Kirk-Othmer Encyclopedia of Chemical Technology.

HYDROCARBON OXIDATION

Oxidation has been of great interest to humanity since the discovery of fire (1). Some understanding of the subject began at the time of Lavoisier (2). Hydrocarbon oxidation has been studied for well over 100 years, but modern understanding of the mechanisms of free-radical chain reactions did not begin until the 1930s (3–12). Since that time, a vast body of multilingual literature has accumulated. There is significant agreement on underlying principles, but sharp controversies on various important points remain and, indeed, are probably growing, undoubtedly because the oxidation of even simple materials is complex. One simplification, however, is that radical reactions in the gas phase and in not strongly polar solvents do not differ appreciably in kinetic parameters. Differences can usually be traced to well-understood kinetic phenomena (13).

The scope of oxidation chemistry is enormous and embraces a wide range of reactions and processes. This article provides a brief introduction to the homogeneous free-radical oxidations of paraffinic and alkylaromatic hydrocarbons. Heterogeneous catalysis, biochemical and biomimetic oxidations, oxidations of unsaturates, anodic oxidations, etc, even if used to illustrate specific points, are arbitrarily outside the purview of this article. There are, even so, many unifying features among these areas.

1. Kinetics of Chain Reactions

One characteristic of chain reactions is that frequently some initiating process is required. In hydrocarbon oxidations radicals must be introduced and to be self-sustained, some source of radicals must be produced in a chain-branching step. Moreover, new radicals must be supplied at a rate sufficient to replace those lost by chain termination. In hydrocarbon oxidation, this usually involves the hydroperoxide cycle (eqs. 1–5).

$$\mathrm{RH + In\cdot \longrightarrow R\cdot + HIn} \qquad (1)$$

$$\mathrm{R\cdot + O_2 \longrightarrow ROO\cdot} \qquad (2)$$

$$\mathrm{ROO\cdot + RH \xrightarrow{k_p} ROOH + R\cdot} \qquad (3)$$

$$\mathrm{ROOH \xrightarrow{k_d} RO\cdot + OH\cdot} \qquad (4)$$

$$\mathrm{ROO\cdot + ROO\cdot} \xrightarrow{k_t} \text{nonradical products} \qquad (5)$$

In reaction 1, some initiating fragment (In·) reacts with the substrate hydrocarbon by abstracting a hydrogen atom, generating a carbon-centered radical with the structure of the original hydrocarbon. The origin of the initiating fragment has remained largely unresolved. A direct reaction of the hydrocarbon wit oxygen (eq. 6) is frequently proposed (1, 14). This reaction has such a high energy of activation that a termolecular alternative (eq. 7) is sometimes suggested (15, 16).

$$\mathrm{RH + O_2 \longrightarrow R\cdot + HOO\cdot} \qquad (6)$$

$$\mathrm{2RH + O_2 \longrightarrow 2R\cdot + HOOH} \qquad (7)$$

However, reaction 7 suffers other shortcomings, eg, entropy problems. Other proposals range from trace peroxidic contaminants to ionic mechanisms for generating peroxides (1) to cosmic rays (17). In any event, the initiating reactions are significant only during the induction period (18).

Carbon-centered radicals generally react very rapidly with oxygen to generate peroxy radicals (eq. 2). The peroxy radicals can abstract hydrogen from a hydrocarbon molecule to yield a hydroperoxide and a new radical (eq. 3). This new radical can participate in reaction 2 and continue the chain. Reactions 2 and 3 are the propagation steps. Except under oxygen starved conditions, reaction 3 is rate limiting.

New radicals are introduced by thermolysis of the hydroperoxide by chain-branching decomposition (eq. 4). Radicals are removed from the system by chain-termination reaction(s) (eq. 5). Under steady-state conditions, the production of new radicals is in balance with the rate of radical removal by termination reactions and equation 8 applies for the scheme of equations 1–5 where r_i = rate of new radical introduction (eq. 4).

$$-d\,[RH]\,/dt = k_p\,[RH]\,\sqrt{r_i/2k_t} \qquad (8)$$

New radicals come exclusively from the decomposition of the intermediate hydroperoxide (eq. 4), provided no other radical sources, eg, peroxidic impurities, are present. Hydroperoxides have varying degrees of stability, depending on their structure. They decompose by a variety of mechanisms and are not necessarily efficient generators of new radicals via thermolysis (19, 20).

Deliberate use of a different radical source with a known radical generation rate, under conditions where the product hydroperoxide does not contribute appreciably to new radical generation, permits evaluation of $k_p/\sqrt{2k_t}$ by using equation 8. This factor, usually called the oxidizability of the hydrocarbon, is a measure of the relative susceptibilities of substrates to oxidation. It is independent of rates of initiation. The term oxidizability refers to oxidations of single substrates. A material with low oxidizability may actually have a high propagation rate constant but oxidize slowly because it also has a high termination rate constant. When cooxidized with a material of higher oxidizability, it may very well cooxidize faster than the more highly oxidizable substrate, depending on the ratio of propagation rate constants. Such ratios may be estimated in a number of ways (1, 22, 23) and can be useful in predicting product distributions. In cooxidations the high termination rate constant for the peroxy radicals produced from the low oxidizability component generally retards the rate of the cooxidation (22–24).

If a self-sustained oxidation is carried out under limiting rate conditions, the hydroperoxide provides the new radicals to the system (by reaction 4 or analogues) and is maintained at a low concentration (decomposition rate = generation rate). For these circumstances, the rate equation 9 holds, where

n = average number of initiating radicals produced (by any means) per molecule of ROOH decomposed and f = fraction of RH consumed which disappears by ROO· attack (25).

$$-d\,[RH]\,/dt = nk_p^2\,[RH]^2\,/2fk_t \qquad (9)$$

Under these conditions, a component with a low rate constant for propagation for peroxy radicals may be cooxidized at a higher relative rate because a larger fraction of the propagation steps is carried out by the more reactive (less selective) alkoxy and hydroxy radicals produced in reaction 4.

The simple hydroperoxide mechanism so far discussed is incomplete for representing reactions with significant products other than hydroperoxides. It can be adequate for oxidations of certain unsaturates, aldehydes, and alkylaromatics where the yield of the corresponding hydroperoxide can exceed 90%.

An important descriptor of a chain reaction is the kinetic chain length, ie, the number of cycles of the propagation steps (eqs. 2 and 3) for each new radical introduced into the system. The chain length for a hydroperoxide reaction is given by equation (10) where HPE = efficiency to hydroperoxide, %, and $2f$ = number of effective radicals generated per mol of hydroperoxide decomposed. For 100% radical generation efficiency, $f = 1$. For 90% efficiency to hydroperoxide, the minimum chain length ($f = 1$) is 14.

$$\text{chain length} = (HPE + 100/2f)\,/\,(100 - HPE) \qquad (10)$$

Chain lengths of some oxidations can be quite long (>100), especially for substrates with easily abstractable hydrogens when they are oxidized under mild conditions at low conversions. Aldehydes are good examples of such substrates (26). Many other oxidations have chain lengths estimated from 3 to 10. At limiting rates, the chain length is near 1 (25).

Products other than hydroperoxides are formed in oxidations by reactions such as those of equations 11 and 12. Hydroxyl radicals (from eq. 4) are very energetic hydrogen abstractors; the product is water (eq. 11).

$$\mathrm{OH\cdot + RH \longrightarrow R\cdot + H_2O} \qquad (11)$$

Alkoxy radicals, such as those produced in reaction 4, can be vigorous hydrogen abstractors and may produce alcohols (eq. 12), but they can undergo other reactions as well.

$$\mathrm{RO\cdot + RH \longrightarrow R\cdot + ROH} \qquad (12)$$

The predominant radicals in hydrocarbon oxidation are usually alkylperoxy radicals, particularly when sufficient oxygen is present to scavenge alkyl radicals by reaction 2. These radicals are weak hydrogen abstractors and they build up to relatively high concentrations (27), becoming the dominant species in the radical flux. Depending on their structures, they can participate in various reactions other than chain propagation. They are usually the main participants in bimolecular radical reactions. Other radicals are less involved in bimolecular radical reactions because their high reactivities cause them to be present at very low concentrations.

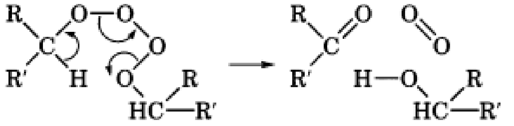
There are two especially important radical–radical reactions of alkylperoxy radicals (28) both believed to proceed via formation of a transient tetroxide (eqs. 13 and **15**).

$$\mathrm{ROO\cdot + \cdot OOR \longrightarrow ROOOOR} \qquad (13)$$

One decomposition of the tetroxide is not terminating, producing alkoxy radicals and oxygen (eq. 14).

$$\mathrm{ROOOOR \longrightarrow RO\cdot + O_2 + \cdot OR} \qquad (14)$$

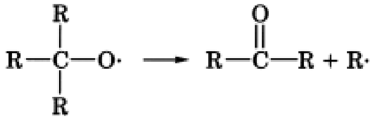
An alternative chain-terminating decomposition of the tetroxide, known as the Russell mechanism (29), can occur when there is at least one hydrogen atom in an alpha position; the products are a ketone, an alcohol and oxygen (eq. **15**). This mechanism is troubling on theoretical grounds (1). Questions about its validity remain (30), but it has received some recent support (31).



(15)

Bimolecular reactions of peroxy radicals are not restricted to identical radicals. When both peroxy radicals are tertiary, reaction **15** is not possible. When an α-hydrogen is present, reaction **15** is generally the more effective competitor and predominates.

Alkoxy radicals can abstract hydrogen (eq. 12), but they may undergo a β-scission reaction (eq. **16**).



$$R-\underset{R}{\overset{R}{C}}-O\cdot \longrightarrow R-\overset{O}{\overset{\|}{C}}-R + R\cdot \qquad (16)$$

Under moderate conditions, primary alkoxy radicals tend to undergo reaction 12 whereas secondary and tertiary alkoxys tend to undergo β-scission. In general, the alkyl group that can form the lowest energy radical tends to become the departing radical. The β-scission of secondary alkoxy radicals yields aldehydes as the nonradical products; tertiary alkoxy radicals yield ketones.

2. Product Sequences in Hydrocarbon Oxidation

The products discussed so far (alcohols, aldehydes, and ketones) are produced by radical reactions involving the hydrocarbon substrate or from further reactions of the intermediate (and frequently transitory) hydroperoxides. Under conditions of low rates and high chain lengths, hydroperoxides may be the principal precursors for all other products. At high rates, however, significant quantities of chain-termination products (alcohols, ketones, and aldehydes) can be produced directly from peroxy radicals (eqs. 14 and **15**) without going through hydroperoxides (25). In any event, there is a sense in which these products may be thought of as primary (22).

All components of the reaction mixture, whatever their source, are subject to the same kind of radical attacks as the starting substrate(s). Any free-radical oxidation is inevitably a cooxidation of substrate(s) and products. The yields of final products are determined by two factors: (*1*) how much is produced in the reaction sequence, and (*2*) how much product survives the reaction environment. By kinetic correlations and radiotracer techniques, it is possible to estimate these relationships and develop a mathematical model of the system (22).

Primary and secondary alcohols oxidize rapidly (frequently ca 6–10 times as fast as the parent hydrocarbon (22, 32)), and probably efficiently, to the corresponding carbonyl compounds (22, 33–35) (Fig. 1). The initial attack is highly selective for the hydrogen in the alpha position relative to the hydroxyl group. The addition of oxygen to the resulting radical is reversible (36). If the peroxy radical abstracts hydrogen (Path I), the hydroxyalkylhydroperoxide decomposes to hydrogen peroxide and the corresponding carbonyl compound (37, 38). If, however, hydrogen is abstracted from the hydroxyalkyl radical by oxygen (Path II), the production of the carbonyl component is accompanied by the formation of a hydroperoxy radical. This radical is notable in that it has an exceptionally high chain-termination rate constant (1); hydroperoxy radicals may react readily with almost any other radical in the system to given oxygen and a nonradical product (eg, eq. 17).

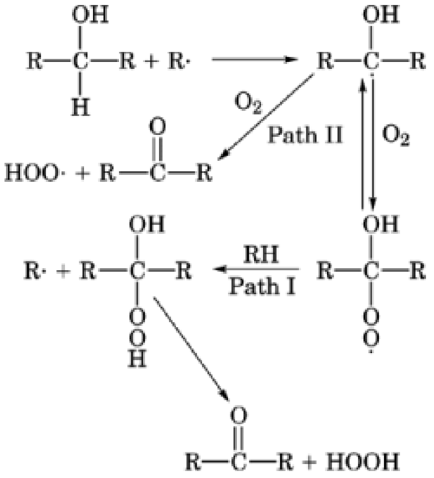
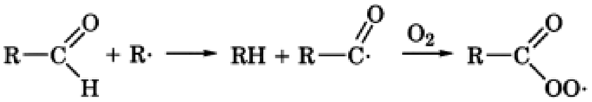


Fig. 1. Production of carbonyl compounds from alcohols by various oxidation routes.

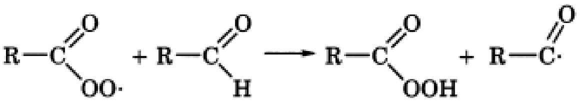
$$HOO\cdot + R\cdot \longrightarrow RH + O_2 \qquad (17)$$

Carbonyl compounds can be primary (from radicals or hydroperoxides) or secondary (from alcohols). Thus the picture emerges of hydrocarbon oxidations occurring through complicated series-sequential pathways as in Figure 1, where clearly other reactions could be going on as well. All possible pathways are pursued to some extent; traffic along any pathway is a function of energy requirements and relative concentrations.

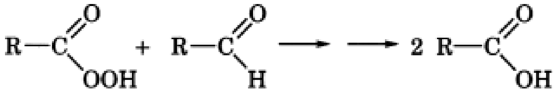
Carbonyl intermediates are also susceptible to further oxidation. Aldehydes can oxidize very rapidly to acids (39–42); peracids are likely intermediates.



(18)



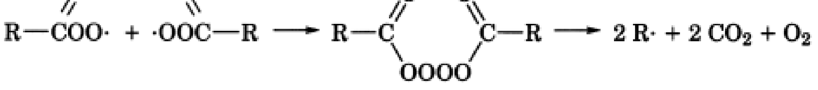
(19)



(20)

Two important inefficient routes for aldehyde oxidation are (eqs. **21** and **22**).

(21)



(22)

Reaction **21** is the decarbonylation of the intermediate acyl radical and is especially important at higher temperatures; it is the source of much of the carbon monoxide produced in hydrocarbon oxidations. Reaction **22** is a bimolecular radical reaction analogous to reaction 13. In this case, acyloxy radicals are generated; they are unstable and decarboxylate readily, providing much of the carbon dioxide produced in hydrocarbon oxidations. An in-depth article on aldehyde oxidation has been published (43).

