[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STEVENS INSTITUTE OF TECHNOLOGY]

THE COMMON BASIS OF ORGANIC OXIDATIONS IN ACIDIC SOLUTION[1]

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The view is prevalent that oxidation in organic chemistry is very often the equivalent of dehydrogenation (1), and this has led to the belief that the intimate mechanistic representation of such reactions should portray the removal of a pair of neutral hydrogen atoms *per se* from the substance oxidized and their transfer to the substance reduced (2–6). Theories of organic oxidation founded on the free-radical thesis (2–6), which require homolytic cleavage of valence bonds with the accompanying unpairing of electron spins fail to take into account the fact that the great majority of oxidations brought about by the common strong inorganic oxidants exhibit little of the character of radical reactions,[2] and are most effective in strongly polar media where the intermediate formation of ions and their incipient solvolysis is a process requiring a considerably smaller expenditure of energy (9) than formation of a radical pair.[3]

A cursory consideration of the simple fact that paraffin hydrocarbons are the most oxidatively resistant organic compounds known suffices to reveal immediately that the abstraction of hydrogen atoms (of which the paraffins have the most) has little if, indeed, anything to do with the process of oxidation.

The organic compounds most easily oxidized, such as olefins, acetylenes, alcohols, phenols, aldehydes, amines, alkyl halides, thiols, sulfides, disulfides, and sulfoxides, all have one thing in common, namely—an excess of valence electrons over and above those needed for bonding. This, of course, suggests at once 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.*

But if this be the case, how, then, can there be a plausible explanation for the fact that the partially oxidized terminal carbon atom of RCH_2OH or RCH_2NH_2 is more susceptible to oxidation than the corresponding C atom in the paraffin RCH_3; for, based on a consideration of the relative electronegativities of the atoms involved, one would necessarily reach the conclusion that, by reason of the inductive effect, the resulting polarities are $R\overset{\delta+}{C}H_2\overset{\delta-}{O}H$ and $R\overset{\delta+}{C}H_2\overset{\delta-}{N}H_2$, (both having C's with a lower electron density than in RCH_3) and that consequently, the alcohol and amine should be less susceptible to oxidative attack at

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[1] This discussion will be limited to so-called chemical oxidation, which denotes oxidation by well-recognized strong (generally inorganic) oxidizing agents other than molecular oxygen. Oxidations brought about by the latter are known as autoxidations, and proceed by way of a free radical chain mechanism, as do most oxidations which take place in the gas phase and in non-ionizing solvents.

[2] For instance, molecular oxygen has no effect on the rate of permanganate oxidation of oxalate or formate (7), nor on the rate of persulfate oxidation of sulfoxides or of water (8).

[3] "The general pattern of organic chemistry, as we know it, is based largely on heterolytic reactions."—C. K. Ingold (10).

the C atom than the hydrocarbon. This paradox is encountered only because we have become accustomed to regarding the transformation $RCH_2OH \rightarrow RCH{=}O$ as one in which the only essential change occurring is oxidation of the terminal carbon atom. Therefore, one is inclined to conclude, the C atom must have been the immediate site of the oxidative attack. If, however, in the transformation $RCH_2{-}CH_3 \xrightarrow{-2H} RCH{=}CH_2$, both C atoms have been oxidized, then in the formally analagous reaction $RCH_2OH \xrightarrow{-2H} RCH{=}O$ have not both C and O been oxidized? Here, indeed, may be the key to the whole problem; for, if adjacent C and O atoms *are* both oxidized in the process, the initial point of attack may presumably be at one or the other of these atoms. Considering now that the oxidative species is, of necessity, an electron-seeking substance, and that in the molecule RCH_2OH, the *highest electron density*, as well as *the only free electron pairs* have their location at the O atom, one is forced to the conclusion that the *initial site of oxidative attack is at the oxygen atom* (or other relatively electronegative center) and *not* at the carbon atom. Paraffin hydrocarbons, therefore, cannot be oxidized by ordinary chemical means because they have no such point of attack.

This conclusion may be arrived at even more readily by examination of reactions wherein RSH, R_2S, R_3N, and ArI, for example, are oxidized unambiguously and exclusively at the center of electronegativity (S, N, or I) to give, respectively, RSSR, R_2SO, R_3NO and ArIO.

A decrease in the magnitude of the partial negative charge on the atom susceptible to oxidation results in a greatly enhanced resistance toward oxidation. Such a decrease may be accomplished by introducing strongly inductive groups (themselves not too easily susceptible to oxidation) into the molecule close to the atom in question. For example, in the order of ease of oxidation at the sulfur atom: $Et_2S > Et{-}S{-}CH_2CH_2Cl > (ClCH_2CH_2)_2S$ (11); $Et_2S > (C_6H_5CH_2)_2S > (C_6H_5)_2S$ (12); and $Et_2SO > (C_6H_5)_2SO$ (8). This is because the strongly inductive (electron-attracting) Cl atom or phenyl group causes a decrease in electron density at the S atom. For a similar reason, in ease of oxidation $R_2S \gg R_2SO$ (8, 13). Even more effective in increasing the resistance toward oxidation is to render completely unavailable the free electron pair(s) which the oxidizing agent seeks to remove. Thus, in ease of oxidation, $R_2\ddot{S}O \gg R_2SO_2$ (8, 14), and $R\ddot{N}H_2 \gg R\overset{+}{N}H_3$ (15), because in the case of both a sulfone and an alkyl ammonium ion, *there are no unshared electron pairs to remove* from the S or N atom.

The exact nature of the oxidizing species in solutions of the various strong inorganic oxidants has been the subject of much investigation and speculation. According to the present hypothesis, since the point of attack on the reductant is assumed to be an electronegative site, such attack is obviously favored by the presence of a full positive charge, or at least a partial electropositive site, on the oxidizing species. Direct reaction of the negative center of the reductant with a negatively charged oxidant may be possible, but certainly not probable, just as reaction between two like-charged ions is considered rather unlikely (7). The probability is much greater that the oxidizing species is in all cases a positive ion or a neutral molecule containing one relatively positively charged atom.

