

Catalytic oxidation : an introduction

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CATALYTIC OXIDATION, AN INTRODUCTION

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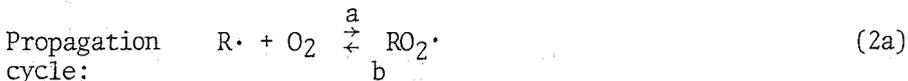
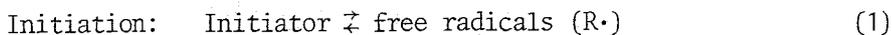
1. INTRODUCTION

Catalytic oxidation provides perhaps the most intricate and challenging terrain in the whole field of catalysis. One reason for the complexity is that there is almost always a noncatalytic ("thermal") reaction occurring simultaneously with the catalytic reaction; it may be an almost-negligible background reaction, but it sometimes can accelerate and even overwhelm the catalytic reaction. Oxidation reactions of hydrocarbons are strongly exothermic and consequently tend to be auto accelerating, which makes them difficult to control. If there are two competing reactions, one thermal and another catalytic, control can become even more difficult; catalytic reactions can ignite thermal processes, and homogeneous gas-phase reactions can lead to the combustion of products of catalytic reactions. There is at least one group of important catalytic oxidation processes for which the "catalyst" is nothing but a modifier of the thermal process. All these complications make it necessary to take a hard look at the thermal reactions before considering the subject of pure catalytic oxidation.

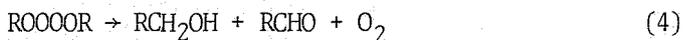
2. THERMAL (NONCATALYTIC) OXIDATION AND COMBUSTION

The following description of the mechanisms of noncatalytic oxidation is based largely on the recent survey of Benson and Nangia [1]. Combustion proceeds by a sequence of elementary reactions (steps) leading from one intermediate to another, each

intermediate being richer in oxygen than the preceding one. To unravel the sequence of steps, one usually starts with a study of slow reactions proceeding at low temperatures. Thermal oxidations take place via chain reactions, with free radicals serving as chain carriers, and in the lower temperature range the products are chiefly hydroperoxides. A simplified representation of the low-temperature ($\leq 100^\circ\text{C}$) chain mechanism is as follows:



ROOOOR can decompose into products, as follows:



The initiation reaction is not well understood. It is usually supposed that there is a unimolecular decomposition of the organic reactant involving fission of a C-H bond; because of the high activation energies of such reactions (Table 1), the initiation is very slow. As one would expect, there is often a correlation between increasing tendency of reactants to be oxidized and decreasing strength of the C-H bond in the reactant.

Table 1. X-H bond dissociation energies

<u>Structure</u>	<u>Bond Energy</u> (kcal mole ⁻¹)	<u>Structure</u>	<u>Bond Energy</u> (kcal mole ⁻¹)
CH ₃ -H	103	CH ₂ =CH-CH ₂ -H	85
n-C ₃ H ₇ -H	99	Ph-CH ₂ -H	85
i-C ₃ H ₇ -H	94	RCO-H	86
t-C ₄ H ₉ -H	90	PhO-H	88
CH ₂ =CH-H	105	ROO-H	90
C ₆ H ₅ -H	103		

The rate of oxidation of a reactant can be increased by adding compounds (initiators) that easily decompose into radicals. Such compounds are well known, also serving as initiators for free-radical vinyl polymerization reactions. One of the most reactive initiators is azoisobutyronitrile, $(\text{CH}_3)_2\text{C}=\text{N}=\text{C}(\text{CH}_3)_2$,

which decomposes to form N_2 and two $(\text{CH}_3)_2\overset{\text{CN}}{\underset{\text{CN}}{\text{C}}}\cdot$ radicals with an

activation energy of $30 \text{ kcal mole}^{-1}$ and a half-life of 1 h at 85°C . Another initiator is t-butylhyponitrite, $\text{t-BuO-N}=\text{N-O-t-Bu}$, which reacts similarly with an activation energy of $28 \text{ kcal mole}^{-1}$ and a half-life of 1 h at 60°C .