Ketones oxidize about as readily as the parent hydrocarbons or even a bit faster (32). Although the reactivities of hydrogens on carbons adjacent to carbonyl groups are perhaps doubled, the effect is small because one methylene group is missing in comparison to the parent hydrocarbon. Ketones oxidize less readily than similar primary or secondary alcohols (35).

Acids are usually the end products of ketone oxidations (41–44) but vicinal diketones and hydroperoxyketones are apparent intermediates (45). Acids are readily produced from vicinal diketones, perhaps through anhydrides (via, eg, a Bayer-Villiger reaction) (46, 47). The hydroperoxyketones reportedly decompose to diketones as well as to aldehydes and acids (45). Similar products are expected from radical—radical reactions of the corresponding peroxy radical precursors.

The carboxyl group of acids appears to deactivate the hydrogens on the alpha carbon atom toward attack by the free-radical flux in oxidation reactions. Acetic acid, therefore, is particularly inert toward further oxidation (hydrogens are both primary and deactivated) (48). For this reason, it is feasible to produce acetic acid by the oxidation of butane (in the liquid phase), even under rather severe oxidation conditions under which most other products are further oxidized to a significant extent (22).

Beginning with propionic acid, all the higher saturated acids are significantly less resistant to oxidation than acetic. For longer chain acids, all carbons in the gamma or higher positions are essentially equivalent to the corresponding carbons in the parent hydrocarbon with regard to susceptibility to oxidation (49–51). For the β-position, however, the picture is not so clear. Some investigators indicate deactivation of the β-position for hydrogen abstraction in autoxidation (49, 50), but others report activation (by a factor of about 2) of this position for abstraction by hydroxyl radicals (51).

Esters are also formed in hydrocarbon oxidations. Although their source is still a matter of debate, there is rather convincing evidence that esters generally do not form in the early stages of an oxidation before the appearance of significant quantities of acids (41, 42, 52, 53). The clear implication is that most esters come from esterification reactions of free acids and alcohols produced by the oxidation. There is widespread agreement that, once formed, most esters are exceptionally resistant to further oxidation, at least in the region of the ester group. Indeed, the consumption of lower molecular weight esters probably proceeds largely through prior hydrolysis and rapid oxidation of the liberated alcohol (54, 55). Since primary and secondary alcohols oxidize readily $(\text{secondary} > \text{primary})$ and also esterify $(\text{primary} > \text{secondary})$, the role of alcohols in hydrocarbon oxidation can be even more complex than the role of many other intermediates.

Earlier reports have indicated that esters can form before significant amounts of acids accumulate (16). The Bayer-Villiger oxidations of ketones with intermediate hydroperoxides and/or peracids have been suggested as ester forming mechanisms (34, 56). However, the reactions of simple aliphatic ketones with peracetic acid are probably too slow to support this mechanism (57, 58). Very early proposals for ester formation, although imaginative, appear improbable (59).

In addition to production of simple monofunctional products in hydrocarbon oxidation there are many complex, multifunctional products that are produced by less well-understood mechanisms. There are also important influences of reactor and reaction types (plug-flow or batch, back-mixed, vapor-phase, liquid-phase, catalysts, etc).

2.1. Efficiency of Intermediate Formation

The variation of the efficiency of a primary intermediate with conversion of the feed hydrocarbon can be calculated (22). Ratios of the propagation rate constants (k_2/k_1) and reactor type (batch or plug-flow vs back-

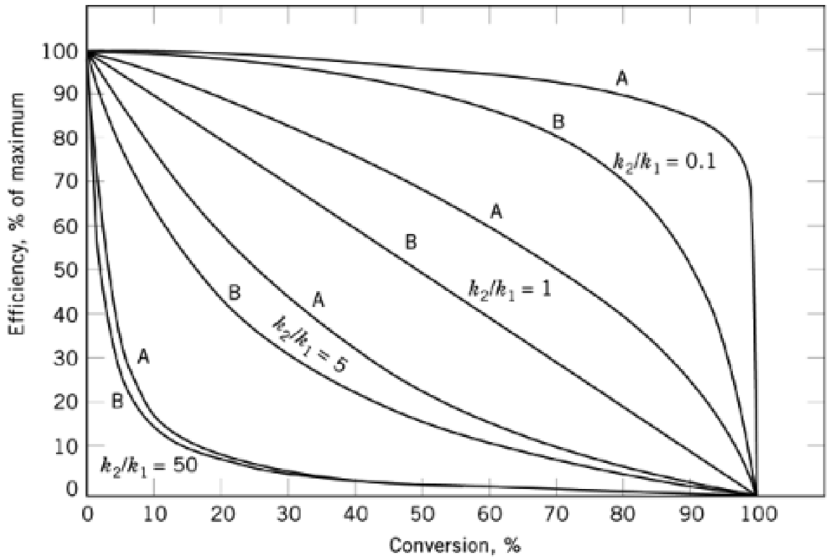


Fig. 2. Efficiency to a primary intermediate as % of maximum (zero conversion) efficiency; x axis is feed conversion. Parameters are oxidation rate-constant ratios (k_2/k_1) for primary intermediate vs feed and reactor type: A, plug-flow or batch; B, back-mixed.

mixed) are important parameters. Figure 2 shows that even materials which are rather resistant to oxidation ($k_2/k_1 = \sim 0.1$) are consumed to a noticeable degree at high conversions. Also the use of plug-flow or batch reactors can offer a measurable improvement in efficiencies in comparison with back-mixed reactors. Intermediates that cooxidize about as readily as the feed hydrocarbon (eg, ketones with similar structure) can be produced in perhaps reasonable efficiencies but, except at very low conversions, are subject to considerable loss through oxidation. They may be suitable coproducts if they are also precursors to more oxidation-resistant desirable materials. Intermediates which oxidize relatively rapidly ($k_2/k_1 = 5 - 50$; eg, alcohols and aldehydes) are difficult to produce in appreciable amounts, even in batch or plug-flow reactors. Indeed, for $k_2/k_1 = 50$, to isolate 90% or more of the intermediate made, the conversion must not be greater than about 0.4%, even for a batch or plug-flow reactor.

The maximum yield of a primary intermediate, as well as the efficiency (and conversion) at maximum yield, can also be calculated (22). Maximum yield plots are shown in Figure 3.

3. Vapor-Phase Oxidation

Above about 250°C, the vapor-phase oxidation (VPO) of many organic substances becomes self-sustaining. Such oxidations are characterized by a lengthy induction period. During this period, peroxides accumulate until they can provide a source of new radicals to sustain a chain reaction. Once a critical threshold peroxide concentration is reached, the reaction accelerates very rapidly.

3.1. The NTC Phenomenon

VPO reactions of typical alkanes may be considered conveniently in three temperature regions. Under some circumstances, particularly at pressures not greatly exceeding atmospheric, a curious and fundamentally

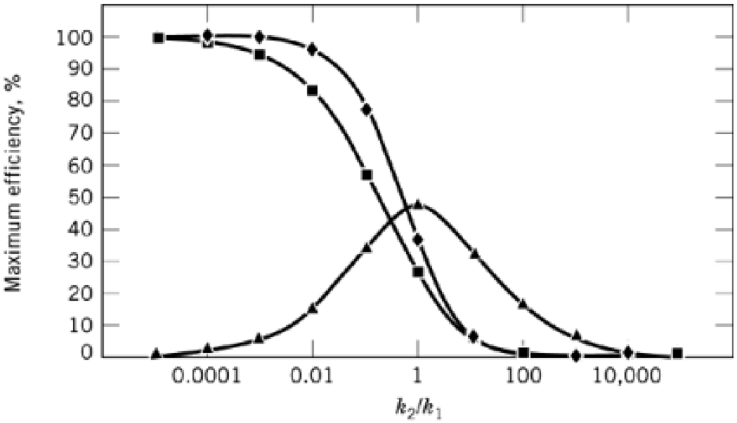


Fig. 3. Plot of maximum yield as a % of maximum (zero conversion) efficiency to a primary intermediate; x axis is ratio of oxidation rate constants (k_2/k_1) for primary intermediate vs feed: (♦) plug-flow or batch reactor; (■) back-mixed reactor; (▲) plug-flow advantage, %.

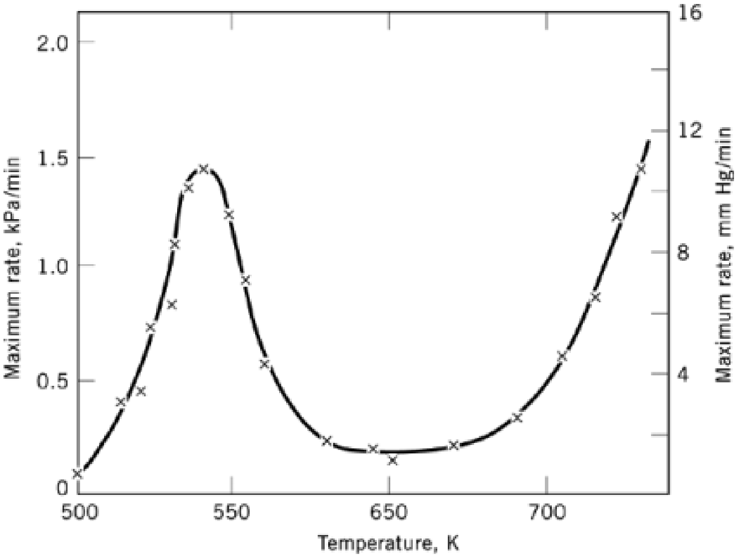


Fig. 4. Plot of maximum rate of pressure change for propane VPO showing NTC region; 5.33 kPa propane, 13.33 kPa O_2. Courtesy of Blackwell Scientific Publications, Ltd., Oxford (60). To convert kPa to mm Hg, multiply by 7.5.

important phenomenon known as the negative temperature coefficient (NTC) region is observed between the low and intermediate temperature ranges. In the NTC zone, increasing temperature actually results in lower reaction rates. A typical plot for propane VPO is presented in Figure 4. In the lower temperature regions, oxygenated materials are usually the principal products. As one progresses through the NTC zone, unsaturated products, usually with the same carbon skeleton as the feed (conjugate olefins), begin to predominate. Further increases in temperature are usually accompanied by production of lower molecular weight olefins as well as products derived from methyl radicals. Figure 5 illustrates these relationships for the VPO of butane.

At still higher temperatures, when sufficient oxygen is present, combustion and "hot" flames are observed; the principal products are carbon oxides and water. Key variables that determine the reaction characteristics

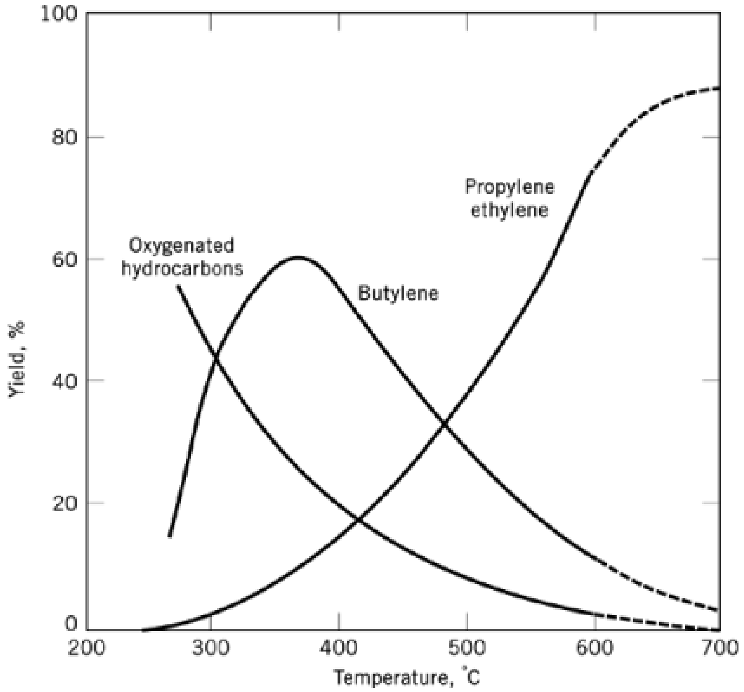


Fig. 5. The effect of temperature on product distribution in VPO of butane with air.

are fuel-to-oxidant ratio, pressure, reactor configuration and residence time, and the nature of the surface exposed to the reaction zone. The chemistry of hot flames, which occur in the high temperature region, has been extensively discussed (60–62) (see Combustion science and technology).

Modern real time instrumental methods permit analyses of unstable transient species and the free-radical intermediates as well. These methods have greatly expanded the scope and power of VPO studies, but important basic questions remain unresolved. Another complication is the role of surface. Peroxide decompositions and radical termination reactions can occur on a surface so that, depending on circumstances, surfaces can have either an inhibiting or accelerating effect. Each surface has varying amounts of adventitious contaminants and also accumulates deposits during reaction. Thus no two surfaces are exactly alike and each changes with time.

3.1.1. Reversibility of Equation 2

Notwithstanding the problems and conflicts, there is widespread agreement that the NTC phenomenon may well be related to the reversibility of equation 2 (13, 60, 63–67): $R\cdot + O_2 \xrightleftharpoons{} ROO\cdot$. In the low temperature regime, the equilibrium lies to the right and alkylperoxy radicals are the dominant radical species. They form hydroperoxides, the chain-branching agent, by reaction 3.

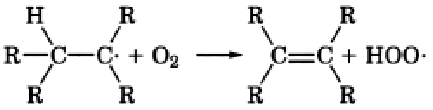
The principal isolated products are alcohols, aldehydes, and ketones, formed by reactions shown in equations 12, **15**, **16**, and Figure 1. Although aldehydes are very susceptible to further oxidation, acids are not usually significant products in low pressure VPO (below ~1.4 MPa (200 psig) in many cases). This appears to be because the decarbonylation of acyl radicals (eq. **21**) competes very effectively with the addition of oxygen (eq. **18**) under these conditions. As a result, carbon monoxide is a prominent product, along with lower molecular weight alcohols and ketones produced from the alkyl radical made in reaction **21**. At higher pressures, reaction **18** becomes more competitive and acid yields rise (Table 1).

Table 1. Products from the Reaction of a Propane: Air Mixture[a] at Various Pressures, %[b]

Compounds	At 0.101 MPa,[c] 378°C	At 2.03 MPa,[c] 281°C	At 6.08 MPa,[c] 251°C	At 10.1 MPa[c] 250°C
total aldehydes	20.5	21.8	13.5	13.7
n-alcohols	19.7	21.0	17.5	15.2
isopropyl alcohol	1.3	2.8	6.2	16.0
acetone	0.5	4.3	12.5	7.9
acids	4.3	17.0	19.0	18.9
carbon dioxide	7.3	17.1	21.4	20.6
carbon monoxide	21.3	16.0	9.9	7.7
propylene	25.1	0	0	0

[a] Ref. 68. Propane : air ratio = 1 : 3.6.
[b] Values are % carbon of propane burned.
[c] To convert MPa to atm, divide by 0.101.