Thus the oxidizing entity in nitric acid solutions is almost certainly $H_2NO_3^+$, NO_2^+, or $\overset{\delta+\delta-}{NO_2}$, and not NO_3^-.[4] In every case the positive ion is formed readily in acidic solutions by reactions which are typified by the following examples:

$$2HONO_2 \rightleftharpoons NO_3^- + H_2\overset{+}{O}NO_2 \rightleftharpoons H_2O + \overset{+}{N}O_2$$

$$2HOCl \rightleftharpoons OCl^- + H_2\overset{+}{O}Cl \rightleftharpoons H_2O + \overset{+}{Cl}$$

$$H^+ + HOOH \rightleftharpoons H_2\overset{+}{O}OH \rightleftharpoons H_2O + OH^+$$

$$H^+ + O_3 \rightleftharpoons O_3H^+ \rightleftharpoons O_2 + OH^+$$

$$2H^+ + MnO_4^- \rightleftharpoons H_2\overset{+}{O}MnO_3 \rightleftharpoons H_2O + \overset{+}{Mn}O_3$$

$$3H^+ + CrO_4^{=} \rightleftharpoons H_2\overset{+}{O}CrO_3H \rightleftharpoons H_2O + \overset{+}{Cr}O_3H$$

The ease with which these positive ions are formed in the presence of a proton donor may be one of the principal reasons that all common oxidizing agents are, without exception, the more powerful the greater the acidity of the solution in which they are used.

Table I shows the most probable and the least probable specific oxidants in solutions of the various common oxidizing agents.

Many of the positive ionic species, (such as NO_2^+, SO_3H^+, NO^+, Cl^+) will be recognized as those responsible for electrophilic aromatic substitutions (16). Evidence that $H_2\overset{+}{O}OH$ or HO^+ is the oxidizing species in acidic hydrogen peroxide solutions has been obtained (17), and transfer of HO^+ from organic peracids to various substrates has been well established (18). In like manner, sulfur tetroxide (SO_4)[5] has been postulated as the active species in persulfate solutions (19, 20) and it has recently been demonstrated that $H_2\overset{+}{O}NO$ or $\overset{+}{N}O$ is responsible for oxidative attack on formate (23). The species $\overset{+}{Mn}O_3$ is the permanganyl ion, and there can be little doubt of its existence in the recently prepared permanganyl fluoride $\overset{+}{Mn}O_3\overset{-}{F}$ (24) which is (as would be predicted on the basis of the present view) a much stronger oxidant (24) than $KMnO_4$. The same reasoning would lead one to expect that nitronium salts such as (16) $(\overset{+}{N}O_2)(ClO_4^-)$, $(\overset{+}{N}O_2)_2(S_2O_7^{=})$, and $(\overset{+}{N}O_2)(NO_3^-)$ (nitrogen pentoxide), as well as the nitronium (nitryl) halides like NO_2Cl, are all stronger oxidants than

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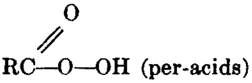
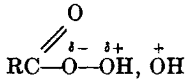
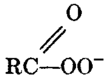
[4] Both nitrate and chromate ion in basic or neutral solution have standard oxidation potentials very close to zero and are therefore no stronger as oxidants than is H_3O^+ ion. On the other hand, both become strong oxidants in 1 *N* acid solution, and very powerful oxidants indeed in concentrated acid solutions.

[5] Sulfur tetroxide, the anhydride of Caro's acid (H_2SO_5) has been prepared (21). It is also believed to be present in the strongly oxidizing solution of $H_2SO_4 + Mn^{+2}$ electrolyzed in the glow discharge (22).

TABLE I

List of Probable Oxidizing Species of Oxidants

Oxidizing Agent	**Precise Oxidizing Species**	
	Most Probable	**Least Probable**
HNO_3	$H_2\overset{+}{O}NO_2$, $\overset{+}{N}O_2$, $\overset{\delta+}{N}\overset{\delta-}{O}_2$	NO_3^-
HNO_2	$H_2\overset{+}{O}NO$, $\overset{+}{N}O$, $\overset{\delta+}{N}\overset{\delta-}{O}$	NO_2^-
H_2SO_4	$H_2\overset{+}{O}SO_3H$, $\overset{+}{S}O_3H$, $\overset{\delta+}{S}\overset{\delta-}{O}_3$	HSO_4^-, $SO_4^{=}$
HIO_4	$H_2\overset{+}{O}IO_3$, $\overset{+}{I}O_3$	IO_4^-
$HClO$	$H_2\overset{+}{O}Cl$, Cl^+, $\overset{\delta+}{Cl}—\overset{\delta-}{O}H$	ClO^-
H_2O_2	$H_2\overset{+}{O}OH$, $\overset{+}{O}H$, $\overset{\delta+}{HO}—\overset{\delta-}{O}H$	OOH^-, $O_2^{=}$
H_2SO_5	SO_4H^+	HSO_5^-, $SO_5^{=}$
Br_2	Br^+, $\overset{+\delta}{Br}—\overset{\delta-}{Br}$	
$K_2S_2O_8$ $(+H^+)$	SO_4H^+, $\overset{+}{O}SO_3^{-}$	$HS_2O_8^-$, $S_2O_8^{=}$
K_2CrO_4 $(+H^+)$	$\overset{+}{Cr}O_3H$, $\overset{\delta+}{Cr}\overset{\delta-}{O}_3$	$HCrO_4^-$, $CrO_4^{=}$, $Cr_2O_7^{=}$
$KMnO_4$ $(+H^+)$	$H_2\overset{+}{O}MnO_3$, $\overset{+}{Mn}O_3$	MnO_4^-
$Pb(OAc)_4$	$\overset{+}{Pb}(OAc)_3$, $\overset{++}{Pb}(OAc)_2$, $\overset{\delta+}{Pb}(\overset{\delta-}{OAc})_4$	
 $RC(=O)—O—OH$ (per-acids)	 $RC(=O)—\overset{\delta-}{O}—\overset{\delta+}{O}H$, $\overset{+}{O}H$	 $RC(=O)—OO^-$

