1509.
13. STAUFF, J., and LOHMANN, F., *Z. physikal. Chem.*, N.F., 1964, **40**, 123.
14. YEATTS, L. B., and TAUBE, H., *J. Am. Chem. Soc.*, 1949, **71**, 4100.
15. ALYEA, H. N., and BÄCKSTRØM, H. L. J., *J. Am. Chem. Soc.*, 1929, **51**, 90.
16. RUSSELL, G. A., MOYE, A. J., and NAGPAL, K. L., *J. Am. Chem. Soc.*, 1962, **84**, 4154.
17. METHOFF, R. C., and BRANCH, G. E. K., *J. Am. Chem. Soc.*, 1930, **52**, 255.
18. PETRY, R. C., and VERHOEK, F. H., *J. Am. Chem. Soc.*, 1956, **78**, 6416. DEMUTH, R., and MEYER, V., *Ber. chem. Ges.*, 1890, **23**, 396.
19. HANSEN, R. L., and HAMANN, R. R., *J. Physic. Chem.*, 1963, **67**, 2868.
20. BAMFORD, C. H., and NEVITT, D. M., *J. Chem. Soc.*, 1946, 695.
21. BAMFORD, C. H., and NEVITT, D. M., *J. Chem. Soc.*, 1946, 688.
22. DAVIES, A. G., HARE, D. G., and KHAN, O. R., *J. Chem. Soc.*, 1963, 1125.
23. AVRAMENKO, L. I., and POSTNIKOV, L. M., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1960, 1921 (*Chem. Abstr.*, 1962, **56**, 14969). BARBER, M., FARREN, J., and LINNETT, J. W., *Proc. Roy. Soc. London, Series A*, 1963, **274**, 306.
24. CLYNE, M. A., and THRUSH, B. A., *Proc. Roy. Soc. London, Series A*, 1963, **275**, 559.
25. TAUBE, H., *J. Am. Chem. Soc.*, 1946, **68**, 611.
26. SIGLER, P. B., and MASTERS, B. J., *J. Am. Chem. Soc.*, 1955, **79**, 6353.
27. TSAO, MAAK-SANG, and WILMARTH, W. K., *Advances Chemistry Series*, 1962, **36**, 113.
28. KUNZ, A. H., *J. Am. Chem. Soc.*, 1931, **50**, 98.
29. LATIMER, W. M., Oxidation Potentials, Englewood Cliffs, New Jersey, Prentice-Hall, Inc., 2nd edition, 1952.
30. CZAPSKI, G., and BIELSKI, B. H. J., *J. Physic. Chem.*, 1963, **67**, 2180.
31. WHITAKER, R. A., and DAVIDSON, N., *J. Am. Chem. Soc.*, 1953, **75**, 3081.
32. GEORGE, P., *J. Chem. Soc.*, 1954, 4349.
33. BELOPAL'SKI, A. P., and URUSOV, V. V., *Zh. Prikl. Khim.*, 1948, **21**, 903.
34. EVANS, M. G., GEORGE, P., and URI, N., *Tr. Faraday Soc.*, 1949, **45**, 230.
35. CHER, M., and DAVIDSON, N., *J. Am. Chem. Soc.*, 1955, **77**, 793.
36. NEWTON, T. W., and BAKER, F. B., *J. Physic. Chem.*, 1958, **60**, 1417.
37. HALPERN, J., AND SMITH, J. G., *Canad. J. Chem.*, 1956, **34**, 1419.
38. SWINEHART, J., private communication.
39. KRUSE, W., and EIGEN, M., private communication.
40. NEWTON, T. W., and BAKER, F. B., *Inorg. Chem.*, 1964, **3**, 569.
41. HAIM, A., and WILMARTH, W. K., *J. Am. Chem. Soc.*, 1961, **83**, 509.
42. JOYNER, T. B., and WILMARTH, W. K., *J. Am. Chem. Soc.*, 1961, **83**, 516.
42 *a*. KOLACZKOWSKI, R. W., and PLANE, R. B., *Inorg. Chem.*, 1964, **3**, 322.
43. OGARD, A. E., and TAUBE, H., *J. Physic. Chem.*, 1958, **62**, 357.
44. MEYER, T. J., and TAUBE, H., work in progress.
45. ENDICOTT, J. F., and TAUBE, H., *Inorg. Chem.*, 1965, in press.
46. WANG, J. H., private communication.
47. GRIFFITH, J. S., *Proc. Roy. Soc. London, Series A*, 1956, **235**, 23.
48. IBERS, J. A., and LAPLACA, S. J., *Proc. 8th Internat. Conf. Coordination Chemistry*, Vienna, September 7, 1964.

49. VASKA, L., *Science*, 1963, **140**, 809.
50. BROSSET, C., and VANNERBERG, N. G., *Nature*, 1961, **190**, 714.
51. WANG, J. H., Hemoglobin and myoglobin, *in* Oxygenases, (O. Hayaishi, editor), New York, Academic Press, Inc., 1962, 464.
52. VOGT, L. H., *Chem. Rev.*, 1963, **63**, 269.
53. CALVIN, M., BAILES, R. H., and WILMARTH, W. K., *J. Am. Chem. Soc.*, 1946, **68**, 2254.
54. WERNER, A., and MYLIUS, A., *Z. anorgan. Chem.*, 1898, **16**, 245.
55. HAIM, A., and TAUBE, H., *J. Am. Chem. Soc.*, 1963, **85**, 495.
56. HALPERIN, J., and TAUBE, H., *J. Am. Chem. Soc.*, 1952, **74**, 380.
57. NOYES, A. A., AND DAHL, T. J., *J. Am. Chem. Soc.*, 1937, **59**, 1337.
58. BAWN, C. E. H., and WHITE, A. G., *J. Chem. Soc.*, 1951, 331.
59. WEISER, D. W., Ph.D. Dissertation, University of Chicago, Department of Chemistry, 1956.
60. BAXENDALE, J. H., and WELLS, C. F., *Tr. Faraday Soc.*, 1957, **53**, 800.
61. THUSIUS, D., and TAUBE, H., experiments in progress.