As the temperature approaches the NTC zone, the reversibility of reaction 2 comes into play and the steady-state concentration of alkyl radicals rises. There is a competing irreversible reaction of oxygen with radicals containing an alpha hydrogen which produces a conjugate olefin (eq. **23**).



$$\mathrm{R{-}C(H)(R){-}\dot{C}R_2 + O_2 \longrightarrow R_2C{=}CR_2 + HOO\cdot} \qquad (23)$$

Alternatively, a number of investigators (69–73) have proposed, on the basis of plausible kinetic arguments, that the conjugate olefin is produced by a rearrangement of alkylperoxy radicals (eq. 24).

$$\mathrm{RCH_2CH_2OO\cdot \longrightarrow [R\dot{C}CHCH_2OOH] \longrightarrow RCH{=}CH_2 + HOO\cdot} \qquad (24)$$

This proposal, however, has been criticized on the basis of transition state theory (74). Hydroperoxy radicals produced in reaction **23** or 24 readily participate in chain-terminating reactions (eq. 17) and are only weak hydrogen abstractors. When they succeed in abstracting hydrogen, they generate hydrogen peroxide:

$$\mathrm{HOO\cdot + RH \longrightarrow HOOH + R\cdot} \qquad (25)$$

$$\mathrm{HOO\cdot + HOO\cdot \longrightarrow HOOH + O_2} \qquad (26)$$

The sequence that makes alkylhydroperoxide has thus been diverted to make hydrogen peroxide, and with lower efficiency. Hydrogen peroxide generates radicals thermally but its decomposition temperature is higher than that of alkyl-hydroperoxides. The overall effect is that the rate of generation of new radicals drops, the reaction rate is reduced, and the oxygenated products are displaced by olefins (mostly conjugate).

$$\mathrm{HOOH \longrightarrow 2OH\cdot} \qquad (27)$$

As the temperature is increased through the NTC zone, the contribution of alkylperoxy radicals falls. Little alkyl hydroperoxide is made and hydrogen peroxide decomposition makes a greater contribution to radical generation. Eventually the rate goes through a minimum. At this point, reaction 2 is highly displaced to the left and alkyl radicals are the dominant radical species.

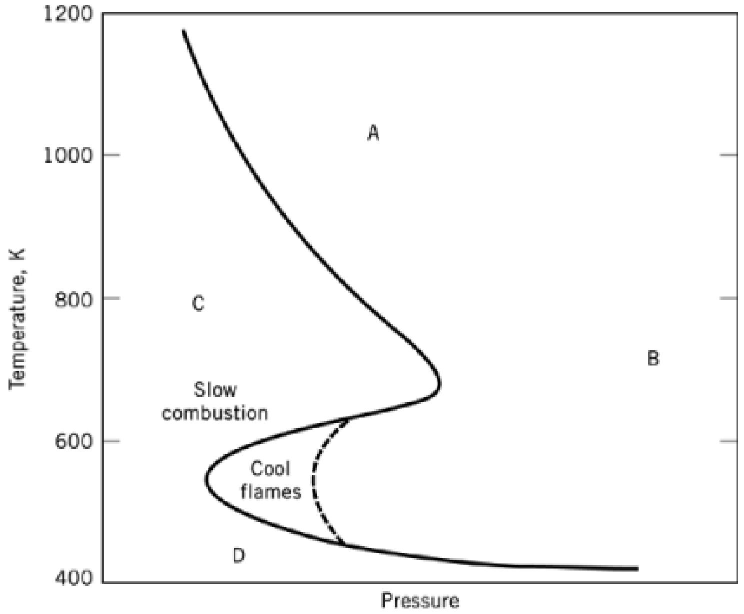
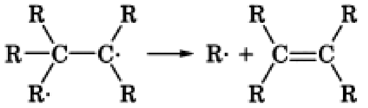


Fig. 6. Schematic ignition diagram for a hydrocarbon+ O_2 mixture, with applications. Region A, very rapid combustion, eg, a jet engine; region B, low temperature ignition, eg, internal combustion engine, safety hazards; regions C and D, slow oxidation to useful chemicals, eg, *O*-heterocyclic compounds in C and alcohols and peroxides in D. Courtesy of Blackwell Scientific Publications, Ltd., Oxford (60).

At the higher temperatures a decomposition of alkyl radicals, which is an olefin-producing variation of the β-scission reaction, becomes competitive with reaction **23** (or sequence 2, 24):



$$\mathrm{R{-}\overset{R}{\underset{R\cdot}{C}}{-}\overset{R}{\underset{R}{C}}\cdot \longrightarrow R\cdot + \overset{R}{\underset{R}{C}}{=}\overset{R}{\underset{R}{C}}} \qquad (28)$$

In principle, this degradation can continue until the residual radical contains only hydrogen or methyl groups attached to the carbon with the odd electron. Those radicals which still contain a carbon–carbon bond can form an olefin via reaction **23** (or sequence 2, 24). Methyl radicals are a special case with limited options.

3.1.2. Cool Flames

An intriguing phenomenon known as “cool” flames or oscillations appears to be intimately associated with NTC relationships. A cool flame occurs in static systems at certain compositions of hydrocarbon and oxygen mixtures over certain ranges of temperature and pressure. After an induction period of a few minutes, a pale blue flame may propagate slowly outward from the center of the reaction vessel. Depending on conditions, several such flames may be seen in succession. As many as five have been reported for propane (75) and for methyl ethyl ketone (76); six have been reported for butane (77). As many as 10 cool flames have been reported for some alkanes (60). The relationships of cool flames to other VPO domains are depicted in Figure 6.

Below a certain critical temperature, which varies with pressure and stoichiometry, cool flames for several hydrocarbons propagate from the wall inward; above this temperature, they propagate from the center of the vessel (78). This transition is interpreted as evidence for a changeover from a predominantly heterogeneous preflame mechanism to a homogeneous one.

When the necessary conditions are met, a cool flame seems to arise when heat generation during the low temperature oxidation exceeds heat losses. This leads to increasing temperature and increasing rates because of a higher radical generation rate by the low temperature chain-branching agent, ROOH. At a critical temperature, a cool flame appears. This causes the temperature to rise into the NTC region. Provided the temperature does not rise enough to permit the intermediate temperature chain-branching agent, HOOH, to become effective in providing new radicals, the flame can be quenched and the temperature drops. When the temperature returns to the low temperature reaction region, if sufficient amounts of the reactants remain, the whole process can proceed through another cycle (79). If, on the other hand, the temperature rise is great enough to bring about significant reaction of the intermediate temperature chain-branching agent, two-stage ignition occurs, ie, the cool flame is followed, after ca 1 s, by a hot flame (explosion or rapid combustion) (80).

The blue luminescence observed during cool flames is said to arise from electronically excited formaldehyde (60, 69). The high energy required indicates radical—radical reactions are producing hot molecules. Quantum yields appear to be very low (10^{-6} to 10^{-16}) (81). Cool flames never deposit carbon, in contrast to hot flames which emit much more intense, yellowish light and may deposit carbon (82).

The composition of an oxidizing mixture is altered extensively by the passage of a cool flame (66, 83, 84). Before passage of the flame, oxygenated materials are present. In the case of hexane oxidation, ROO· radicals are reportedly displaced by HOO· radicals above 563 K (85), in concordance with previous work (86, 87). After the passage of a cool flame, olefins, some conjugate and others of lower molecular weight, are observed.

The relationships that give rise to cool flames in static reactors are also associated with oscillations in flow reactors (88–91). Flow reactors offer significant advantages in studying these phenomena because, during stable operation, greater quantities of intermediates are available for sampling and sampling probes can be moved to points of interest. Moreover, stationary temperatures can be much more accurately determined. Such systems are characterized by sudden shifts from one stable state to another or oscillations between them. Hysteresis is frequently encountered in approaching a particular steady state.

Using the flow technique, one group of investigators report evidence that ROO· radicals are not unstable at higher temperatures (ie, reaction 2 is not readily reversible) (88). The concentration of ROO· radicals is drastically reduced by the passage of a cool flame, but can be quite high, even at elevated temperatures, prior to the actual flame passage. The ROO· radicals may decrease because they are destroyed by RO· and HO· radicals generated in the cool flame and not because of the reversibility of reaction 2 (88).

Even though there is some challenge, the reversibility of reaction 2 as the root cause of the NTC and cool flame phenomena is widely accepted. It is also generally accepted that, as a consequence of reversibility, there is a temperature-dependent switchover from a low temperature chain-branching agent, ROOH, to an intermediate temperature chain-branching agent, HOOH. However, there are some instances where NTCs and cool flames are reported, but the generation of HOO· by either reaction **23** or 24 is not possible. The oxidations of acetone and methane are notable examples (76, 92–94). These cases apparently require the presence of some other intermediate that can trigger the switchover to HOO· radicals. This role is often assigned to formaldehyde.

Additional evidence indirectly supports the reversibility of reaction 2. The addition of oxygen to a highly conjugated radical is readily reversible even at 40°C according to a study of the isomerization of methyl linolenate hydroperoxides in the presence of $^{18}O_2$ (95).

3.1.3. Effect of Pressure

The effect of pressure in VPO has not been extensively studied but is informative. The NTC region and cool flame phenomena are associated with low pressures, usually not far from atmospheric. As pressure is increased, the production of olefins is suppressed and the NTC region disappears (96, 97). The reaction rate also increases significantly and, therefore, essentially complete oxygen conversion can be attained at lower temperatures.

The product distribution shifts toward oxygenated materials that retain the carbon skeleton of the parent hydrocarbon.

3.2. Molecular Structure

Molecular structure strongly influences the reaction rate in low temperature VPO but has less effect in the intermediate and high temperature regions (96, 98). At low temperature and low pressure, relative rates vary from 1.0 for pentane to 1380 for decane (96, 99). This variation is much greater than the variation in the ease of abstractability of the hydrogen atoms. The relative efficiency of production of chain-branching agents is also involved (96). This is further borne out by the observation that branched-chain isomers oxidize more slowly than their straight-chain counterparts (96, 98) even though the ease of hydrogen abstractability increases in the series primary < secondary < tertiary. Reaction 2 is more readily reversible for 3° radicals (63). Furthermore, they produce ketones (through reactions 2, 13, 14, and **16**) rather than aldehydes. Aldehydes oxidize very rapidly and are more effective in subsequent chain branching.

The similarity of oxidation rates of different hydrocarbons in the higher temperature regions is probably related to the predominance of alkyl radical cracking reactions under these conditions (reaction **28**). The products of such reactions would be similar for most common hydrocarbons (96).

3.2.1. Methane

As our most abundant hydrocarbon, methane offers an attractive source of raw material for organic chemicals (see Hydrocarbons). Successful commercial processes of the 1990s are all based on the intermediate conversion to synthesis gas. An alternative one-step oxidation is potentially very attractive on the basis of simplicity and greater energy efficiency. However, such processes are not yet commercially viable (100).

At ordinary pressures, the rate of homogeneous oxidation of methane [74-82-8] is not very high (<500 °C) (101). Reaction 2 is highly reversed, ie, the ratio of $CH_3\cdot$ to $CH_3OO\cdot$ is very high. The radicals present in highest concentration tend to be the principal participants in radical–radical reactions. The generation of intermediate ethane from methyl radicals has been found to be a significant path in the oxidation of methane (102). In oxidations near 1100 K, roughly half of the methyl radicals are directly oxidized; the remainder dimerize before oxidation. Moreover, the methyl radicals that are directly oxidized under these conditions tend not to react with oxygen molecules but with $HOO\cdot$ radicals or atomic oxygen. The principal reactions producing methyl radicals involve $HO\cdot$ or atomic oxygen.

A previous proposal for the initiation mechanism at temperatures up to 2000 K is an analogue of equation 6 (103):

$$CH_4 + O_2 \longrightarrow CH_3\cdot + HOO\cdot$$

An alternative suggestion, based on a mathematical model fitted to experimental data, is that initiation occurs by thermolysis of a carbon–hydrogen bond:

$$CH_4 + M^* \longrightarrow CH_3\cdot + H\cdot + M \qquad (29)$$

where M* represents an energy-rich molecule (102).

Methane oxidations occur only by intermediate and high temperature mechanisms and have been reported not to support cool flames (104, 105). However, others have reported that cool flames do occur in methane oxidation, even at temperatures >400 °C (93, 94, 106, 107). Since methyl radicals cannot participate in reactions **23** or 24, some other mechanism must be operative to achieve the quenching observed in methane cool flames. It has been proposed that the interaction of formaldehyde and its products with radicals decreases their concentrations and inhibits the whole oxidation process (93).

The reported characteristics of methane oxidation at high pressures are interesting. As expected,the reaction can be conducted at lower temperatures; eg, 262°C at 334 MPa (3300 atm) (100). However, the cool flame phenomenon is observed even under these conditions. At high pressures, in excess of about 5 MPa (50 atm), the product distribution shifts toward methanol (100, 108–110).

Very extensive investigations have been conducted on the oxidation of methane over a number of heterogeneous catalysts, particularly Li^+—MgO (111, 112). A typical oxidation is conducted at 700°C (113). Methyl radicals generated on the surface are effectively injected into the vapor space before further reaction occurs (114). Under these conditions, methyl radicals are not very reactive with oxygen and tend to dimerize. Ethane and its oxidation product ethylene can be produced in good efficiencies but maximum yield is limited to ca 20%. This limitation is imposed by the susceptibility of the intermediates to further oxidation (see Figs. 2 and 3). A conservative estimate of the lower limit of the oxidation rate constant ratio for ethane and ethylene with respect to methane is one, and the ratio for methanol may be at least 20 (115).

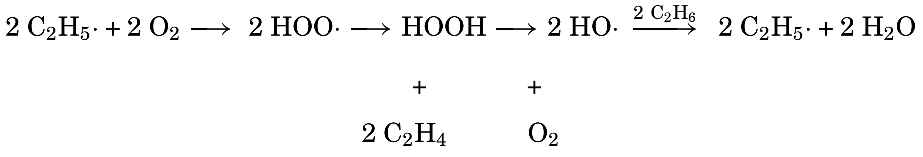
Some control over the split between methyl radical oxidation (to HCHO) and dimerization in heterogeneous oxidation can be achieved by varying conditions (116). For homogeneous oxidation, an efficiency of 70–80% to methanol has been claimed at 8–10% conversions (110). This is the high end of the reported range and is controversial. Even so, such technology appears unlikely to be competitive for regular commercial use until further advances are made (117). The critical need is to protect the products from further oxidation (118).

Although there are no new methane VPO competitive processes, current technology may be useful for the production of impure methanol in remote areas for use as a hydrate inhibitor in natural gas pipelines (119, 120).