nitric acid just as they are more powerful aromatic nitrating agents. Similarly, chromyl halides would be expected to be [and are (25)] stronger oxidants than chromic acid, and chlorosulfonic acid should be more powerful than sulfuric acid[6]. In agreement with the requirements of the present view, most of these positively charged or neutral oxidizing species are capable of undergoing a simple two electron transfer[7] which results in their reduction to the common stable anions or molecules actually observed as the products. (In this connection there is little need to point out the fact that the organic reductant always suffers in a net loss of two electrons).

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[6] On the other hand, the presence of chloride ion causes a retardation in the rate of the persulfate oxidation of sulfoxides (26), due, presumably, to combination of Cl^- with $\overset{+}{O}SO_3^-$ to form$ClOSO_3^-$, thereby reducing the concentration of active oxidizing species.

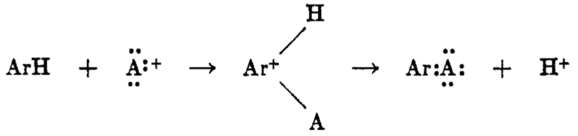
[7] Two-electron oxidation-reduction reactions have been well established in certain instances, such as in the chlorate oxidation of sulfite (27, 28), and in the chromic acid oxidation of isopropyl alcohol (29, 30).

For example:

$$
\begin{gathered}
NO_2^+ + 2e \rightarrow NO_2^- \\
NO_2 + 2e \rightarrow NO + O^= \\
NO^+ + 2e \rightarrow NO^- \xrightarrow{NO^+} 2N\dot{O} \\
OH^+ + 2e \rightarrow OH^- \\
MnO_3^+ + 2e \rightarrow MnO_3^- \\
CrO_3H^+ + 2e \rightarrow CrO_3H^- \\
SO_3H^+ + 2e \rightarrow SO_3H^- \\
SO_4H^+ + 2e \rightarrow SO_4H^- \\
IO_2^+ + 2e \rightarrow IO_2^- \\
Cl^+ + 2e \rightarrow Cl^- \\
\overset{+}{Pb}(OAc)_3 + 2e \rightarrow Pb^{++} + 3OAc^-
\end{gathered}
$$

The formation of Cr^{IV} (as in CrO_3H^-, $CrO_3^=$, or CrO_2) as the first reduction product of Cr^{VI} has been postulated[8] in the oxidation of secondary alcohols (29, 30, 38). Similarly, Mn^V in the ion MnO_3^- has previously been proposed as the immediate reduction product of Mn^{VII} in the oxidation of formate (32–34).

It thus appears reasonable that the active oxidizing substances are always cationoid or electrophilic species generally identical with those responsible for substitution reactions on the aromatic ring. As further justification for this assumption, the following analogy may be made. The mechanism of aromatic substitutions generally comprises two steps, which are very likely the same two steps involved in the initial stages of most oxidations of organic molecules. The first step in aromatic substitutions, upon attack by the electrophilic species $\ddot{\underset{\cdot\cdot}{A}}{:}^{+}$, is the formation of a positively charged intermediate complex; and the second is the loss of a proton:



$$ArH + \ddot{\underset{\cdot\cdot}{A}}{:}^{+} \rightarrow Ar^{+}\begin{matrix} H \\ A \end{matrix} \rightarrow Ar{:}\ddot{\underset{\cdot\cdot}{A}}{:} + H^+$$

The formation of $Ar{:}\ddot{\underset{\cdot\cdot}{A}}{:}$, the substituted aromatic compound, then is in reality only the first stage of an oxidation which generally proceeds no further because of the great stability of the aromatic product, which can be considered as an intermediate in the oxidative process. That this view is justified may readily be seen from the following well known examples in which the subsequent stages of the oxidative sequence are *forced* to take place.

$$ArH \xrightarrow{SO_3H^+} ArSO_3H \xrightarrow[Fuse]{OH^-} ArOH + SO_3H^-$$

also

$$ArH \xrightarrow{Cl^+} ArCl \xrightarrow{OH^-} ArOH + Cl^-$$

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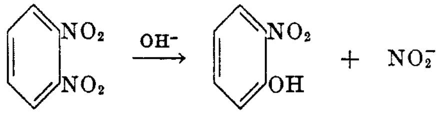
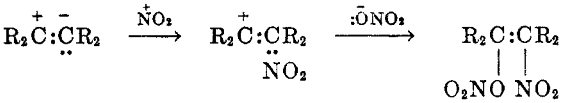
[8] Furthermore, the existence of $Cr^{IV}O_2$ has been established (31).

and, as a final example:



In each case, it will be observed, the over-all effect of the sequence has been to oxidize ArH to ArOH, and simultaneously reduce $\overset{..}{\underset{..}{A}}{:}^{+}$ to ${:}\overset{..}{\underset{..}{A}}{:}^{-}$. Therefore, it may be concluded that all electrophilic aromatic substitutions are the first stages of oxidations which come to an abrupt halt because the intermediate formed is an extremely stable molecule.