Peroxides and hydroperoxides belong to this class of initiators, and they are also common reaction intermediates in hydrocarbon oxidation; we return later to the consequences of this important complication of the scheme of oxidation reactions.

The first propagation step (2a) is invariably very fast and takes place with almost no activation energy; its rate is around $10^5 \text{ l mole}^{-1} \text{ sec}^{-1}$. The bond strength of $\text{R-O}_2\cdot$ is only about $28 \text{ kcal mole}^{-1}$, which indicates that the bond formation is a reversible process. The second propagation step (2b) is much slower and is strongly dependent on the nature of RH; the activation energy is about $10\text{-}20 \text{ kcal mole}^{-1}$, and the rate constant for some common reactants is about $1 \text{ l mole}^{-1} \text{ sec}^{-1}$ at 30°C .

The termination reaction is puzzling, and Benson and Nangia [1] discussed it in some detail, suggesting an acceptable microscopic formulation. Its formulation (3) is unquestionably real and relevant. It is strongly dependent on the nature of the peroxide, being fast for $\text{HO}_2\cdot$ (with a rate constant of about $2 \times 10^9 \text{ l mole}^{-1} \text{ sec}^{-1}$) but quite slow for tertiary radicals $\text{t-RO}_2\cdot$ (with a rate constant of about $10^3 \text{ l mole}^{-1} \text{ sec}^{-1}$ and an activation energy of 8 kcal mole^{-1}).

The total enthalpy of reaction of the hydroperoxide formation



is around -18 to $-24 \text{ kcal mole}^{-1}$. This is exothermic enough that we expect secondary reactions to set in as temperatures increase during reaction.

At temperatures around 100°C , the hydroperoxides begin to react with the radicals appearing in the chain of propagation steps. They do this via reactions such as



and



The occurrence of chain transfer steps changes the distribution of the products but does not substantially change the nature of the chain propagation.

At somewhat higher temperatures ($\sim 150^\circ\text{C}$), however, the hydroperoxides begin to decompose unimolecularly, forming new radicals:



That is, the products begin to act as initiators, which, formally, amounts to a type of chain branching. This was named "degenerate chain branching" by Semenov to account for the delay between formation and decomposition of the product. The strength of the O-O bond determines the rate of decomposition; for most hydroperoxides the activation energy for bond breaking is about 42 kcal mole⁻¹, but for H₂O₂ it is 57 kcal mole⁻¹. Unimolecular decomposition of most hydroperoxides is therefore rather rapid even at 300°C, but for H₂O₂ it begins to be important only at temperatures $\geq 500^\circ\text{C}$.

To illustrate the consequence of the degenerate branching, it is helpful to consider a simple approximate analysis. The rate of the oxidation reaction is the product of the number of chains (n) operating at a given time and the rate of product formation per chain, p. For each chain there is one radical, so that the number of radicals present at a given time is equal to the number of chains running simultaneously. Therefore, the reaction rate is

$$\frac{d^2x}{dt^2} = p \frac{dn}{dt} \quad \text{where } x = \text{concentration of product molecules (hydroperoxides)} \quad (9)$$

The number of chains being initiated at a certain time is determined by the spontaneous rate of formation of radicals from the reactant (or initiator) (n_0) plus the rate of formation of new radicals resulting from decomposition of the hydroperoxides. The latter reaction is first order in the hydroperoxide concentration x (with a rate constant k), so that

$$\frac{dn}{dt} = n_0 + kx \quad (10)$$

$$\begin{aligned} \frac{d^2x}{dt^2} &= pn_0 + pkx \\ &\equiv pn_0 + f^2 \cdot x \end{aligned} \quad (11)$$

Integration gives

$$x = \frac{n_0}{k} (e^{ft} - 1) \quad (12)$$

If f is very small $\exp(ft) \approx 1 + ft$, and thus the conversion grows linearly with time. At higher temperatures, however, $\exp(ft)$ is much greater than 1 since the decomposition has a considerable activation energy. In the limiting case,

$$x = \frac{n_0}{k} \exp(ft) \quad (14)$$

The conversion therefore grows exponentially with time, and since $\frac{n_0}{k}$ is typically very small, some considerable time--called the induction period--will be required before the reaction products become observable. Once the product concentration is appreciable, the conversion increases very fast (Fig. 1), and around 300°C most oxidation reactions of hydrocarbons and aldehydes tend to become explosive, or to give rise to flames (sometimes called "cool flames").