3.2.2. Ethane

Ethane VPO occurs at lower temperatures than methane oxidation but requires higher temperatures than the higher hydrocarbons (121). This is a transition case with mixed characteristics. Low temperature VPO, cool flames, oscillations, and a NTC region do occur. At low temperatures and pressures, the main products are formaldehyde, acetaldehyde ($HCHO{:}CH_3CHO =$ ca 5) (121–123), and carbon monoxide. These products arise mainly through ethylperoxy and ethoxy radicals (see eqs. 2 and 12–16and Fig. 1).

As the temperature is raised, ethylene and hydrogen peroxide become important products. In the 600–630°C region, hydrogen peroxide is a significant product but it is isolated in much smaller quantities than ethylene (124). There is strong evidence that hydrogen peroxide must be made primarily by reaction 26 rather than reaction 25. In this mode, it does not serve as a chain-branching agent but rather as a delayed chain carrier through the following reaction scheme.



$$2\,C_2H_5\cdot + 2\,O_2 \longrightarrow 2\,HOO\cdot \underset{\substack{+\\ 2\,C_2H_4}}{\longrightarrow} HOOH \underset{\substack{+\\ O_2}}{\longrightarrow} 2\,HO\cdot \xrightarrow{2\,C_2H_6} 2\,C_2H_5\cdot + 2\,H_2O$$

Chain-branching requirements are met by HOOH formed in reaction 25 and by HCHO oxidation (eqs. 30 and 31).

$$HCHO + O_2 \longrightarrow HOO\cdot + H\dot{C}O \qquad (30)$$

$$HOO\cdot + HCHO \longrightarrow HOOH + H\dot{C}O \qquad (31)$$

Ethylene oxide is a coproduct, probably formed by the reaction of ethylene and HOO· (124–126). Chain branching also occurs through further oxidation of ethylene; hydroxyl radicals are the main chain centers of propagation (127).

Most HCHO ($>75\%$) is formed directly from ethane [74-84-0] (perhaps via reactions 2, 13, 14, **16**, etc) without going through ethylene (126, 128), although this is controversial (129).

Increasing pressure increases yields of methanol and ethanol, increases the C_2H_5OH:CH_3OH ratio, and reduces yields of acetaldehyde and formaldehyde (96, 97, 130). Ethylene is insignificant at 790 kPa (7.8 atm) even at 460°C (96).

3.2.3. Propane

The VPO of propane [74-98-6] is the classic case (66, 89, 131–137). The low temperature oxidation (beginning at ca 300°C) readily produces oxygenated products. A prominent NTC region is encountered on raising the temperature (see Fig. 4) and cool flames and oscillations are extensively reported as complicated functions of composition, pressure, and temperature (see Fig. 6) (96, 128, 138–140). There can be a marked induction period. Product distributions for propane oxidation are given in Table 1.

Aldehydes are important products at all pressures, but at low pressures, acids are not. Carbon monoxide is an important low pressure product and declines with increasing pressure as acids increase. This is evidence for competition between reaction sequence **18–20** and reaction **21**. Increasing pressure favors retention of the parent carbon skeleton, in concordance with the reversibility of reaction 2. Propylene becomes an insignificant product as the pressure is increased and the temperature is lowered. Both acetone and isopropyl alcohol initially increase as pressure is raised, but acetone passes through a maximum. This increase in the alcohol:carbonyl ratio is similar to the response of the methanol:formaldehyde ratio when pressure is increased in methane oxidation.

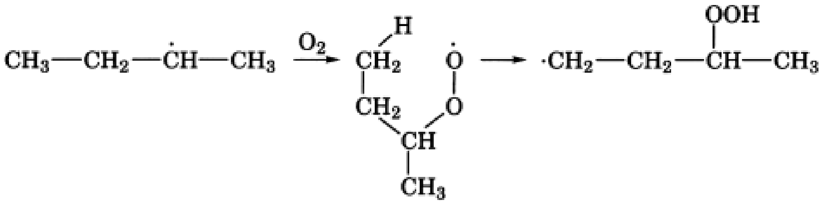
The changeover from ROO· radicals to HOO· radicals and the switch from organic peroxides to HOOH has been shown as temperature is increased in propane VPO (87, 141). Tracer experiments have been used to explore product sequences in propane VPO (142–145). Propylene oxide comes exclusively from propylene. Ethylene, acetaldehyde, formaldehyde, methanol, carbon monoxide, and carbon dioxide come from both propane and propylene. Ethanol comes exclusively from propane.

Commercial VPO of propane–butane mixtures was in operation at Celanese Chemical Co. plants in Texas and/or Canada from the 1940s to the 1970s. The principal primary products were acetaldehyde, formaldehyde, methanol, and acetone. The process was run at low hydrocarbon conversion (3–10%) and a pressure in excess of 790 kPa (7.8 atm). These operations were discontinued because of various economic factors, mainly the energy-intensive purification system required to separate the complex product streams.

A process to produce propylene by VPO of propane was patented in the former USSR in 1987 (146). Similar processes have the potential to coproduce hydrogen peroxide. Yields of hydrogen peroxide as high as 1 mol/mol propylene produced have been reported with 60–70% propylene selectivity (147).

3.2.4. Butane

The VPO of butane (148–152) is, in most respects, quite similar to the VPO of propane. However, at this carbon chain length an important reaction known as back-biting first becomes significant. There is evidence that a β-dicarbonyl intermediate is generated, probably by intramolecular hydrogen abstraction (eq. **32**). A postulated subsequent difunctional peroxide may very well be the precursor of the acetone formed.



(32)

At combustion temperatures, the oxidation of butane [106-97-8] is similar to that of propane (153). This is because most butyl radicals are consumed by carbon–carbon bond scission (reaction **28**).

3.2.5. Isobutane

The VPO of isobutane [75-28-5] is similar to the VPO of other low molecular weight paraffins; however, among the significant differences, conjugate olefin can be a main product even in the low temperature region (78). The selectivity of isobutylene is ca 50% at 1% conversion at ca 290°C. The selectivity decreases with increasing temperature, passing through a minimum of ca 20% at ca 350°C. In the NTC range, the selectivity to isobutylene increases as expected. The low temperature mechanism for isobutylene is postulated as heterogeneous (78, 154), whereas the higher temperature mechanism is the usual homogeneous one. In contrast, 80% selectivities of isobutylene have been reported in the initial products (<1% conversion) (155) over the range 270–330°C by a mechanism that was postulated to be mainly homogeneous. Increasing surface-to-volume ratio has a significant impact on product distribution (156).

Isobutane shows the usual NTC and cool flame phenomena (78, 154, 157, 158). As the pressure is increased, the expected increase in oxygenated products retaining the parent carbon skeleton is observed (96). Under similar conditions, isobutane oxidizes more slowly than *n*-butane (159). There are still important unresolved questions concerning isobutane VPO (160).

3.2.6. Higher Hydrocarbons

The VPO of higher hydrocarbons is similar to that of the lower members of the series with two significant additional complications: (*1*) the back-biting reactions of alkylperoxy radicals (eq. **32**), particularly at positions 2 or 3 carbons removed from the peroxy position, and (*2*) above the NTC region, radical fragmentation (eq. **28**).

Below the NTC region, intramolecular abstraction appears to generate β-dicarbonyl intermediates that are consumed during cool flames (161–164). Secondary attack on nonradical monofunctionals does not appear to be a significant source for these difunctional intermediates.

In the NTC region, back-biting reactions appear to be responsible for the formation of cyclic ethers (60, 165–170). In addition to oxetanes and tetrahydrofurans, tetrahydropyrans, oxiranes, and others are also observed (60, 96, 169); the tetrahydrofurans are favored. *O*-Heterocycle yields of 25 to 30% have been reported for *n*-pentane (165, 171). Conjugate and other olefins are also prominent products in this region (60, 169–172).

More complete understanding of VPO of hydrocarbons, especially in the fuel range, is vital for continued development of modern technology (60). The quenching phenomena associated with NTC regions and cool flames have been recognized as producing significant emissions of unburned and partially oxidized fuel (102). A significant correlation between cool flame phenomena and octane number has been reported. The use of a flow reactor under cool flame conditions has been suggested as a rapid method for octane number determination (173).

4. Liquid-Phase Oxidation

Although there are many similarities between VPO and liquid-phase oxidation (LPO), there are sharp distinctions. First, of course, in LPO with a gaseous oxidant (such as air), it is necessary that the oxidant (oxygen) be transported from the vapor phase into the liquid phase before LPO can occur. Moreover, it is possible to have a homogeneous catalyst dissolved in the liquid phase. If the solvent and/or products are volatile, they may be vaporized in significant amounts into any vent gas issuing from the reactor. Thus each individual component may have its own residence time in the system. Under these conditions, the hydrocarbon conversion no longer has a simple relationship with the exposure of individual components to oxidation conditions and alternative relationships are needed for kinetic studies (22). LPOs generally occur at lower temperatures than VPOs. LPOs do not exhibit NTC phenomena; oscillations are known to occur (174, 175), but these seem to be related to catalyst valence shift cycles and involve oxygen mass-transfer rate limitations. Another rate reduction effect is encountered if the temperature increases enough so that the vapor pressure approaches the imposed system pressure. In this case, oxygen is swept out of solution and the reaction stops; a boiling liquid does not support LPO. Generally, olefins are not significant products of the LPO of saturated materials. The high heat capacity and high heat of vaporization of the solvent, combined with limited oxygen supply, tend to damp temperature excursions in the liquid. Of course, runaway VPO reactions are possible if the LPO is quenched and unconverted oxygen collects in the vapor space.

The lower temperatures and reduced degree of oxygen starvation in LPO (vs VPO) generally reduce carbon monoxide production markedly by promoting reaction **18** and suppressing reaction **21**. As a consequence, acids, from further oxidation of aldehydes, are usually the main products.

4.1. Mass Transfer

The transfer of oxygen from the vapor to the liquid phase is a critical part of any LPO involving a gaseous oxidant. A simplified view of this process can provide a rationalization of the observed system behavior when air is the oxidant (176, 177). The typical air-sparged LPO system can be considered to consist of two zones. The zone near the sparger is chemically rate limited since the liquid contains enough dissolved oxygen to scavenge alkyl radicals by reaction 2. Under these conditions, the reaction is zero order with respect to oxygen (178); the kinetics are thus determined by the initiating and chain-branching, chain-terminating, and chain-propagating reactions.

As the concentration of oxygen in the ascending bubbles falls, a point is reached where the mass transfer of oxygen from the bubble becomes rate limiting. Above this transition region (assumed to be negligible), if the partial pressure of oxygen in equilibrium with the dissolved oxygen is negligible compared to the partial pressure of oxygen in the bubble and if the bubbles are of constant size and rise at a uniform rate, the delivery of oxygen to the solution is approximately first order, in both time and distance, with respect to the oxygen in the bubble. The system therefore has a characteristic transfer height. As the bubbles rise through this distance, they deliver ca 63.2% $(100 \times (1 - 1/e))$ of the oxygen they contained at the start. The transfer characteristics of a mixed zone system can be approximated with a relatively simple equation (177).

In the chemically rate-limited zone, the energy of activation is on the order of 105 kJ/mol (25 kcal/mol) (25, 176, 177). Mass transfer, since it is a physical process, is likely to have an energy of activation <21 kJ/mol (5 kcal/mol) (179). The effective overall energy of activation for the oxygen-transport process is even lower because increasing temperature results in larger bubbles that rise faster (less surface per unit volume, lower contact time). The two zones can interact in such a way that the activation energy for the oxidation process can be very low as long as both zones are present. This lends stability to the operation. If the chemically rate-limited zone is so large that the energy of activation is significant, the operation becomes unstable because a small temperature fluctuation (reduction) can result in a significantly reduced reaction rate. This causes a reduction in the heat evolution rate and a further reduction of temperature ensues. The minimum stable operating temperature for a given system and set of conditions may be sharply defined; a reduction of as little as a few tenths of a degree in temperature may mean the difference between stable operations and loss of the reaction. The lowest minimum stable operating temperature can be approached when the temperature distribution in the reactor approaches uniformity.

Stable operation of LPO reactors thus requires the presence of a mass-transfer rate-limited zone. It is usually desirable to limit this zone to minimize oxygen starvation problems.

4.2. Pressure

Within limits, pressure may have little effect in air-sparged LPO reactors. Consider the case where the pressure is high enough to supply oxygen to the liquid at a reasonable rate and to maintain the gas holdup relatively low. If pressure is doubled, the concentration of oxygen in the bubbles is approximately doubled and the rate of oxygen delivery from each bubble is also approximately doubled in the mass-transfer rate-limited zone. The total number of bubbles, however, is approximately halved. The overall effect, therefore, can be small. The optimum pressure is likely to be determined by the permissible maximum gas holdup and/or the desirable maximum vapor load in the vent gas.

4.3. Reactor Configuration

The horizontal cross-sectional area of a reactor is a critical parameter with respect to oxygen mass-transfer effects in LPO since it influences the degree of interaction of the two types of zones. Reactions with high intrinsic rates, such as aldehyde oxidations, are largely mass-transfer rate-limited under common operating conditions. Such reactions can be conducted effectively in reactors with small horizontal cross sections. Slower reactions, however, may require larger horizontal cross sections for stable operation.

4.4. Catalysts and Promoters

The function of catalysts in LPO is not well understood. Perhaps they are not really catalysts in the classical sense because they do not necessarily speed up the reaction (25). They do seem to be able to alter relative rates and thereby affect product distributions, and they can shorten induction periods. The basic function in shortening induction periods appears to be the decomposition of peroxides to generate radicals (eq. 33).

$$\text{ROOH} + \text{M}^{n+} \longrightarrow \text{RO}\cdot + \text{OH}^- + \text{M}^{(n+1)+} \qquad (33)$$

Although the decomposition rate of peroxide is thus increased, the consequent lowering of steady-state peroxide concentration leaves the effective rate unchanged in the simple peroxide cycle kinetic scheme (25). In real systems, at certain critical levels, a catalyst can become an inhibitor (2, 180).

An important function of manganous ions is the ready reduction of alkylperoxy radicals (181) (eq. 34).

$$\text{ROO}\cdot + \text{Mn}^{2+} \longrightarrow \text{ROO}^- + \text{Mn}^{3+} \qquad (34)$$

Higher valence-state metal ions can abstract hydrogen from a hydroperoxide (25) (eq. 35) or from a substrate (eq. 36).

$$\text{ROOH} + \text{M}^{(n+1)+} \longrightarrow \text{ROO}\cdot + \text{H}^+ + \text{M}^{n+} \qquad (35)$$

$$\text{RH} + \text{M}^{(n+1)+} \longrightarrow \text{R}\cdot + \text{H}^+ + \text{M}^{n+} \qquad (36)$$

Reaction 36 may occur through a peroxy radical complex with the metal ion (2, 25, 182). In any event, reaction 34 followed by reaction 36 is the equivalent of a metal ion-catalyzed hydrogen abstraction by a peroxy radical.