Oxidative addition to olefins furnishes another powerful argument that the initial attack is by a positive ion at the most electronegative center. The mechanism here is clear-cut and well established. Thus oxidation by HOX to give the chlorohydrin proceeds by way of initial addition of $\overset{..}{\underset{..}{X}}{:}^{+}$ in accord with Markovnikov's rule. Similarly, Br_2 will oxidize ethylene to $BrCH_2CH_2Br$ only in the presence of a trace of water (35), in which case formation of Br^+ is facilitated. Again, oxidative addition of nitric acid gives the sequence,



$$R_2\overset{+}{C}{:}\underset{..}{\overset{-}{C}}R_2 \xrightarrow{\overset{+}{NO_2}} R_2\overset{+}{C}{:}\underset{NO_2}{\underset{..}{C}}R_2 \xrightarrow{:\bar{O}NO_2} \begin{array}{cc} R_2C & {:}CR_2 \\ | & | \\ O_2NO & NO_2 \end{array}$$

forming the β-nitro nitrate ester (35). Nitrogen tetroxide, N_2O_4, gives the corresponding β-nitroso nitrate ester (35) by attack of $\overset{+}{NO}$ followed by NO_3^-. Glycol formation by permanganate oxidation can be formulated in analogous manner, assuming initial attack by $\overset{+}{MnO_3}$ to form a cyclic intermediate, followed by two consecutive attacks by $\overset{-}{OH}$ or H_2O. All permanganate oxidations, however, are unusually complicated because of the many different oxidation states of Mn (7^+, 6^+, 5^+, 4^+, 3^+, and 2^+) which can participate in the reactions. Initial attack by Mn^{+3} or its complexes, MnX_2^+, has been postulated in the oxidation of oxalate (36).

In the case of the more easily oxidized organic molecules, such as alcohols, aldehydes, sulfides, etc., the reaction does *not* stop at the first stage, because the second stage can be attained with extreme ease and rapidity.

A few examples of ionic oxidative mechanisms will clearly illustrate why this is so. It should be pointed out that in all four of the examples presented below the mechanisms are essentially identical with those previously proposed for the reactions. The main purpose of the present paper is to define the common basis of the mechanistic course of these reactions and to indicate how the same sort of reasoning can be applied with equal success to many additional well-known oxidations for which logical mechanisms, in agreement with kinetic and other data, have not previously been devised.

The common characteristics of these four mechanisms are (37):

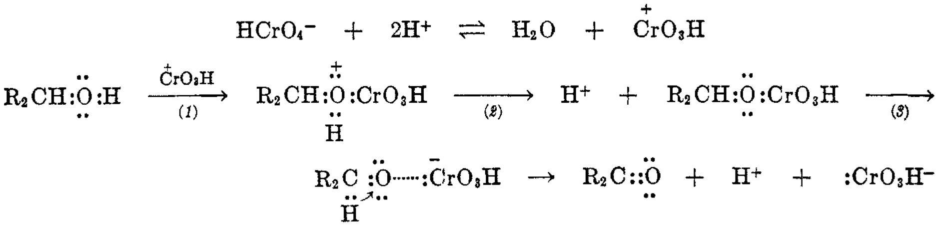
1. The positively charged atom of the oxidant always attacks a free electron pair of the reductant at a center of high electron density, forming a coordinate bond, and the atom initially attacked (in some cases the adjacent atom) becomes positively charged.

2. The positive charge is removed by expulsion of a positive fragment (usually H+) or by combination with a readily available anion.

3. The oxidizer begins to move off with the electron pair of the coordinate bond, resulting in a transition state in which a newly forming positive organic species is simultaneously expelling a second positive fragment or combining with a second negative ion.

The examples follow:[9]

Example 1: The chromic acid oxidation of secondary alcohols (29, 30, 38).

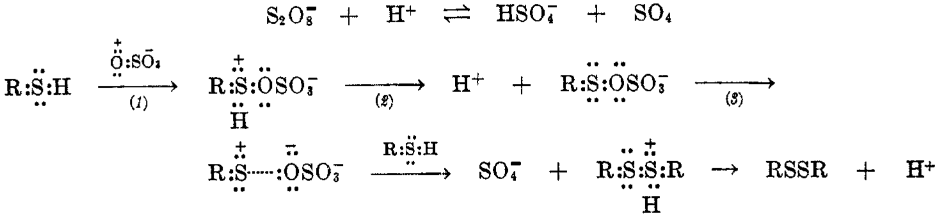


$$HCrO_4^- + 2H^+ \rightleftharpoons H_2O + \overset{+}{Cr}O_3H$$

$$R_2CH{:}\underset{\cdot\cdot}{\ddot{O}}{:}H \xrightarrow[(1)]{\overset{+}{Cr}O_3H} R_2CH{:}\underset{\underset{H}{\cdot\cdot}}{\overset{+}{\ddot{O}}}{:}CrO_3H \xrightarrow[(2)]{} H^+ + R_2CH{:}\underset{\cdot\cdot}{\ddot{O}}{:}CrO_3H \xrightarrow[(3)]{}$$

$$R_2\underset{H}{C}\,{:}\ddot{O}\cdots{:}\overset{-}{Cr}O_3H \rightarrow R_2C{::}\underset{\cdot\cdot}{\ddot{O}} + H^+ + {:}CrO_3H^-$$

Example 2: The persulfate oxidation of mercaptans (20).