Surprisingly, these reactions often slow down again at higher temperatures, illustrating the well-known negative temperature coefficient of thermal oxidation. At temperatures $\geq 250^\circ\text{C}$, the reaction mechanism is no longer the same, the chain of propagation steps being represented instead as

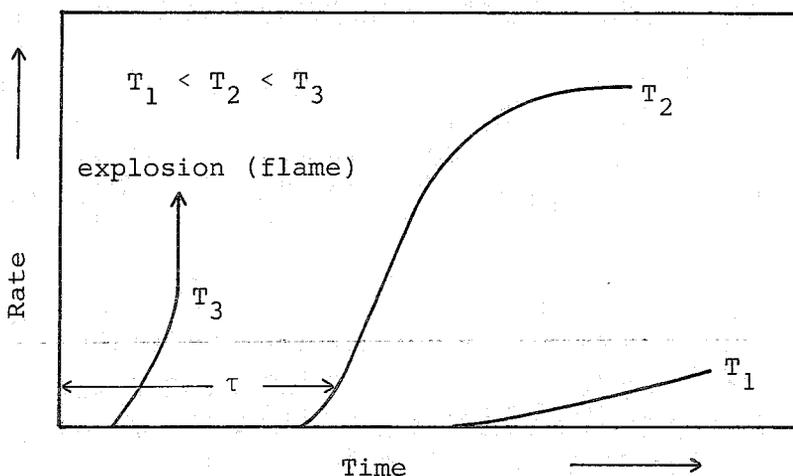
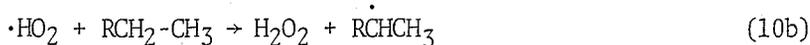
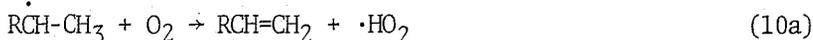
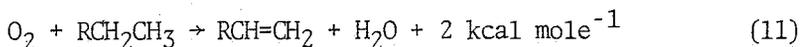


Figure 1. Thermal oxidation of a paraffin in the temperature range 200 to 300°C. τ is the induction period.



The overall stoichiometry is



Whereas the low-temperature reaction is decidedly exothermic and therefore potentially autocatalytic, the high-temperature reaction is nearly thermoneutral; it is typically an oxidative dehydrogenation. The hydroperoxide now formed is H_2O_2 , which because of its relatively strong O-O bond ($57 \text{ kcal mole}^{-1}$), does not decompose readily. At the higher temperature, the rate of branching is decreased, and the rate of termination is presumably increased, since termination by $\cdot\text{HO}_2$ recombination is fast. The shift from an organic hydroperoxide to H_2O_2 as the main peroxidic intermediate is ultimately due to the reversibility of reaction (2a); at higher temperatures the superoxide radical ($\text{RO}_2\cdot$) does not last long enough to allow a reaction with the hydrocarbon molecule to occur at a significant rate.

From this cursory review of thermal oxidation we learn that there are two temperature ranges where catalytic oxidation might compete successfully with the thermal process: At temperatures $\leq 150^\circ\text{C}$ the thermal process is relatively slow, and at temperatures $\geq 350^\circ\text{C}$ it is probably not too fast and, more important, it has no strong tendency to lead to an explosion. At intermediate temperatures, thermal oxidation can cause the many complications mentioned above, including explosions.

Using these generalizations as a basis, we anticipate that catalytic oxidation processes fall into two classes:

(1) Low-temperature processes: The reactants could be used in high concentrations in the liquid state, and the catalysts might be expected to be homogeneously dispersed in the reactant solution.