Reactions 33 and 35 constitute the two principal reactions of alkyl hydroperoxides with metal complexes and are the most common pathway for catalysis of LPOs (2). Both manganese and cobalt are especially effective in these reactions. There is extensive evidence that the oxidation of intermediate ketones is enhanced by a manganese catalyst, probably through an enol mechanism (34, 96, 183–185).

Mn(II) is readily oxidized to Mn(III) by just bubbling air through a solution in, eg, nonanoic acid at 95°C, even in the absence of added peroxide (186). Apparently traces of peroxide in the solvent produce some initial Mn(III) and alkoxy radicals. Alkoxy radicals can abstract hydrogen to produce R· radicals and Mn(III) can react with acid to produce radicals. The R· radicals can produce additional alkylperoxy radicals and hydroperoxides (reactions 2 and 3) which can produce more Mn(III). If the oxygen feed is replaced by nitrogen, the Mn(III) is rapidly reduced to Mn(II).

Chromium compounds decompose primary and secondary hydroperoxides to the corresponding carbonyl compounds, both homogeneously and heterogeneously (187–191). The mechanism of chromium catalyst interaction with hydroperoxides may involve generation of hexavalent chromium in the form of an alkyl chromate, which decomposes heterolytically to give ketone (192). The oxidation of alcohol intermediates may also proceed through chromate ester intermediates (193). Therefore, chromium catalysis tends to increase the ketone:alcohol ratio in the product (194, 195).

Cupric ion has a unique ability to compete with oxygen for a carbon-centered free radical (compare reaction 2):

$$R\cdot + CuX_2 \longrightarrow [\mathit{complex}] \longrightarrow RX + CuX \text{ or } R'CH{=}CH_2 + hX + CuX \qquad (37)$$

Depending on the nature of the radical and the copper ligands, the complex formed in reaction 37 may form an olefin or a ligand-substituted product (2, 196, 197) where X can be acetate, halide, etc. When the radical is acyl, reaction 37 can compete with reaction **21** and improve efficiencies, especially for alpha-branched aldehydes (43, 198). Since the acylium ion intermediate reacts with carboxyl groups to produce anhydride this approach has been used to make anhydrides (199, 200). Copper catalysts generally retard LPOs, but soluble copper ions from corrosion have been identified as a primary cause of oxidative degradation of lubricating oils (201–203).

Zirconium and other nonmultivalent metal ions can act as promoters in some manner not currently clearly defined. For zirconium, the effect may be related to changes in monomer–dimer equilibria of Co(II) complexes (2, 204, 205).

Increasing efforts to heterogenize homogeneous catalysts for LPO are apparent (2, 206–209). Significant advantages in product recovery, catalyst use, and catalyst recovery are recognized. In some instances, however, the active catalyst is reported to be material dissolved from the solid catalyst (210).

The selectivity to alcohol in LPO may be significantly increased when boric acid, *meta*-boric acid, or boric anhydride is present in stoichiometric amounts (2). The boron compounds appear to convert alkylhydroperoxides to alkyl borates and may also intercept alkylperoxy radicals, converting them to alkylperoxyboron compounds; these are later converted to alkyl borates. The alkyl borates are resistant to further oxidation; they are hydrolyzed to recover alcohols.

4.5. Propane

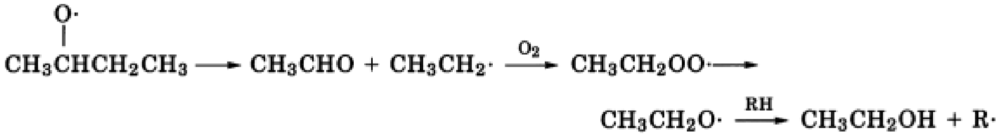
Propane is difficult to oxidize in LPO because of its volatility and lack of reactivity. It can, however, be oxidized with a suitable solvent and sufficiently high pressures and temperatures (211). The principal products are acetone and isopropyl alcohol.

4.6. Butane

Butane LPO has been a significant source for the commercial production of acetic acid and acetic anhydride for many years. At various times, plants have operated in the former USSR, Germany, Holland, the United States, and Canada. Only the Hoechst-Celanese Chemical Group, Inc. plants in Pampa, Texas, and Edmonton, Alberta, Canada, continue to operate. The Pampa plant, with a reported annual production of 250,000 t/yr, represents about 15% of the 1994 installed U.S. capacity (212). Methanol carbonylation is now the dominant process for acetic acid production, but butane LPO in established plants remains competitive.

The production of acetic acid from butane is a complex process. Nonetheless, sufficient information on product sequences and rates has been obtained to permit development of a mathematical model of the system. The relationships of the intermediates throw significant light on LPO mechanisms in general (22). Surprisingly, ca 25% of the carbon in the consumed butane is converted to ethanol in the first reaction step. Most of the ethanol is consumed by subsequent reaction.

The proposed mechanism for producing ethanol [64-17-5] from butane involves β-scission of a *sec*-butoxy radical (eq. **38**). The *sec*-butoxy radicals are derived from *sec*-butylperoxy radicals (reaction 14 (213)) and/or through some sequence involving reaction 33. If 25% of the carbon forms ethanol, over 50% must pass through the *sec*-butoxy radical. Furthermore, the principal fate of *sec*-butoxy radicals must be the β-scission reaction; the ethoxy radical, on the other hand, must be converted to ethanol efficiently.



$$CH_3\overset{O\cdot}{\overset{|}{C}}HCH_2CH_3 \longrightarrow CH_3CHO + CH_3CH_2\cdot \xrightarrow{O_2} CH_3CH_2OO\cdot \longrightarrow CH_3CH_2O\cdot \xrightarrow{RH} CH_3CH_2OH + R\cdot \tag{38}$$

Methyl ethyl ketone, a significant coproduct, seems likely to arise in large part from the termination reactions of *sec*-butylperoxy radicals by the Russell mechanism (eq. **15**, where $R = CH_3$ and $R' = CH_2CH_3$). Since alcohols oxidize rapidly vs paraffins, the *sec*-butyl alcohol produced (eq. **15**) is rapidly oxidized to methyl ethyl ketone. Some of the *sec*-butyl alcohol probably arises from hydrogen abstraction by *sec*-butoxy radicals, but the high efficiency to ethanol indicates this is a minor source.

Although it appears that methyl ethyl ketone [78-93-3] cannot be the principal product in butane LPO, it has been reported that the ratio of methyl ethyl ketone to acetic acid [64-19-7] can be as high as 3:1 in a plug-flow-type reactor (214). However, this requires a very unusual reactor (length : dia = $16,640 : 1$). The reaction is very unstable and wall reactions may influence mechanisms.

Water has a strong inhibiting effect above ca 3% concentration in the feed (214); in contrast, others report that 14–16 wt % water increases the rate (215).

Acetone is a coproduct of butane LPO. Some of this is produced from isobutane, an impurity present in all commercial butane (by reactions 2, 13, 14, and **16**). However, it is likely that much of it is produced through the back-biting mechanisms responsible for methyl ketone formation in the LPO of higher hydrocarbons (216).

Propionic acid made in butane LPO probably comes by a minor variation of reaction **38** that produces methyl radicals and propionaldehyde. It is estimated that up to 18% of the *sec*-butoxy radicals may decompose in this manner (213); this may be high since propionic acid is a minor product.

Between 6 and 30% of the radical attack on butane may occur at the primary hydrogen atoms (213). Since ca 6% of the butane goes to or through butyric acid (22), the middle of this range does not seem unreasonable. Because it is much more resistant to oxidation than its precursors or coproducts, Acetic acid (qv) is the main product of butane LPO.

Butane LPO conducted in the presence of very high concentrations of cobalt catalyst has been reported to have special character (2, 205, 217–219). It occurs under mild conditions with reportedly high efficiency to acetic acid. It is postulated to involve the direct attack of Co(III) on the substrate. Various additives, including methyl ethyl ketone, *p*-xylene, or water, are claimed to be useful.

4.7. Isobutane

Isobutane can be oxidized noncatalytically to give predominantly *t*-butyl hydroperoxide [75-91-2] (TBHP) (reactions 2 and 3). The temperature is kept within the range 100 to 140°C. TBHP can serve as the initiator. At low rates of initiation and low conversions (which favor propagation reactions 2 and 3 over termination reaction 5), efficiencies greater than 90% can be achieved (2). Under practical conditions, the reaction is conducted at 125°C using di-*tert*-butyl peroxide, a more efficient initiator. TBHP is obtained in 75% efficiency at 8% isobutane conversion. *tert*-Butyl alcohol (21%), acetone (2%), and isobutyl derivatives (1%) are formed as side products. Using cobalt catalyst at 135°C gives predominantly *tert*-butyl alcohol (77%). Other branched-chain paraffins give mainly cleavage products under these conditions, indicating the *tert*-butoxy radical is more resistant to the β-scission reaction (reaction **16**) than other *tert*-alkoxy radicals (205). With no catalyst at 150–180°C and 5 MPa (50 atm) in acetic acid solvent, the principal products are acetone and methyl acetate (220). Addition of a manganese catalyst lowers acetone and increases formic acid.

A significant outlet for TBHP is the molybdenum-complex catalyzed production of propylene oxide, a process developed by Oxirane (221–224). The reported U.S. capacity in 1991 was 0.55×10^6 t/yr (225). The *tert*-butyl alcohol coproduct is used mostly to make methyl *tert*-butyl ether, a gasoline additive.

4.8. Higher Paraffins

The LPO of paraffins to produce synthetic fatty acids (SFAs) has been practiced extensively in the former USSR and Eastern bloc countries. Production capacity reportedly exceeded 0.45×10^6 t/yr in 1975 (226). Elsewhere, varying degrees of interest in the process have been evident in Germany, Japan, China (227), and a number of other countries. Although the basic mechanisms are similar, several difficulties are encountered in higher paraffin LPO that are not so evident in the LPO of, eg, butane. For one thing, the desired product SFAs have virtually the same susceptibility to further oxidation, on a per carbon atom basis, as the feed hydrocarbon, contrasting sharply with acetic acid from butane LPO. The minimum impact of this lack of oxidation resistance can be viewed in Figure 2. As a limiting optimistic case, the SFAs can be treated as if they were primary products, made straightforwardly by a single oxidative attack (neither of these assumptions is true); the k_2/k_1 ratio would be about 1. Efficiency would be limited to ca 80% at a conversion of ca 35%, even with a plug-flow or batch reactor. The real situation would, of course, be worse.

An even more significant limitation is that a higher paraffin, once attacked, is highly susceptible to the back-biting reaction (eq. **32**) before being converted to nonradical products (42, 216). Keeping the conversion low reduces secondary attack on nonradical products by keeping the concentration of such products low with respect to the feed; however, the site of a back-biting attack cannot be diluted with respect to the attacking radical. Some of the products of back-biting attack are inevitably multifunctional products. Some are monofunctionals, such as methyl ketones, which can be subsequently converted to acids of lower molecular weight. Many of the multifunctionals, however, are essentially lost.

The typical SFA process uses a manganese catalyst with a potassium promoter (for solubilization) in a batch reactor. A manganese catalyst increases the relative rate of attack on carbonyl intermediates. Low conversions are followed by recovery and recycle of complex intermediate streams. Acid recovery and purification involve extraction with caustic and heat treatment to further decrease small amounts of impurities (particularly carbonyls). The fatty acids are recovered by freeing with sulfuric acid and, hence, sodium sulfate is a by-product.

4.9. Cyclohexane

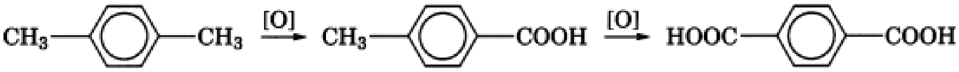
The LPO of cyclohexane [110-82-7] supplies much of the raw materials needed for nylon-6 and nylon-6,6 production. Cyclohexanol (A) and cyclohexanone (K) may be produced selectively by using a low conversion process with multiple stages (228–232). The reasons for low conversion and multiple stages (an approach to plug-flow operation) are apparent from Figure 2. Several catalysts have been reported. The selectivity to A as well as the overall process efficiency can be improved by using boric acid (2, 232, 233). K/A mixtures are usually oxidized by nitric acid in a second step to adipic acid (233) (see Cyclohexanol and cyclohexanone).

A one-step LPO of cyclohexane directly to Adipic acid (qv) has received a lot of attention (233–238) but has not been implemented on a large scale. The various versions of this process use a high concentration cobalt catalyst in acetic acid solvent and a promoter (acetaldehyde, methyl ethyl ketone, water).

Until the 1960s, adipic acid [124-04-9] was virtually the sole intermediate for nylon-6,6. However, much hexamethylenediamine is now made by hydrodimerization of Acrylonitrile (qv) or via hydrocyanation of Butadiene (qv). Cyclohexane remains the basis for practically the entire world output of adipic acid. The U.S. capacity for adipic acid for 1993 was 0.97×10^6 t/yr (233).

4.10. Alkylaromatics

The aromatic ring is fairly inert toward attack by oxygen-centered radicals. Aromatic acids consisting of carboxyl groups substituted on aromatic rings are good candidates for production by LPO of alkylaromatics since their k_2/k_1 ratios are low. Terephthalic acid [100-21-0] (TPA) and dimethyl terephthalate [120-61-6] (DMT) are the outstanding examples of high volume chemicals made in this way; efficiencies are ca 95%. The 1989 U.S. capacity for TPA was reported to be 4.0×10^6 t/yr (206). TPA is produced mostly by the LPO of *p*-xylene:



(39)

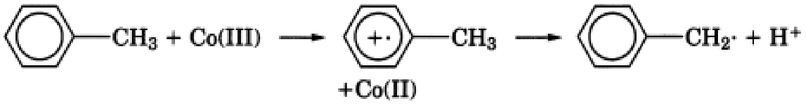
The intermediate *p*-toluic acid [99-94-5] (PTA) does not oxidize readily; its concentration builds up and the oxidation tends to stop before reaching high conversions to TPA (239, 240). A common explanation is deactivation of the methyl group by the electron-withdrawing carboxyl group making the methyl particularly resistant to oxidation (2). This conclusion is questionable, however, since methyl *p*-toluate is readily oxidized even though the electron-withdrawing capability of simple carboalkoxy groups is equivalent to that of the carboxyl group (241, 242). An appealing alternative explanation is that some phenolic material is produced during the oxidation of PTA. It is known that the oxidation of substituted aromatics may produce aryl radicals, probably through decarbonylation of aroyl radicals and decarboxylation of aroyloxy radicals (analogues of reactions **21** and **22**); that some phenols are produced (perhaps via aryl radicals through analogues of reactions 2 and **15**); and that phenols are powerful inhibitors of this type of reaction (54, 240, 243–247).

Various ways of overcoming the PTA oxidation problem have been incorporated into commercial processes. The predominant solution is the use of high concentrations of manganese and cobalt ions (2, 248–254), optionally with various cocatalysts (204, 255, 256), in the presence of an organic or inorganic bromide promoter in acetic acid solvent. Operational temperatures are rather high (ca 200°C). A lesser but significant alternative involves isolation of intermediate PTA, conversion to methyl *p*-toluate, and recycle to the reactor. The ester is oxidized to monomethyl terephthalate, which is subsequently converted to DMT and purified by distillation (248, 257–264).