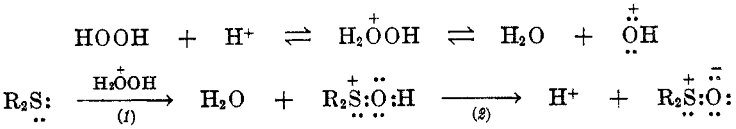


$$S_2O_8^= + H^+ \rightleftharpoons HSO_4^- + SO_4$$

$$R{:}\underset{\cdot\cdot}{\ddot{S}}{:}H \xrightarrow[(1)]{\overset{+}{\ddot{O}}{:}\overset{-}{SO_3}} R{:}\underset{\underset{H}{\cdot\cdot}}{\overset{+}{\ddot{S}}}{:}\underset{\cdot\cdot}{\ddot{O}}SO_3^- \xrightarrow[(2)]{} H^+ + R{:}\underset{\cdot\cdot}{\ddot{S}}{:}\underset{\cdot\cdot}{\ddot{O}}SO_3^- \xrightarrow[(3)]{}$$

$$R{:}\underset{\cdot\cdot}{\overset{+}{\ddot{S}}}\cdots{:}\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}SO_3^- \xrightarrow{R{:}\ddot{S}{:}H} SO_4^= + R{:}\underset{\cdot\cdot}{\ddot{S}}{:}\underset{\underset{H}{\cdot\cdot}}{\overset{+}{\ddot{S}}}{:}R \rightarrow RSSR + H^+$$

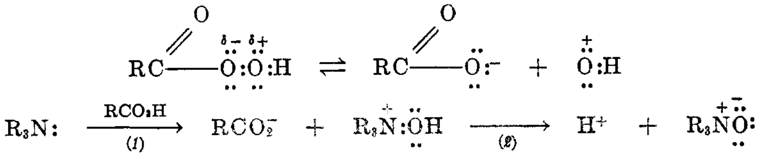
Example 3: The oxidation of sulfides by hydrogen peroxide (17).



$$HOOH + H^+ \rightleftharpoons H_2\overset{+}{O}OH \rightleftharpoons H_2O + \underset{\cdot\cdot}{\overset{+}{\ddot{O}}}H$$

$$R_2\underset{\cdot\cdot}{S}{:} \xrightarrow[(1)]{H_2\overset{+}{O}OH} H_2O + R_2\underset{\cdot\cdot}{\overset{+}{S}}{:}\underset{\cdot\cdot}{\ddot{O}}{:}H \xrightarrow[(2)]{} H^+ + R_2\underset{\cdot\cdot}{\overset{+}{S}}{:}\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}{:}$$

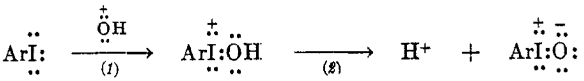
Example 4: The oxidation of tertiary amines and aryl iodides by organic peracids (18, 39).



$$RC(=O)-\underset{\cdot\cdot}{\overset{\delta-}{\ddot{O}}}{:}\underset{\cdot\cdot}{\overset{\delta+}{\ddot{O}}}{:}H \rightleftharpoons RC(=O)-\underset{\cdot\cdot}{\ddot{O}}{:}^- + \underset{\cdot\cdot}{\overset{+}{\ddot{O}}}{:}H$$

$$R_3N{:} \xrightarrow[(1)]{RCO_3H} RCO_2^- + R_3\overset{+}{N}{:}\underset{\cdot\cdot}{\ddot{O}}H \xrightarrow[(2)]{} H^+ + R_3\overset{+}{N}\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}{:}$$

and



$$Ar\underset{\cdot\cdot}{\ddot{I}}{:} \xrightarrow[(1)]{\overset{+}{\ddot{O}}H} Ar\underset{\cdot\cdot}{\overset{+}{\ddot{I}}}{:}\underset{\cdot\cdot}{\ddot{O}}H \xrightarrow[(2)]{} H^+ + Ar\underset{\cdot\cdot}{\overset{+}{\ddot{I}}}{:}\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}{:}$$

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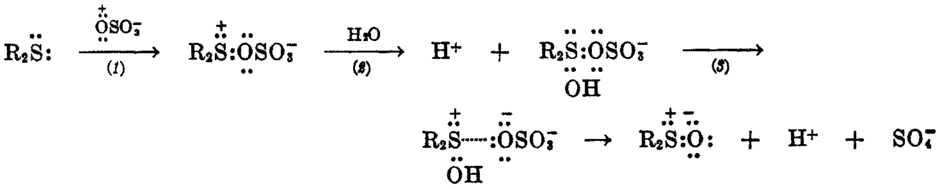
[9] In these examples of ionic oxidation it should be understood that loss of a proton always occurs by direct transfer to a basic species, but for simplicity in formulation this has not been indicated. Only in certain instances, as in the last step of Ex. 1, are such proton removals kinetically significant.

(In the last two examples, no third step need take place.)

The following additional examples of reactions for which plausible mechanisms have not previously been worked out will illustrate the applicability of the generalized approach outlined here.

Example 5: The persulfate oxidation of sulfides and sulfoxides (8, 26, 40–42).

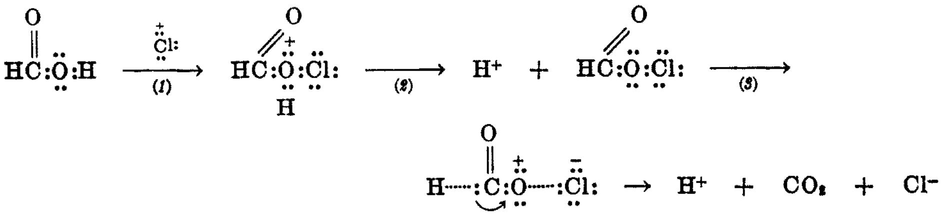
$$S_2O_8^= \rightleftharpoons SO_4^- + SO_4$$



This mechanism is in agreement with the kinetics (41, 42) of the reaction, which are first-order with respect to persulfate and first-order in substrate concentration at low concentrations. At higher concentrations of substrate, the reaction remains first-order in persulfate, but becomes zero-order in sulfur compound, presumably because of the slow rate of formation of the active oxidizing species.