(2) High-temperature processes: Unless very high pressures were to be applied (which requires expensive reactors) the reactants would be in the gaseous state, and the catalysts would be high-surface-area solids.

We consider these classes of catalytic oxidation processes in turn.

3. LOW-TEMPERATURE CATALYTIC OXIDATION

There are a number of good reviews of low-temperature catalytic oxidation [2-5], and here we mainly follow the development given by Sheldon and Kochi [2]. There are two principal classes of reaction mechanisms describing the oxidations:

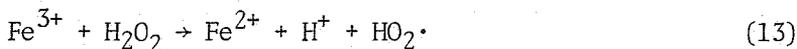
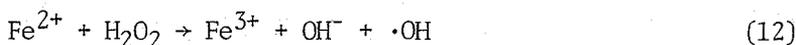
(1) Homolytic processes involve one-electron processes and outer sphere electrons. They are the kinds of reactions we encountered in free-radical oxidation, but now, for the first time, we consider how transition metal ions can play a role. The reactions proceed via a series of one-electron changes, the metals undergoing redox processes such as $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$.

(2) Heterolytic processes involve two-electron rather than one-electron changes of metals. They are the kinds of reactions we associate with coordination catalysis, involving reactants bonded in the coordination spheres of transition metals and exemplified by elementary steps like oxidative additions, discussed elsewhere in this volume.

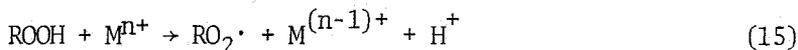
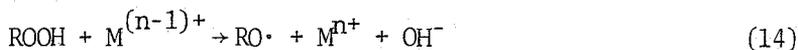
We now consider these two classes of processes in detail.

3.1 Homolytic catalytic processes

To illustrate how transition-metal ions can cooperate in chemical reactions, let us consider Fenton's reagent, a Fe^{2+} -salt used in aqueous solution with H_2O_2 to initiate polymerization reactions by producing radicals:



In a similar type of reaction, organic hydroperoxides can also be involved in the formation of radicals according to the following cycle:



The metal M is not consumed here, and its role is therefore catalytic. The result of this catalytic cycle is a branching process which produces two radicals at the expense of one ROOH molecule. The second ROOH molecule is rapidly replenished by the reaction



Kinetically, therefore, this metal-catalyzed process has an effect that is equivalent to the chain branching resulting from unimolecular decomposition in thermal oxidation. The catalytic reaction, even in the presence of only small amounts of the appropriate metal ions, is substantially faster than the thermal process, which indicates that the catalytic reactions (14) and (15) are faster than the thermal branching by unimolecular decomposition

reaction (8).

It is important that catalytic branching consists of separate steps, namely (14), in which the hydroperoxide oxidizes the cation, and (15), in which it reduces the cation. Hydroperoxides are usually strong oxidizing agents but only mild reducing agents, and so (14) is presumably faster than (15) under comparable conditions. For those cations that are commonly applied, i.e., Co, Mn, Fe, and Cu, reaction (14) is indeed found to be much faster than the thermal branching, reaction (8). Its activation energy is about 10-12 kcal mole⁻¹ (compared with about 40 kcal mole⁻¹ for thermal decomposition). (This result applies to reactions in both polar and nonpolar solvents in the presence of very small amounts of catalyst.)

Information about reactions like (15) is sparse, but they are presumably slower than reactions like (14) when the same concentrations of reactants are present for each. For a rough guess as to how the rates of reactions (14) and (15) compare, the redox potentials of the systems $M^{n+} + e^- \rightleftharpoons M^{(n-1)+}$ (Table 2) might serve as a guide. The greater this potential, the more the rate of reaction (15) might be expected to approach that of reaction (14).