A third method utilizes cooxidation of an organic promoter with manganese or cobalt-ion catalysis. A process using methyl ethyl ketone (248, 252, 265–270) was commercialized by Mobil but discontinued in 1973 (263, 264). Other promoters include acetaldehyde (248, 271–273), paraldehyde (248, 274), various hydrocarbons such as butane (270, 275), and others. Other types of reported activators include peracetic acid (276) and ozone (277), and very high concentrations of cobalt catalyst (2, 248, 278).

The aromatic core or framework of many aromatic compounds is relatively resistant to alkylperoxy radicals and inert under the usual autoxidation conditions (2). Consequently, even somewhat exotic aromatic acids are resistant to further oxidation; this makes it possible to consider alkylaromatic LPO as a selective means of producing fine chemicals (206). Such products may include multifunctional aromatic acids, acids with fused rings, acids with rings linked by carbon–carbon bonds, or through ether, carbonyl, or other linkages (279–287). The products may even be phenolic if the phenolic hydroxyl is first esterified (288, 289).

Using high concentrations of cobalt catalysts under mild conditions, it is even possible, when oxidizing a methylaromatic, to isolate relatively high yields of the aldehyde intermediate with consequently less production of the corresponding acid. This is possible because the initial attack on the aromatic substrate may occur through an electron-transfer mechanism (eq. **40**) (2, 205) rather than through direct hydrogen abstraction by a radical.



(40)

The cation–radical intermediate loses a proton to become, in this case, a benzyl radical. The relative rate of attack (via electron transfer) on an aromatic aldehyde with respect to a corresponding methylarene is a function of the ionization potentials (8.8 eV for toluene, 9.5 eV for benzaldehyde); it is much lower than one would expect if the competition involved hydrogen abstraction by, eg, alkylperoxy radicals. For example, it has been reported that a 90% efficiency to benzaldehyde can be obtained at 10% conversion in the oxidation of toluene using a $Co(OOCCH_3)_2$ catalyst and a NaBr or paraldehyde promoter (290). From Figure 2, this implies a k_2/k_1 ratio near 1, which is orders of magnitude less than the ratio of reported propagation rate constants (291). By varying catalysts and conditions to take advantage of this effect, a wide variety of simple to complex aromatic aldehydes can be synthesized directly from the corresponding methylarenes with surprising efficiency (2, 290–296).

An additional curious feature of alkylaromatic oxidation is that, under conditions where the initial attack involves electron transfer, the relative rate of attack on different alkyl groups attached to the same aromatic ring is quite different from that observed in alkane oxidation. For example, the oxidation of *p*-cymene can lead to high yields of *p*-isopropylbenzoic acid (2, 205, 297, 298).

Synthetic phenol capacity in the United States was reported to be ca 1.6×10^6t/yr in 1989 (206), almost completely based on the cumene process (see Cumene; Phenol). Some synthetic phenol [108-95-2] is made from toluene by a process developed by The Dow Chemical Company (2, 299–301). Toluene [108-88-3] is oxidized to benzoic acid in a conventional LPO process. Liquid-phase oxidative decarboxylation with a copper-containing catalyst gives phenol in high yield (2, 299–304). The phenolic hydroxyl group is located ortho to the position previously occupied by the carboxyl group of benzoic acid (2, 299, 301, 305). This provides a means to produce meta-substituted phenols otherwise difficult to make (2, 306). VPOs for the oxidative decarboxylation of benzoic acid have also been reported (2, 307–309). Although the mechanism appears to be similar to the LPO scheme (309), the VPO reaction is reported not to work for toluic acids (310).

Dihydroxyarenes can be produced from the corresponding diisopropylarenes in a manner similar to the production of phenol from cumene (206, 311–315).

An oxirane process utilizes ethylbenzene to make the hydroperoxide, which then is used to make propylene oxide [75-56-9]. The hydroperoxide-producing reaction is similar to the first step of cumene LPO except that it is slower (2, 224, 316–318). In the epoxidation step, α-phenylethyl alcohol [98-85-1] is the coproduct. It is dehydrated to styrene [100-42-5]. The reported 1992 capacity for styrene by this route was 0.59×10^6 t/yr (319).

The corresponding propylene oxide capacity is ca 0.33×10^6 t/yr. The total propylene oxide capacity based on hydroperoxide oxidation of propylene [115-07-1] (coproducts are *t*-butyl alcohol and styrene) is 1.05×10^6 t/yr (225).

BIBLIOGRAPHY

"Hydrocarbon Oxidation" in *ECT* 1st ed., Suppl. 1, pp. 401–418, by F. B. Marcotte and R. L. Mitchell, Celanese Corp. of America; in *ECT* 2nd ed., Vol. 11, pp. 224–241, by H. F. Hamil, Celanese Chemical Co.; in *ECT* 3rd ed., Vol. 12, pp. 826–851, by C. C. Hobbs, Celanese Chemical Co.

Cited Publications

1. S. W. Benson and P. S. Nangia, *Acc. Chem. Res* **12**(7), 223–228 (1979).
2. R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, Inc., New York, 1981.
3. N. Semenov, *Chemical Kinetics and Chain Reactions*, Oxford University Press, London, 1935, p. 68.
4. J. L. Bolland, *Q. Rev. (London)* **3**, 1 (1949).
5. J. L. Bolland, *Trans. Faraday Soc.* **46**, 358 (1950).
6. J. L. Bolland and G. Gee, *Trans. Faraday Soc.* **42**, 236 (1946).
7. J. L. Bolland and H. P. Koch, *J. Chem. Soc.*, 445 (1945).
8. L. Bateman, *Q. Rev. (London)* **8**, 147 (1954).
9. L. Bateman and G. Gee, *Proc. R. Soc. (London) A* **195**, 376 (1948).
10. A. Robertson and W. A. Waters, *Trans. Faraday Soc.* **42**, 201 (1946).
11. F. R. Mayo, *J. Chem. Educ.* **63**(2), 97–99 (1986).
12. C. Walling, *Ibid.*, 99–102.
13. S. W. Benson, in R. R. Gould and F. R. Mayo, eds., *Advances in Chemistry Series 76*, American Chemical Society, Washington, D.C., 1968, 143–153.
14. Ref. 2, p. 20.
15. A. T. Betts and H. Uri, in Ref. 13, 160–181.
16. B. D. Boss and R. N. Hazlett, *Can. J. Chem.* **47**, 4175–4182 (1969).
17. M. G. Simic, *J. Chem. Educ.* **58**(2), 125–131 (1981).
18. L. Sieg, in W. Jost, ed., *Low Temperature Oxidation*, Gordon and Breach, New York, 1965; p. 222.
19. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1957, pp. 503ff.
20. D. Swern, ed., *Organic Peroxides*, John Wiley & Sons, Inc., New York, 1970, p. 214.
21. G. A. Russell, in S. L. Friess, E. S. Lewis, and A. Weissberger, eds., *Technique of Organic Chemistry*, Vol. **8**, Part 1, Interscience Publishers, New York, 1961, p. 344.
22. C. C. Hobbs and co-workers, *Ind. Eng. Chem. Proc. Des. Dev.* **11**, 59 (1972).
23. F. R. Mayo, *Acc. Chem. Res.* **1**(7), 193–201 (1968).
24. G. A. Russell, *J. Am. Chem. Soc.* **77**, 4583 (1955).
25. C. Walling, *J. Am. Chem. Soc.* **91**, 7590 (1969).
26. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
27. Ref. 2, p. 22.
28. Ref. 2, p. 24.
29. G. A. Russell, *J. Am. Chem. Soc.* **79**, 3871 (1957).
30. S. W. Benson, *Oxid. Commun.* **2**(3–4), 169–188 (1982).
31. Q. J. Niu and G. D. Mendenhall, *J. Am. Chem. Soc.* **114**(1), 165–172 (1992).
32. B. D. Boss and R. N. Hazlett, *Ind. Eng. Chem., Prod. Res. Dev.* **14**(2), 135–138 (1975).
33. Ref. 26, p. 145.
34. F. R. Mayo, *Prepr, Div. Pet. Chem. Am. Chem. Soc.* **19**(4), 627 (1974).

35. A. Krzysztoforski and co-workers, *Ind. Eng. Chem. Process Des. Dev.* **25**(4), 894–898 (1986).
36. F. F. Rust, personal communication, 1970.
37. Ref. 2, p. 351.
38. Ref. 26, p. 147.
39. Ref. 26, p. 165.
40. Ref. 19, p. 411.
41. S. Blaine and P. E. Savage, *Ind. Eng. Chem. Res.* **30**(9), 2185–2191 (1991).
42. R. K. Jensen and co-workers, *J. Am. Chem. Soc.* **103**(7), 1742–1749 (1981).
43. D. R. Larkin, *J. Org. Chem.* **55**(5), 1563–1568 (1990).
44. F. Garcia-Ochoa, A. Romero, and J. Querol, *Ind. Eng. Chem. Res.* **28**(1), 43–48 (1989).
45. Ref. 26, 154–155.
46. R. Stewart, *Oxidation Mechanisms*, W. A. Benjamin, New York, 1964, p. 30.
47. B. Plesnicar, in W. S. Trahanovsky, ed., *Oxidation in Organic Chemistry*, Academic Press, Inc., New York, 1978, p. 264.
48. C. Walling, *Pure Appl. Chem.* **15**(1), 69 (1967).
49. W. Pritzkow and V. Voerckel, *Oxid. Commun.* **4**(1–4), 223–228 (1983).
50. W. Pritzkow and V. Voerckel, *J. Prakt. Chem.* **326**(4), 572–578 (1984).
51. F. R. Hewgill and G. M. Proudfoot, *Aust. J. Chem.* **34**(2), 335–342 (1981).
52. S. Blaine and P. E. Savage, *Ind. Eng. Chem. Res.* **31**(1), 69–75 (1992).
53. S. Blaine and P. E. Savage, *Prepr. Div. Pet. Chem., Am. Chem. Soc.* **35**, 239–244 (1990).
54. P. Roffia, P. Calini, and L. Motta, *Ind. Eng. Chem. Prod. Res. Dev.* **23**(4), 629–634 (1984).
55. P. Roffia, P. Calini, and S. Tonti, *Ind. Eng. Chem. Res.* **27**, 765–770 (1988).
56. F. Broich and co-workers, *Erdöl Kohle* **16**, 284 (1963).
57. T. Horlenko, unpublished data, Celanese Chemical Co., 1964.
58. Ref. 47, p. 262.
59. A. W. Dawkins, *Eur. Chem. News, Norm. Paraffins Suppl.*, 49–58 (1966).
60. R. W. Walker, *Sci. Prog.* **74**(294, Pt. 2), 163–187 (1990).
61. C. K. Westbrook and F. L. Dryer, *Prog. Energy Combust. Sci.* **10**(1), 1–57 (1984).
62. T. S. Norton and F. L. Dryer, *Symp. (Int.) Combust. [Proc.]*, **23**, 179–185 (1991).
63. S. W. Benson, *J. Am. Chem. Soc.* **87**(5), 972–979 (1965).
64. D. N. Koert and N. P. Ceransky, *Chem. Phys. Processes Combust.*, 17/1–17/4 (1991).
65. E. I. Finkel'shtein and G. N. Gerasimov, *Zh. Fiz. Khim.* **58**(4), 942–946 (1984).
66. R. D. Wilk, N. P. Ceransky, and R. S. Cohen, *Combust. Sci. Technol.* **49**(1–2), 41–78 (1986).
67. R. D. Wilk, N. P. Ceransky, and R. S. Cohen, *Combust. Sci. Technol.* **52**(1–3), 39–58 (1987).
68. D. M. Newitt and W. G. Schmidt, *J. Chem. Soc.*, 1665 (1937).
69. R. R. Baker and D. A. Yorke, *J. Chem. Ed.* **49**(5), 351 (1972); R. A. Geisbrecht and T. E. Daubert, *Ind. Eng. Chem. Prod. Res. Dev.* **15**(2), 115 (1976).
70. J. C. Dechaux and L. Delfosse, *Combust. Flame* **34**(2), 169–185 (1979).
71. R. I. Moshkina and co-workers, *Kinet. Katal.* **21**(6), 1379–1384 (1980).
72. R. D. Wilk, *Chem. Phys. Processes Combust.*, 11-1–11-4 (1991).
73. I. R. Slagle, J. Y. Park, and D. Gutman, *Symp. (Int.) Combust. [Proc.]*, 733–741 (1984).
74. S. W. Benson, in Ref. 13, 143–153.
75. D. M. Newitt and L. S. Thornes, *J. Chem. Soc.*, 1656–1665 (1937).
76. J. A. Barnard, in Ref. 13, 98–110.
77. T. Berry and co-workers, in Ref. 13, 86–97.
78. J. G. Atherton and co-workers, *Symp. (Int.) Combust. [Proc.]* **14**, 513 (1973).
79. Ref. 18, 197–198.
80. Ref. 18, p. 226.
81. S. W. Benson, *The Foundation of Chemical Kinetics*, McGraw Hill Book Co., Inc., New York, 1960, p. 485.
82. A. D. Walsh in Ref. 18, 285–327.
83. Ref. 18, p. 224.
84. J. W. Falconer, D. E. Hoare, and Z. F. Savaya, *Oxid. Commun.* **4**(1–4), 299–315 (1983).