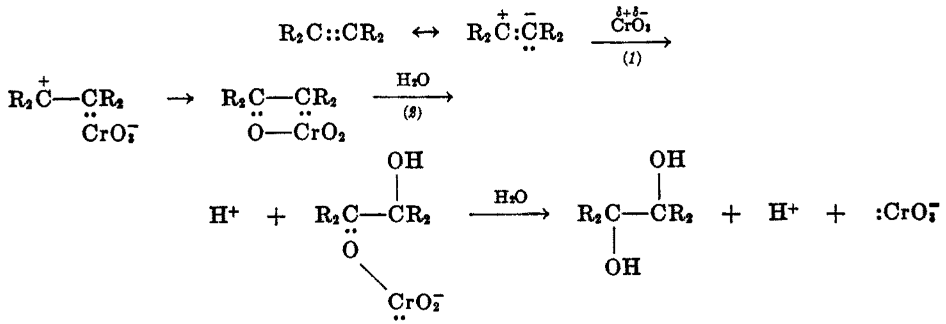
Example 6: The oxidation of formic acid by hypochlorous acid (43).

$$2HOCl \rightleftharpoons OCl^- + H_2\overset{+}{O}Cl \rightleftharpoons H_2O + \overset{+}{Cl}$$



This mechanism is in accord with the kinetics (43) which are second-order in HOCl and first-order in HCOOH. Above *p*H 13 there is no reaction, because Cl^+ cannot be formed. Addition of H^+ ion accelerates hypochlorite oxidations (44) by assisting in the formation of $H_2\overset{+}{O}Cl$ and Cl^+.

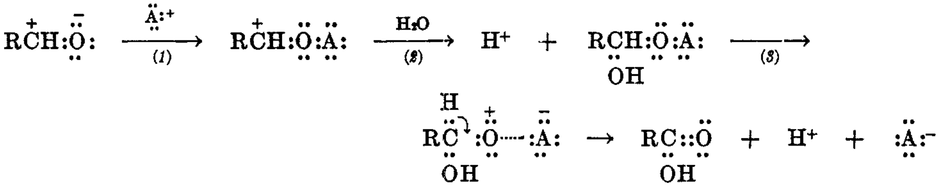
Example 7: The chromic acid oxidation of olefins (45).



In this reaction a *trans* glycol is produced (45). The intermediate formation of an organochromium complex has been established (45).

Example 8: The oxidation of aldehydes.

In general, these oxidations probably proceed in the following manner (where $\underset{\cdot\cdot}{\ddot{A}}{:}^+$ is the active oxidant):



$$R\overset{+}{C}H{:}\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}{:} \xrightarrow[(1)]{\ddot{A}{:}^+} R\overset{+}{C}H{:}\underset{\cdot\cdot}{\ddot{O}}{:}\underset{\cdot\cdot}{\ddot{A}}{:} \xrightarrow[(2)]{H_2O} H^+ + R\underset{OH}{\underset{\cdot\cdot}{C}}H{:}\underset{\cdot\cdot}{\ddot{O}}{:}\underset{\cdot\cdot}{\ddot{A}}{:} \xrightarrow[(3)]{}$$

$$R\underset{OH}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}{:}\underset{\cdot\cdot}{\overset{+}{\ddot{O}}}\cdots{:}\underset{\cdot\cdot}{\overset{-}{\ddot{A}}}{:} \rightarrow R\underset{OH}{\underset{\cdot\cdot}{C}}{::}\underset{\cdot\cdot}{\ddot{O}} + H^+ + {:}\underset{\cdot\cdot}{\ddot{A}}{:}^-$$

When bromine (46) is the oxidant A^+ is Br^+, and the key intermediate in aqueous solution would be RCH(OH)OBr. In ethanol solution (46) RCH(OEt)OBr would be formed instead. This explains the direct formation of ethyl acetate when acetaldehyde is oxidized in ethanol solution, without the preliminary formation of acetic acid (46). The reaction does *not* proceed *via* the intermediate formation of acetyl bromide (47).

In any of these oxidative reactions, if the step in which the active oxidizing species is formed is the slowest step in the entire sequence of events, it will be the rate-controlling step. In this circumstance, with a constant initial concentration of oxidant and increasingly higher initial concentrations of reductant, a limiting rate should be attained at higher concentrations of reductant, and the rate of oxidation will become independent of the concentration of reductant. Such limiting rates have been observed in the persulfate oxidation of mercaptans (48), sulfides (40), sulfoxides (41, 42), and secondary alcohols (37); in the oxidation of sulfides by peracetic acid (13); and in the periodic acid oxidation of glycols (49). A limiting rate is also reached in the chlorination of aromatic compounds by HOCl, in which case it has been proved that the rate-controlling step is the slow reversible formation of Cl^+ or H_2O^+Cl (16).

In the oxidation of alcohols, the reaction appears always to go thru the intermediate stage of ester formation. For example, when CrO_3, $S_2O_8^=$, HNO_3, HOCl, H_2O_2, or HIO_4 is the oxidizing agent, the esters formed are, respectively, $ROCrO_3H$, $ROOSO_3H$, $RONO_2$, ROCl, ROOH, and $ROIO_3$. These intermediate esters are relatively stable only when R is a tertiary alkyl group; the primary and secondary esters generally decompose in the cold and are violently explosive on heating (50). The reason for this is that the subsequent oxidative steps can proceed rapidly when a proton can be expelled from the incipiently forming ions,[10] $RCH{:}\underset{\cdot\cdot}{\ddot{O}}{}^+$ or $R_2CH{:}\underset{\cdot\cdot}{\ddot{O}}{}^+$, whereas a tertiary ester can only expel a carbonium ion (R^+) from $R_3C{:}\underset{\cdot\cdot}{\ddot{O}}{}^+$, which is, energetically, more difficult to do. Thus, *tert*-butyl hypochlorite (52, 53), and chromate (54) are surprisingly stable.