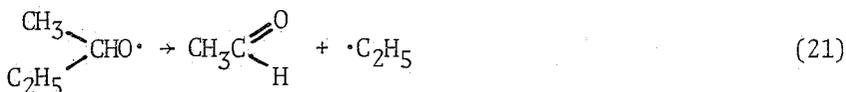
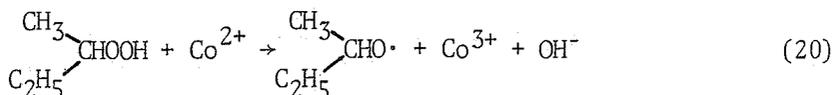
Although the redox potentials are expected to be only a rough guide to reactivity (and these are not even the correct redox potentials, being applicable to reactions in aqueous solution, whereas the reactions are usually performed in nonpolar hydrocarbon media), it is nevertheless striking that the cations with the higher redox potentials are indeed the ones most often applied as catalysts.

Alternatives to reaction (15) have been proposed for reduction of the cation. Long ago, Haber and Weiss suggested that the catalytic chain for the oxidation of alkyl aromatics consists of an attack of the more highly charged species on the alkyl aromatic:

Table 2. Redox potentials [2]

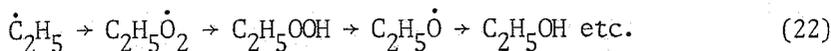
<u>Reaction</u>	<u>E⁰, volt</u>
Co ³⁺ + e ⁻ → Co ²⁺	1.82
Mn ³⁺ + e ⁻ → Mn ²⁺	1.51
Fe ³⁺ + e ⁻ → Fe ²⁺	0.77
Cu ²⁺ + e ⁻ → Cu ⁺	0.15

followed by the usual formation of the hydroperoxide. The cleavage of the peroxide seems to be more complicated since it leads also to a cleavage of C-C bonds. Parshall [5] proposed the following mechanism:



(β -bond fission)

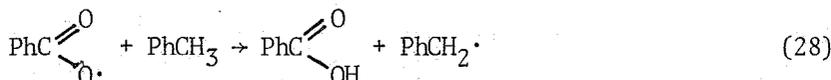
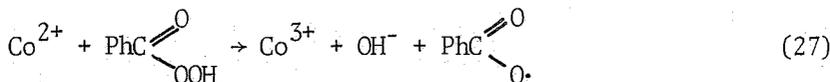
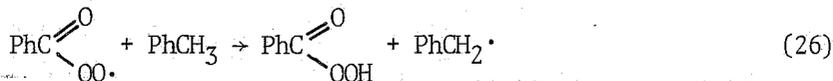
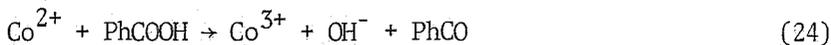
and, further (with details left out),



and (via radical intermediates and cationic catalysis),



The oxidation reactions of toluene and p-xylene follow the route indicated by reactions (17) and (18), i.e., the Co^{3+} attacks the hydrocarbon. The remainder of the reaction sequence is probably as follows:



It has been reported that the reaction does not start unless Co^{3+} is present, which is a strong indication that the first step in the reaction is as given in reaction (17).

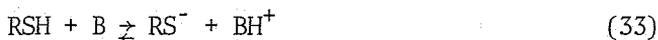
A most interesting detail in the oxidation of *p*-xylene is that it does not proceed further than the oxidation of one methyl group to give $\text{CH}_3\text{-C}_6\text{H}_4\text{-COOH}$. However addition of NaBr to the solution (as in the Amoco process) in the presence of Co and Mn cations leads to oxidation of both methyl groups, presumably because of the rate enhancement of the hydrogen addition to $\text{RO}_2\cdot$:



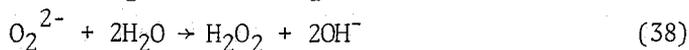
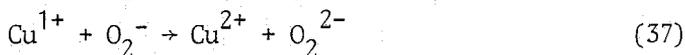
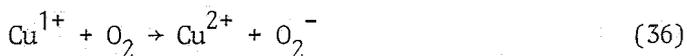
The last process we consider in this category is the oxidative dehydrogenation of mercaptans to give disulfides:



The process is carried out under the trade name Merox and serves as a sweetening operation. There is no consensus as to whether the reaction is of the one-electron or two-electron type. The cations operating as catalysts are similar to those discussed earlier, i.e., Co, Mn, Fe, and Cu, and this fact seems to support the suggestion of a one-electron process. It is clear that the reaction requires two different catalyst functions; the first step is the loss of a proton to the first function, a base (B):