85. Z. A. Mansurov and D. U. Bodykov, *Khim. Fiz.* **7**(10), 1430–1431 (1988).
86. M. Carlier and L. R. Sochet, *J. Chim. Phys. Phys.-Chim. Biol.* **72**, 623–630 (1975).
87. G. A. Sachyan, G. Sh. Alaverdyan, and A. B. Nalbandyan, *Dokl. Akad. Nauk SSSR* **204**, 883 (1972).
88. K. A. Sahetchian and co-workers, *Combust. Flame* **34**(2), 153–159 (1979).
89. A. A. Mantashyan, P. S. Gukasyan, and R. H. Sayadyan, *Arch. Termodyn. Spalania* **9**(2), 273–278 (1978).
90. A. A. Mantashyan, S. G. Bernatosyan, and T. R. Simonyan, *Oxid. Commun.* **5**(1–2), 207–223 (1983).
91. V. Caprio, A. Insola, and P. G. Lignola, *Fiamme Reaz. Flusso, Simp. Int. Din. Reaz. Chim.* **2**, 47–51 (1978).
92. J. A. Barnard and M. A. Sheikh, *Pak. J. Sci. Ind. Res.* **16**(3–4), p. 93 (1973).
93. V. Ya. Basevich and S. M. Kogarko, *Oxid. Commun.* **3**(3–4), 199–209 (1983).
94. G. A. Foulds and co-workers, *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **37**(1), 51–60 (1992).
95. H. W.-S. Chan, G. Levett, and J. A. Matthew, *J. Chem. Soc. Chem. Comm.*, 756 (1978).
96. H. D. Medley and S. D. Cooley, *Adv. Pet. Chem. Ref.* **3**, 309 (1960).
97. U.S. Pat. 5,017,731 (May 21, 1991), H. D. Gesser, and co-workers.
98. Ref. 82, p. 296.
99. C. F. Cullis and co-workers, *Disc. Faraday Soc.* **2**, 111, 114, 117, 128 (1947).
100. H. D. Gesser, N. R. Hunter, and C. B. Prakash, *Chem. Rev.* **85**(4), 235–244 (1985).
101. D. E. Hoare in Ref. 18, 125–167.
102. C. K. Westbrook and co-workers, *J. Phys. Chem.* **81**(25), 2542–2554 (1977).
103. W. M. Heffington and co-workers, *Symp. (Int.) Combust. [Proc.]* **16**, 997 (1977).
104. Ref. 82, p. 481.
105. A. D. Walsh, in Ref. 18, pp. 290, 305, 313.
106. G. G. Torchyan, A. A. Mantashyan, and A. B. Nalbandyan, *Vses. Konf. Kinet. Mekh. Gazofazn. Reakts.* **2**, 17 (1971).
107. L. A. Khachatryan and co-workers, *Dokl. Akad. Nauk SSSR Ser. Khim.* **224**, 1363 (1975).
108. R. I. Moshkina and co-workers, *Arm. Khim. Zh.* **41**(1–2), 32–36 (1988).
109. Can. Pat. 1,267,423 (Oct. 17, 1986), H. D. Gesser, N. R. Hunter, and L. A. Morton (to Canada, Minister of Energy, Mines, and Resources).
110. P. S. Yarlagadda and co-workers, *Ind. Eng. Chem. Res.* **27**(2), 252–256 (1988).
111. *Catal. Today* **6**(4) (1990).
112. *Catal. Today* **13**(4) (1992).
113. C. Shi, M. Hatano, and J. H. Lunsford, *Catal. Today* **13**(2–3), 191–199 (1992).
114. P. F. Nelson, C. A. Lukey, and N. W. Cant, *J. Phys. Chem.* **92**(22), 6176–6179 (1988).
115. J. A. Labinger, *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **37**(1), 289–292 (1992).
116. J. S. J. Hargreaves, G. J. Hutchings, and R. W. Joyner, *Nature* **348**(6300), 428–429 (1990).
117. J. W. M. H. Geerts, J. H. B. J. Hoebink and K. Van der Wiele, *Catal. Today* **6**(4), 613–620 (1990).
118. J. H. Edwards and N. R. Foster, *Fuel Sci. Technol. Int.* **4**(4), 365–390 (1986).
119. P. M. Shcherbakov, S. A. Egorov, and S. F. Bobrova, *Neft. Gazov. Prom-st.*, (1), 40–41 (1986).
120. V. F. Budymka and co-workers, *Khim. Prom-st. (Moscow)*, (6), 330–331 (1987).
121. L. Sieg, in Ref. 18, p. 191.
122. A. B. Nalbandyan, *Dokl. Akad. Nauk SSSR* **66**, 413 (1949).
123. P. Gray, J. F. Griffiths, and S. M. Hasko, *Proc. R. Soc. London* **396**(1811), 227–255 (1984).
124. R. J. Sampson, *J. Chem. Soc.*, 5095 (1963).
125. R. I. Moshkina and co-workers, *Dokl. Akad. Nauk SSSR* **218**, 1147 (1974).
126. R. I. Moshkina and co-workers, *Kinet. Katal.* **19**(4), 830–839 (1978).
127. M. Cathonnet and H. James, *J. Chim. Phys. Phys.-Chim. Biol.* **74**(2), 156–167 (1977).
128. R. I. Moshkina and co-workers, *Kinet. Katal.* **17**, 1057 (1976).
129. J. H. Knox, in Ref. 13, 1–21.
130. M. U. Fedurtsa and S. S. Abedzheva, *Khim. Prom-st., Ser.: Khlornaya Prom-st.*, (1), 5–6 (1980).
131. M. M. Aleksishvili, S. S. Polyak, and V. Ya. Shtern, *Kinet. Katal.* **15**, 290 (1974).
132. M. M. Aleksishvili, S. S. Polyak, and V. Ya. Shtern, *Kinet. Katal.* **17**, 1110 (1976).
133. E. A. Poladyan and A. A. Mantashyan, *Arm. Khim. Zh.* **28**, 949 (1975).
134. E. A. Polyadyan and G. L. Grigoryan, *Kinet. Katal.* **17**, 231 (1976).
135. E. A. Poladyan and A. A. Mantashyan, *Arm. Khim. Zh.* **29**, 131 (1976).

136. D. N. Koert, D. L. Miller, and N. P. Ceransky, *Chem. Phys. Processes Combust.*, 8/1–8/4 (1991).
137. E. A. Poladyan and co-workers, *Kinet. Katal.* **17**, 304 (1976).
138. L. Sieg, in Ref. 18, p. 206.
139. A. A. Mantashyan and P. S. Gukasyan, *Dokl. Akad. Nauk SSSR* **234**, 379 (1977).
140. P. G. Lignola and co-workers, *Ber. Bunsenges. Phys. Chem.* **84**(4), 369–373 (1980).
141. I. K. Shakhnazaryan and co-workers, *Vses. Konf. Kinet. Mekh. Gazofaz. Reakts.* **2**, 4 (1971).
142. R. I. Moshkina and co-workers, *Dokl. Akad. Nauk SSSR* **249**(4), 908–912 (1979).
143. R. I. Moshkina and co-workers, *Oxid. Commun.* **3**(3–4), 241–257 (1983).
144. R. I. Moshkina and co-workers, *Khim. Fiz.*, (7), 976–987 (1982).
145. R. I. Moshkina, S. S. Polyak, and L. B. Romanovich, *Khim. Fiz.* **5**(9), 1249–1258 (1986).
146. Rus. Pat. SU 3719706 (Oct. 30, 1987), A. A. Mantashyan and M. D. Pogosyan (to Institute of Chemical Physics, Academy of Sciences, Armenian SSR).
147. T. Kunugi and co-workers, in Ref. 13, 326–344.
148. J. C. Dechaux, J. L. Flament, and M. Lucquin, *Combust. Flame* **17**, 205 (1971).
149. R. R. Baldwin and R. W. Walker, *Combust. Flame* **21**, 55 (1973).
150. R. R. Baldwin, J. C. Plaistowe, and R. W. Walker, *Combust. Flame* **30**, 13 (1977).
151. M. Carlier and L. R. Sochet, *Combust. Flame* **25**, 309 (1975).
152. V. K. Proudler and co-workers, *Phi. Trans. R. Soc. Lond. A* **337**, 211–221 (1991).
153. W. J. Pitz and Charles K. Westbrook, *Symp. (Int.) Combust. [Proc.]* **20**, 831–843 (1985).
154. G. A. Luckett and R. T. Pollard, *Combust. Flame* **21**, 265 (1973).
155. J. Hay, J. H. Knox, and J. M. C. Turner, *Symp. (Int.) Combust. [Proc.]* **10**, 331 (1965).
156. G. McKay and J. A. Aga, *Combust. Flame* **40**(2), 221–224 (1981).
157. A. J. Brown and co-workers, *Mech. Hydrocarbon React. Symp.*, 751 (1975).
158. V. Caprio, A. Insola, and P. G. Lignola, *Symp. (Int.) Combust. [Proc.]* **16**, 1155 (1977).
159. S. D. Cooley and J. W. Walker, Celanese Chemical Co. Technical Center, Corpus Christi, Tex., unpublished data.
160. B. Vogin, F. Baronnet, and G. Scacchi, *Can. J. Chem.* **67**(5), 759–772 (1989).
161. J. R. Thomas and H. W. Crandall, *Ind. Eng. Chem.* **43**, 2761 (1951).
162. M. R. Barusch and co-workers, *Ind. Eng. Chem.* **43**, 2764 (1951).
163. *Ibid.*, p. 2766.
164. Ref. 18, 222–223.
165. Ref. 77, p. 92.
166. J. H. Jones and D. A. Kurtz, *Am. Chem. Soc. Div. Pet. Chem. Prepr.* **17**, A98 (1972).
167. K. Richter, G. Oehlmann, and W. Schirmer, *Z. Phys. Chem. (Leipzig)* **253**(3–4), 207 (1973).
168. *Ibid.*, p. 217.
169. R. R. Baldwin, J. P. Bennett, and R. W. Walker, *Symp. (Int.) Combust.* **16**, 1041 (1977).
170. C. F. Cullis, M. M. Hirschler, and R. L. Rogers, *Proc. R. Soc. London, [Ser.] A* **382**(1783), 429–440 (1982).
171. R. R. Baldwin, J. P. Bennett, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1* **76**(5), 1075–1092 (1980).
172. M. M. Abdelkafi and A. Baklouti, *J. Soc. Chim. Tunis.* **2**(10), 7–12 (1991).
173. Ya.Yu. Stepanskii and co-workers, *Khim. Tekhnol. Topl. Masel*, (8), 54–56 (1981).
174. M. G. Roelofs and J. H. Jensen, *J. Phys. Chem.* **91**, 3380–3382 (1987).
175. M. G. Roelofs, E. Wasserman, and J. H. Jensen, *J. Am. Chem. Soc.* **109**, 4207–4217 (1987).
176. C. C. Hobbs and co-workers, *Ind. Eng. Chem. Prod. Res. Dev.* **11**, 220 (1972).
177. C. C. Hobbs and M. B. Lakin, in J. J. McKetta and W. A. Cunningham, eds., *Encyclopedia of Chemical Processing and Design*, Vol. **26**, Marcel Dekker, Inc., 1987, 351–373.
178. Ref. 26, p. 24.
179. K. J. Laidler, *J. Chem. Educ.* **49**, 343 (1972).
180. J. F. Black, *J. Am. Chem. Soc.* **100**, 527 (1978).
181. W. J. de Klein and E. C. Kooyman, *J. Catal.* **4**, 626 (1965).
182. I. I. Chuev and E. I. Zhilova, *Isv. Vyssh. Uchebn. Zaved., Khim. Kim. Technol.* **28**(1), 116–117 (1985).
183. J. Skriniarova, M. Hronec, and J. Ilavsky, *Oxid. Commun.* **10**(1–2), 51–68 (1987).
184. S. P. Prokopchuk, S. S. Abadzhev, and V. U. Shevchuk, *Ukr. Khim. Zh.* **49**(5), 505–508 (1983).
185. R. M. Dessau and E. I. Heiba, *Colloq. Int. C.N.R.S.* **278**, 271–274 (1978).

186. L. B. Levy, *J. Org. Chem.* **54**, 253–254 (1989).
187. N. Ikeda and K. Fukuzumi, *J. Am. Oil Chem. Soc.* **54**(3), 105 (1977).
188. U.S. Pat. 3,719,706 (Mar. 6, 1973), J. C. Brunie and co-workers (to Rhône-Poulenc SA).
189. Brit. Pat. 1,304,785 (Dec. 12, 1969), J. C. Brunie and co-workers (to Rhône-Poulenc SA).
190. U.S. Pat. 4,042,630 (Aug. 16, 1977), J. Wolters and J. L. J. P. Hennekens (to Stamicarbon B.V.).
191. Brit. Pat. 1,535,869 (Dec. 13, 1978), W. Voskuil and J. J. M. Van der Donck (to Stamicarbon BV).
192. S. V. Krylova and co-workers, *Oxid. Commun.* **10**(3–4), 243–254 (1987).
193. K. K. Sengupta, T. Samanta, and S. N. Basu, *Tetrahedron* **42**(2), 681–685 (1986).
194. O. A. Borislavskii and co-workers, *Vestn. L'vov. Politekh. Inst.* **211**, 120–122 (1988).
195. I. I. Korsak and co-workers, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, (5), 37–40 (1981).
196. J. K. Kochi, *Pure Appl. Chem.* **4**, 377 (1971).
197. Ger. Offen. 2,704,077 (Aug. 11, 1977), D. W. Edwards and G. H. Jones (to Imperial Chemical Industries, Ltd.).
198. Ger. Offen. 3,029,700 (Feb. 26, 1981), C. C. Hobbs and H. H. Thigpen (to Celanese Corp.).
199. Ger. Offen. 2,757,222 (July 5, 1979), H. Erpenbach and co-workers, (to Hoechst AG).
200. Jpn. Kokai Tokkyo Koho 78 112,804 (Oct. 2, 1978), T. Maki (to Mitsubishi Chemical Industries Co., Ltd.).
201. N. V. Aleksandrov, *Kinet. Katal.* **19**(4), 1057–1060 (1978).
202. H. Yukawa and Y. Fujikawa, *Kenkyu Hokoku-Kanagawa-ken Kogyo Shikensho*, (52), 63–68 (1982).
203. D. A. Hutchison and J. L. Thompson, *Lubr. Eng.* **46**(7), 467–473 (1990).
204. A. W. Chester, E. J. Y. Scott, and P. S. Landis, *J. Catal.* **46**(3), 308–319 (1977).
205. J. E. Lyons, in B. E. Leach, ed., *Applied Industrial Catalysis*, Vol. **3**, Academic Press, Inc., Orlando, Fla., 1984; Chapt. 6, 131–214.
206. R. A. Sheldon, *Stud. Surf. Sci. Catal.* **66**, 573–594 (1991).
207. R. A. Sheldon, *Stud. Surf. Sci. Catal.* **59**, 33–54 (1991).
208. A. Ya. Yuffa and co-workers, *Homogeneous Heterog. Catal.* **5**, 727–739 (1988).
209. B. J. Hwang and T. C. Chou, *Ind. Eng. Chem. Res.* **26**(6), 1132–1140 (1987).
210. M. Hronec and Z. Hrabe, *Ind. Eng. Chem. Prod. Res. Dev.* **25**(2), 257–261 (1986).
211. Can. Pat. 1,058,637 (Oct. 16, 1973), B. W. Kiff and J. B. Saunby (to Union Carbide Corp.).
212. *World Petrochemicals Program, Ethylene and Derivatives 1992*, Vol. **5**, private report from SRI International, Menlo Park, Calif., Jan. 1992, pp. UNIT-15 to UNIT-20.
213. Ref. 34, p. 631.
214. J. B. Saunby and B. W. Kiff, *Hydrocarbon Process* **55**(11), 247–252 (1976).
215. Jpn. Pat. 75 22,531 (July 31, 1975), K. Hori and co-workers (to Daicel Ltd.).
216. R. K. Jensen and co-workers, *J. Am. Chem. Soc.* **101**(25), 7574–7584 (1979).
217. U.S. Pat. 3,644,512 (Feb. 22, 1972), A. Onopchenko, J. G. D. Schulz, and R. Seekircher (to Gulf Research & Development Co.).
218. U.S. Pat. 4,032,570 (June 28, 1977), J. C. D. Schulz and R. Seekircher (to Gulf Research & Development Co.).
219. A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.* **38**(5), 909–912 (1973).
220. M. U. Fedurtsa and S. S. Abadzhev, *Khim. Prom-st., Ser.: Khlornaya Prom-st.*, (5), 11–12 (1982).
221. Fr. Pat. 1,500,728 (Nov. 3, 1967), H. R. Grane (to Atlantic Richfield Co.).
222. Belg. Pat. 718,070 (July 12, 1968), H. R. Grane and L. S. Bitar (to Atlantic Richfield Co.).
223. U.S. Pat. 3,907,902 (Sept. 23, 1975), H. R. Grane (to Atlantic Richfield Co.).
224. *Propylene Oxide, Report 2b,* private report from SRI International's Process Economics Program, Menlo Park, Calif., Feb., 1971.
225. *World Petrochemicals Program, Propylene and Derivatives 1992,* Vol. 3, private report from SRI International, Menlo Park, Calif., Jan. 1992, pp. UNIT-164 to UNIT-170.
226. *Fatty Acids, Report 42,* private report from SRI International's Economic Program, Menlo Park, Calif., Oct. 1968.
227. W. Bao, *Riyong Huaxue Gongye*, (3), 135–137 (1991).
228. Ref. 213, p. 251.
229. Ger. Offen. 2,044,461 (Mar. 23, 1972), M. S. Furman.
230. U.S. Pat. 3,987,100 (Oct. 19, 1976), W. J. Barnette, D. L. Schmitt, and J. O. White (to E. I. du Pont de Nemours & Co., Inc.).
231. U.S. Pat. 3,530, 185 (Sept. 22, 1970), K. Pugi (to E. I. du Pont de Nemours & Co., Inc.).