The formation of carbonium ions in the oxidative cleavage of tertiary alcohols,

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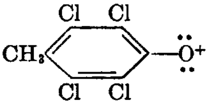
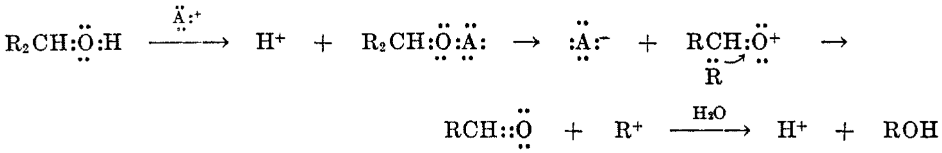
[10] Excellent evidence for the formation of the oxygen cation  during the oxidation of the corresponding phenol has been reported (51). Of course, HO^+ and $\overset{+}{O}SO_3^-$ are themselves oxygen cations.

ketones, and acids is implicit in the generalized approach to organic oxidation presented here. Even primary and secondary alcohols might be expected to expel carbonium ions in competition with proton ejection when the carbonium ion (such as $(CH_3)_3C^+$ or $C_6H_5CH_2^+$) is one that can be formed readily because of its relative stability.

Such cleavage has been observed in the chromic acid oxidation of many secondary alcohols. Thus, methyl *tert*-butyl carbinol gives *tert*-butyl alcohol and acetaldehyde (55), and phenyl *tert*-butyl carbinol yields *tert*-butyl alcohol and benzaldehyde (56, 57). On the other hand, phenyl *n*-butyl carbinol gives only "normal" oxidation to the ketone (56) because a stable carbonium ion cannot be expelled. Wholly comparable results are obtained in the oxidation of secondary alcohols by acidic permanaganate (56).

Similarly, in the oxidative cleavage of tertiary alcohols to ketones by chromic acid (58, 59), and by acidic hydrogen peroxide (60) or *tert*-butyl hydroperoxide (60), the cleaved group is always the one which can most readily be eliminated as a carbonium ion. Thus, diphenyl *p*-nitrophenyl carbinol (58) gives *p*-nitrobenzophenone and phenol; diphenyl *o*-tolyl carbinol (60) yields benzophenone and *o*-cresol; and phenyl dimethyl carbinol (60) gives acetone and phenol.

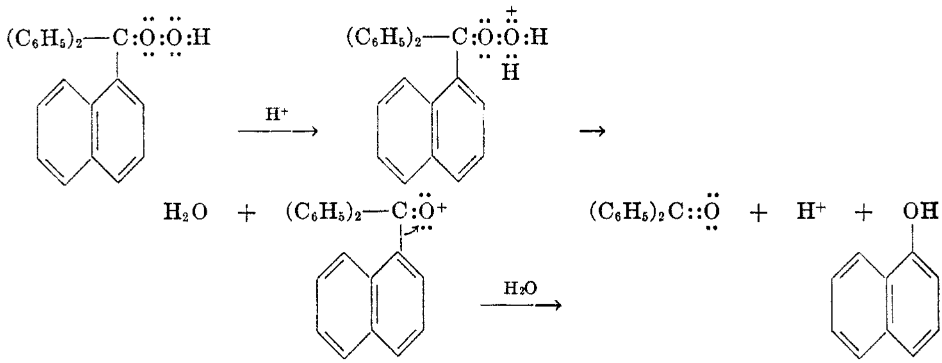
The mechanism of cleavage of secondary alcohols is readily explained on the basis of the present view, and may be simply represented[11] as follows (where A^+ is a general oxidant):



$$R_2CH{:}\underset{..}{\ddot{O}}{:}H \xrightarrow{\ddot{A}{:}^+} H^+ + R_2CH{:}\underset{..}{\ddot{O}}{:}\underset{..}{\ddot{A}}{:} \rightarrow {:}\underset{..}{\ddot{A}}{:}^- + \underset{R}{RCH}{:}\ddot{O}^+ \rightarrow$$

$$RCH{::}\underset{..}{\ddot{O}} + R^+ \xrightarrow{H_2O} H^+ + ROH$$

An example of the oxidative cleavage of a tertiary alcohol is the oxidation of diphenyl α-naphthyl carbinol (60) by acidic hydrogen peroxide, which almost certainly proceeds by way of the hydroperoxide ester in the following manner:



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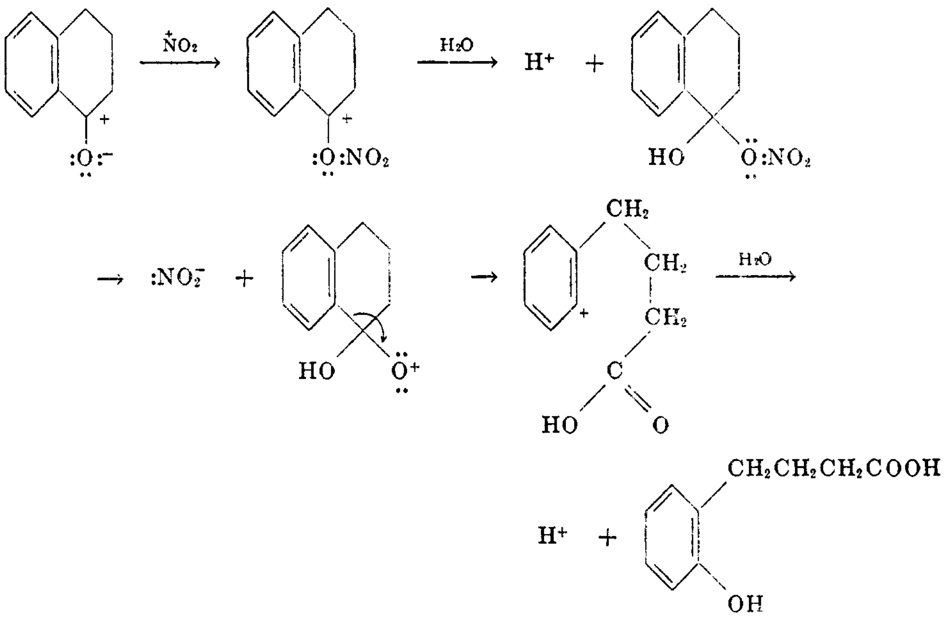
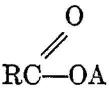
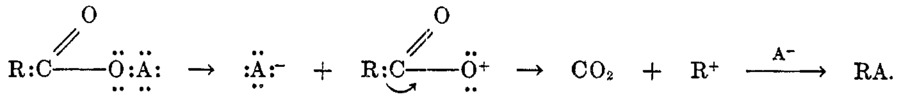
[11] Formation of an oxygen cation as the intermediate in these reactions was proposed by Zeiss (59) and represented in the following manner: $R_3C^+ + HCrO_4^- \rightarrow R_3COCrO_3H \rightarrow R_3CO^+ + HCrO_3^-$. While adequate for tertiary and possibly secondary alcohols, this would not explain the oxidation of primary alcohols. Mosher and Whitmore (55) preferred hydride ion ($:H^-$) extraction from ROH to give directly RO^+, but this seems hardly likely in acidic solution.