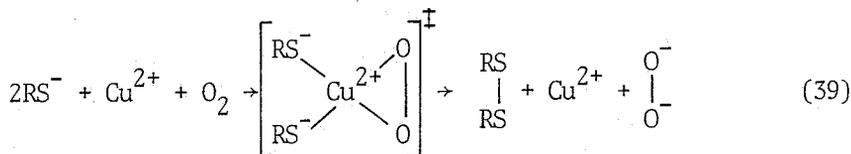


In aqueous media the reaction therefore has to be performed in solution of high pH. The second function (the metal, which is involved in electron transfer) then involves the following (provided that the reaction can be assumed to proceed via one-electron steps):



So far, all attempts to isolate the superoxy ion (O_2^-) and the radicals by ESR have failed. Neither has one arrived at a satisfactory explanation of the reaction kinetics (half order in oxygen and between first and second order in Cu).

An alternative mechanism would be given by a concerted two-electron process



The main objection to this model is that it fails to explain the half-order in oxygen.

The recognition of the functions involved in the solution catalysis (base and metal) has led to the design of solid catalysts for this reaction [6,7]. They are complexes of Co^{3+} with phthalocyanine (CoPc) anchored to polymers incorporating basic groups, $(-CH_2-CHNH_2-)_n$. These bifunctional solid catalysts were found to be 50 times more active per Co atom than CoPc in alkaline solution. The reasons for the high activity are not yet clear, but the important point is that this example provides a simple, easily understood bridge between homogeneous and heterogeneous catalytic oxidation.

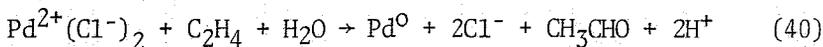
3.2 Heterolytic oxidation reactions

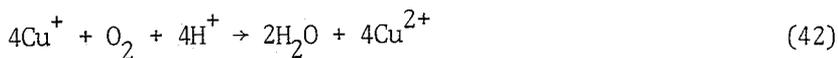
The heterolytic processes differ sharply from the homolytic processes, which are so closely tied in with thermal oxidation. The heterolytic reactions are generally far less well understood, but two subclasses are now relatively well defined:

- (1) Oxidation reactions catalyzed in aqueous solutions of salts of Pd^{2+} and Cu^{2+} (Wacker type reactions).
- (2) Epoxidation reactions of olefins.

We consider these in turn.

The Pd-catalyzed reactions are similar or related to the commercial Wacker process for oxidation of ethylene to give acetaldehyde. The Wacker process proceeds via a sequence of three reactions, and they have been studied separately,

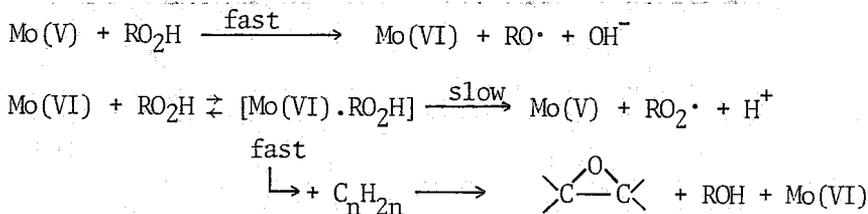




Reaction (40) is discussed in some detail elsewhere in this book. It is important to emphasize at this point that the oxygen for the oxidation of Pd^{2+} is provided not by O_2 , but instead by H_2O , an oxide; the reaction is typically a concerted process with internal transfer of an electron pair. O_2 is introduced in reaction (42), a well-known reaction, which is, however, mechanistically not well understood. It is expected to be similar to reaction (34) in the mercaptan oxidation. Reaction (41) is the electron transfer step; again we are confronted with the difficulty of having to choose between a concerted two-electron process and a merging of one-electron processes into a pairwise process.