232. K. Tanaka, *Chem. Technol.* **4**(9), 555 (1974).
233. A. Castellan, J. C. J. Bart, and S. Cavallaro, *Catal. Today* **9**(3), 237–254 (1991).
234. A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.* **38**(21), 3729–3733 (1973).
235. U.S. Pat. 3,231,608 (Jan. 25, 1966), J. Kollar (to Gulf Research and Development Co.).
236. U.S. Pat. 4,032,569 (June 28, 1977), A. Onopchenko and J. G. D. Schulz (to Gulf Research and Development Co.).
237. A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.* **38**, 3729 (1973).
238. U.S. Pat. 4,263,453 (Dec. 10, 1979), J. G. D. Schulz and A. Onopchenko (to Gulf Research and Development Co.).
239. H. S. Bryant and co-workers, *Chem. Eng. Prog.* **67**(9), 69 (1971).
240. W. H. Starnes, Jr., *J. Org. Chem.* **31**, 1436 (1966).
241. J. March, *Advanced Organic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1985, p. 244.
242. G. Kohnstam and D. L. H. Williams, in Saul Patai, ed., *The Chemistry of Carboxylic Acids and Esters*, Wiley-Interscience, New York, 1969, Chapt. 16, p. 782.
243. I. M. Borisov, Yu. S. Zimin, and V. S. Martem'yanov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **34**(10), 46–49 (1992).
244. W. Partenheimer and J. A. Kaduk, *Stud. Surf. Sci. Catal.* **66**, 613–621 (1991).
245. Jpn. Kokai Tokkyo Koho JP 03 184,931 (Aug. 12, 1991), T. Maki, T. Masuyama, and T. Yokoyama (to Mitsubishi Kasei Corp.).
246. H. Buenger, *Compend.-Dtsch. Ges. Mineraloelwiss. Kohlechem.* **78**–**79**(1), 417–436 (1978).
247. D. E. Van Sickle, *Ind. Eng. Chem. Res.* **27**(3), 440–447 (1988).
248. P. Raghavendrachar and S. Ramachandran, *Ind. Eng. Chem. Res.* **31**(2), 453–462 (1992).
249. U.S. Pat. 2,833,816 (May 6, 1958), A. Saffer and R. S. Barker (to Mid-Century Corp.).
250. D. A. S. Ravens, *Trans. Fr. Soc.* **55**, 1768 (1959).
251. Brit. Pat. 1,063,451 (Mar. 30, 1967), W. J. Zimmerschied, D. E. Hanneman, and C. Serres, Jr. (to Standard Oil, Indiana).
252. Y. Ichikawa and Y. Takeuchi, *Hydrocarbon Process.* **51**(11), 103 (1972).
253. Jpn. Kokai 49-26240 (Mar. 8, 1974), M. Shigeyasu and co-workers (to Maruzen Oil).
254. M. Shigeyasu and T. Kitamura, *Shokubai* **20**(3), 155 (1978).
255. Jpn. Kokai 53 112,830 (Oct. 2, 1978), T. Yamaji and co-workers (to Teijin KK).
256. Jpn. Kokai 76 127,034 (Nov. 5, 1976), K. Teranishi and co-workers (to Mitsui Petrochemical Industries, Ltd.).
257. U.S. Pat. 2,653,165 (Sept. 22, 1953), I. E. Levine (to California Research Corp.).
258. U.S. Pat. 2,772,305 (Nov. 27, 1956), I. E. Levine and W. G. Toland, Jr. (to California Research Corp.).
259. Brit. Pat. 809,730 (Mar. 4, 1959), (to Imhausen Werke GmbH).
260. Ger. Offen. 2,310,824 (July 25, 1974), S. Takeda and co-workers (to Teijin Hercules Chemical).
261. Brit. Pat. 1,313,083 (Sept. 6, 1971), T. Harada and co-workers (to Teijin Hercules Chemical).
262. *Chemical Product Synopsis*, Mannsville Chemical Products, New York, Nov. 1978.
263. *Terephthalic Acid and Dimethyl Terephthalate*, report no. 75-1, Chem. Systems, Inc., New York, July 1975.
264. *Terephthalic Acid and Dimethyl Terephthalate, Report 9,* private report from SRI International's Process Economics Program, Menlo Park, Calif., Feb. 1966, Sept. 1970, and Aug. 1976.
265. W. F. Brill, *Ind. Eng. Chem.* **52**(10), 837–840 (1960).
266. H. S. Bryant and co-workers, *Chem. Eng. Prog.* **67**(9), 69 (1971).
267. U.S. Pat. 2,853,514 (Sept. 23, 1958), W. F. Brill (to Olin Mathieson Chemical Corp.).
268. U.S. Pat. 3,036,122 (May 22, 1962), A. E. Ardis and co-workers (to Olin Mathieson Chemical Corp.).
269. Brit. Pat. 1,129,398 (Oct. 2, 1968), (to Mobil Chem. Co.).
270. J. D. Behun, *Prepr. Div. Pet. Chem., Am. Chem. Soc.* **19**, 698 (1974).
271. U.S. Pat. 3,850,981 (Nov. 26, 1974), J. C. Trebellas, H. H. Thigpen, and W. M. Mays (to Celanese Corp. of America).
272. Fr. Pat. 1,348,386 (Aug. 10, 1962), B. Thompson and S. D. Neely (to Eastman Kodak Co.).
273. Jpn. Kokai 53 034,739 (Mar. 31, 1978), H. Torigata, M. Suematsu, and K. Nakaoka (to Toray Inds., Inc.).
274. K. Nakaoka and co-workers, *Ind. Eng. Chem. Prod. Res. Dev.* **12**, 150 (1973).
275. U.S. Pat. 3,215,733 (Nov. 2, 1975), A. F. MacLean, C. C. Hobbs, and A. L. Stautzenberger (to Celanese Corp. of America).
276. Fr. Pat. 1,549,026 (Dec. 6, 1968), E. R. Witt, K. Y. Zee-Cheng, and J. P. Cave (to Celanese Corp. of America).
277. G. A. Galstyan, V. A. Yakobi, and M. M. Dvortsevoi, *Neftekhimiya* **16**, 465 (1976).
278. O. Kobayashi and co-workers, *Nippon Kagaku Kaishi* **2**, 320 (1975).
279. J. S. Bawa and co-workers, *Proc. Natl. Symp. Catal.* **4**, 319–330 (1978).

280. U.S. Pat. 5,004,830 (Apr. 2, 1991), C. M. Park and W. P. Schammel (to Amoco Corp.).
281. G. N. Kogel and co-workers, *Zh. Org. Khim.* **24**(7), 1499–1504 (1988).
282. C. F. Hendriks, H. C. A. van Beek, and P. M. Heertjes, *Ind. Eng. Chem. Prod. Res. Dev.* **17**(3), 256–260 (1978).
283. U.S. Pat. 4,537,978 (Aug. 27, 1985), P. H. Kilner and co-workers (to Standard Oil, Indiana).
284. Jpn. Kokai Tokkyo Koho JP 61 27,942 (Feb. 7, 1986), M. Suematsu, S. Otoma, and K. Nakaoka (to Toray Industries, Inc.).
285. China Pat. CN 85,103,212 (Jan. 17, 1987), Z. Mi and co-workers (to Liming Chemical Institute).
286. Jpn. Kokai Tokkyo Koho JP 03 271,249 (Dec. 3, 1991), M. Yoshimizu, H. Takeuchi, and T. Kamei (to Nippon Steel Co., Ltd.).
287. Eur. Pat. Appl. EP 317,884 (May 31, 1989), F. Rohrscheid, G. Siegemund, and J. Lau (to Hoechst AG).
288. Jpn. Kokai 76 108,030 (Sept. 25, 1976), T. Aoyama and F. Ishihara (to Mitsubishi Gas Chemical Co., Inc.).
289. Jpn. Kokai Tokkyo Koho JP 61 24,541 (Feb. 3, 1986), S. Naito and K. Abe (to Mitsubishi Gas Chemical Co., Inc.).
290. H. V. Borgaonkar, S. R. Raverkar, and S. B. Chandalia, *Ind. Eng. Chem. Prod. Res. Dev.* **23**(3), 455–458 (1984).
291. R. A. Sheldon and N. De Heij, *Stud. Org. Chem. (Amsterdam)* **33**, 243–256 (1988).
292. K. Shimizu and co-workers, *Sekiyu Gakkaishi* **25**(1) 7–15 (1982).
293. Jpn. Kokai Tokkyo Koho JP 03,190,837 (Aug. 20, 1991), T. Yokoyama, N. Matsuyama, and T. Maki (to Mitsubishi Kasei Corp.).
294. N. Kitajima and co-workers, *Bull. Chem. Soc. Jpn.* **61**(3), 1035–1037 (1988).
295. Jpn. Kokai Tokkyo Koho 80 07,235 (Jan. 19, 1980), H. Imamura and K. Onisawa (to Agency of Industrial Sciences and Technology; Sanko Chemical Industry Co., Ltd.).
296. J. Imamura, *Yuki Gosei Kagaku Kyokaishi* **37**(8), 667–677 (1979).
297. N. N. Basaeva and co-workers, *Osnovn. Org. Sint. Neftekhim.* **6**, 11–16 (1976).
298. A. Onopchenko, J. G. D. Schultz and R. Seekircher, *J. Org. Chem.* **37**(9), 1414–1417 (1972).
299. W. W. Kaeding, *Hydrocarbon Process.* **43**(11), 173 (1964).
300. U.S. Pat. 2,727,926 (Dec. 20, 1955), W. W. Kaeding, R. O. Lindblom, and R. G. Temple (to The Dow Chemical Co.).
301. W. W. Kaeding and co-workers, *Ind. Eng. Chem. Proc. Des. Dev.* **4**(1), 97 (1965).
302. Belg. Pat 868,779 (July 5, 1978), (to Panclor Chemicals).
303. Ger. Offen 2,101,852 (July 29, 1971), L. L. Van Dierendonck, L. Laurentius, and J. P. H. Von den Hoff (to Stamicarbon NV).
304. L. Giuffre and co-workers, *Gazz. Chim. Ital.* **111** (5–6), 227–229 (1981).
305. Fr. Pat. 2,390,413 (Jan. 12, 1979), J. H. Atkinson (to ICI Chem. Ind. Ltd.).
306. Ger. Offen. 2,820,394 (Nov. 23, 1978), J. H. Atkinson (to Imperial Chemical Industries, Ltd.).
307. Ger. Offen. 2,844,195 (Oct. 11, 1978), A. P. Gelbein and A. M. Khonsari (to Lummus Co.).
308. A. P. Gelbein and A. S. Nislick, *Hydrocarbon Process.* **57**(11), 125–128 (1978).
309. M. Stolcova and co-workers, *J. Catal.* **101**(1), 153–161, (1986).
310. M. Hronec and co-workers, *Appl. Catal.* **69**(2), 201–204 (1991).
311. Jpn. Kokai Tokkyo Koho JP 63 27,473 (Feb. 5, 1988), M. Matsuno, K. Yoshiga, and K. Nakamura (to Mitsui Petrochemical Industries, Ltd.).
312. Jpn. Kokai Tokkyo Koho JP 60 84,235 (May 13, 1985), (to Mitsui Petrochemical Industries, Ltd.).
313. Jpn. Kokai Tokkyo Koho JP 60 89,440 (May 20, 1985), (to Mitsui Petrochemical Industries, Ltd.).
314. U.S. Pat. 4,503,262 (Mar. 5, 1985), B. F. Gupton and E. D. Little (to Virginia Chemicals, Inc.).
315. A. Tomita, *Numazu Kogyo Koto Semmon Gakko Kenkyu Hokoku* **13**, 49–59 (1978).
316. Kh. E. Kharlampidi and co-workers, *Khim. Tekhnol. Pererab. Nefti Gaza*, 10–13 (1985).
317. U.S. Pat. 3,459,810 (Aug. 5, 1969), C. Y. Choo and R. L. Golden (to Halcon International).
318. Neth. Pat. Appl. 75 13,860 (Mar. 31, 1976), (to Halcon International).
319. *World Petrochemicals Program, Aromatics and Derivatives 1992,* Vol. 5, private report from SRI International, Menlo Park, Calif., Jan. 1992, pp. UNIT-122 to UNIT-132.

General References

320. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1957.
321. F. R. Mayo, *Acc. Chem. Res.* **1**(7), 193–201 (1968).

322. S. W. Benson and P. S. Nangia, *Acc. Chem. Res.* **12**(7), 223–228 (1979).
323. S. W. Benson, *Thermochemical Kinetics*, 2nd ed., John Wiley & Sons, Inc., New York, 1976.
324. R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, Inc., New York, 1981.
325. R. W. Walker, *Sci. Prog. (Oxford)* **74**(294, Pt. 2), 163–187 (1990).
326. J. E. Lyons, in B. E. Leach, ed., *Applied Industrial Catalysis*, Vol. **3**, Academic Press, Inc., Orlando, Fla., 1984, Chapt. 6, 131–214.

CHARLES C. HOBBS
Consultant, sponsored by Hoechst Celanese Corporation

Related Articles

Combustion science and technology; Hydrocarbons