The oxidation of α-tetralone by strong oxidants such as persulfate, nitric acid, or chromic acid affords an interesting example of ketone cleavage. The reaction, which results in formation of 4-(2-hydroxyphenyl)butanoic acid (61), may be formulated as follows, with HNO_3 as the oxidizing agent.



In similar fashion, periodic acid cleaves diethyl ketone at elevated temperatures to give propionic acid and ethanol (62). This takes place, presumably, by attack of $\overset{+}{IO_3}$ on the oxygen atom.

Oxidative decarboxylation of acids very likely proceeds though formation of an acyl ester,  $R\overset{O}{\overset{\|}{C}}—OA$ as the intermediate (63):


$$R{:}\overset{O}{\overset{\|}{C}}—\ddot{\underset{..}{O}}{:}\ddot{\underset{..}{A}}{:} \rightarrow {:}\ddot{\underset{..}{A}}{:}^- + R{:}\overset{O}{\overset{\|}{C}}—\ddot{\underset{..}{O}}^+ \rightarrow CO_2 + R^+ \xrightarrow{A^-} RA.$$

The acyl nitrates and bisulfates have been isolated, though they are very unstable (64).

If carbonium ions of sufficiently long half-life are actually ejected from molecules undergoing oxidative fission of C—C bonds, one might expect that molecular rearrangements involving certain of them would have been noted.[12] Such Wagner-Meerwein type rearrangements have in fact been observed, for ex-

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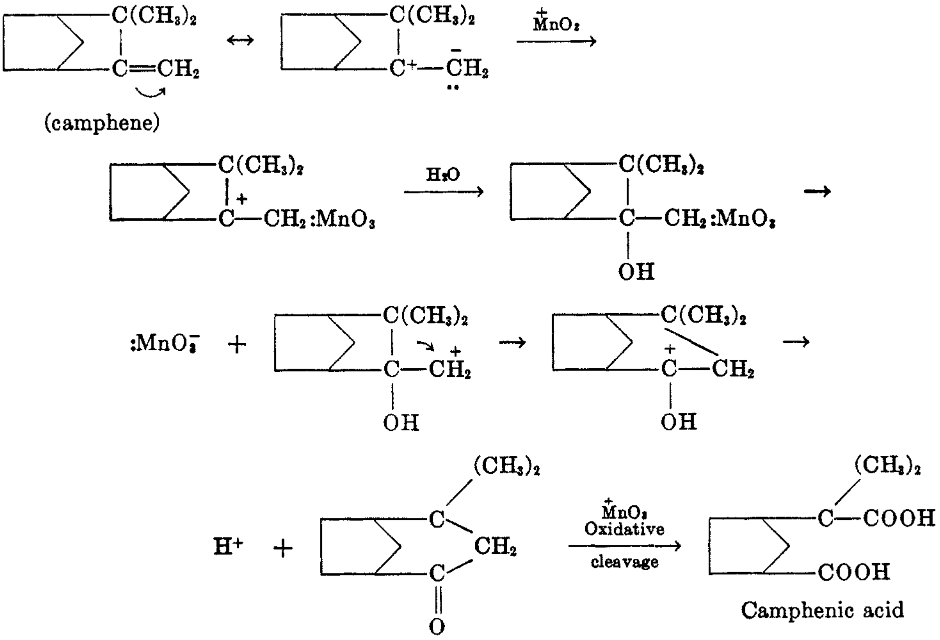
[12] Since this paper was first submitted for publication, a striking confirmation of the carbonium ion nature of the eliminated group has been established by Mosher and Duckworth (65) in the chromic acid oxidation of *l*-3-methyl-3-phenyl-2-pentanol, in which the cleaved carbonium ion was racemized completely to give *d,l*-2-phenyl-2-butanol.

ample in the chromic acid oxidation of cyclooöctatetraene (66) to *p*-phthalic acid, and in the permanganate oxidation of camphene to camphenic acid (67). The mechanism of the latter reaction may be explained as follows:



In many instances, solvolysis may simultaneously accompany the formation of a carbonium ion in a concerted type reaction, so that it never actually becomes a free entity. When molecular rearrangement accompanies its formation, however, it is apparent that the carbonium ion is relatively long-lived. Similarly, in many cases the positively charged electrophilic oxidizing species may never actually have an independent existence (68), but may rather, like a proton, be transferred directly from the oxidizing agent to the organic reductant.

Finally, it is of considerable interest to note the striking analogy between a typical acid-base reaction and the formation of the initial complex postulated here, in which the electronegative atom of the organic molecule plays the role of a Lewis base and the oxidant $\overset{\cdot\cdot}{\underset{\cdot\cdot}{A}}{:}^{+}$ is a typical Lewis acid. The entire phenomenon of oxidation-reduction, from this viewpoint, is just a special case of acid-base behavior. This concept is by no means new or startling, since the same general conclusion was reached some time ago in the most comprehensive of acid-base theories yet proposed (69, 70).

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