We stress that the Wacker reaction is in many respects a strikingly appropriate model for the high-temperature heterogeneous catalytic reactions, even though it is a homogeneous catalytic reaction. The basis for the comparison is as follows: In both the Wacker process and in surface-catalyzed partial oxidation, one catalyst component takes care of the oxidation of the organic reactant, using oxygen atoms from an oxide. In the high-temperature surface reactions, the oxide is a solid. A second cation takes care of the incorporation of O_2 ; since in the surface reactions this cation is incorporated in a second solid oxide, the two oxides are typically applied in the form of a binary compound. Electron transfer and transfer of O^{2-} will then occur in this solid.

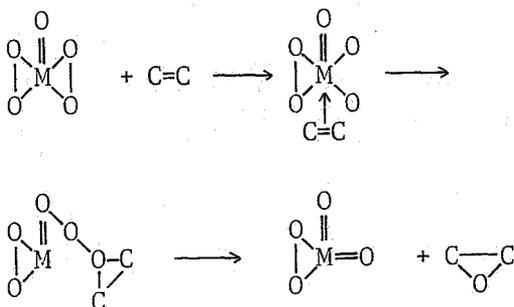
The epoxidation of olefins is catalyzed by oxygen-containing derivatives of W, Mo, V, Os, Se, and Cr. In the presence of O_2 there is only a slow homolytic reaction as could be expected from the redox-potentials of the metals in their highest valence state (table 3). The reduction of the metal-cation by the hydroperoxides would probably be a slow process. However, in the presence of H_2O_2 or hydroperoxides epoxidation becomes important. Hydroperoxides appear to form peroxides of the catalyst-cation that subsequently react with the olefins to form epoxides (Sheldon [11]).



Mimoun et al [12] propose the following mechanism for the reaction of the inorganic peroxide with the olefin.

Table 3. Redox potentials [2]

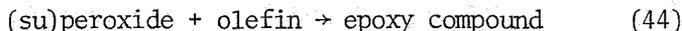
<u>Redox couple</u>	<u>E⁰, volt</u>
Mo ⁺⁶ + e ⁻ → Mo ⁺⁵	~ 0.2
W ⁺⁶ + e ⁻ → W ⁺⁵	- 0.03
V ⁺³ + e ⁻ → V ⁺²	- 0.20
Ti ⁺⁴ + e ⁻ → Ti ⁺³	- 0.37
Cr ⁺³ + e ⁻ → Cr ⁺²	- 0.41



4. COMPARISON OF HIGH-TEMPERATURE AND LOW-TEMPERATURE CATALYTIC OXIDATION

We have seen that there are both similarities and some remarkable differences between low- and high-temperature noncatalytic oxidation. We might anticipate parallels with catalytic oxidation, and indeed they exist, as illustrated briefly in the following paragraphs.

There is one high-temperature oxidation process that produces an epoxide: the oxidation of ethylene to give ethylene oxide catalyzed by silver on an alumina support. Kilty *et al.* [8] proposed a mechanism in which the key intermediate is a surface superoxy species. Since Ag²⁺ has one of the highest known redox potentials (1.98 volt), it is not unexpected that O₂ can form reducing peroxides; once they form, the next step



is similar to the low-temperature case. The real surprise is that the surface-catalyzed reaction is so selective, but this can be understood from the fact that ethylene is not a particu-

larly aggressive reactant and is more or less restricted to epoxide formation under mild conditions. Moreover, in the commercial process, a subterfuge is used to restrict the number of peroxide sites on the surface by partially covering it with Cl^- ions.

By far the greater number of important high-temperature catalytic oxidation reactions, especially those with olefins as reactants, follow the pattern of bifunctionality illustrated by the Wacker process, with oxygen being delivered to the organic reactant by the oxidic catalyst. The first step in the reaction of the olefin leads to the formation of the allyl radical. One may ask whether this radical is formed in the gas phase or on the catalyst surface. (In the former case the catalytic reaction would be viewed as just a modified thermal reaction.) From the weight of evidence [9,10] it is concluded that the allyl is formed on the surface of the mixed oxide catalyst. Further details of the surface reaction are given by van Hooff in this book.

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