

Some Unresolved Problems in Oxidation and Combustion

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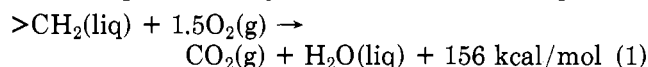
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If it is meaningful to single out one category of chemical reactions as having a unique importance on our planet, that designation would have to go to the reactions included under the heading oxidation. Oxidation reactions became dominant in our evolutionary history with the photochemical transformation of the earth's atmosphere from a reducing to an oxidizing environment. Following the formation of oceans and the production of organic molecules it is surmised that photosynthetic processes (reduction) became of dominant importance in the earliest forms of vegetable and cellular life.

Today oxidation is the major reaction utilized to produce energy for societal and industrial purposes. Oxidative combustion drives our automobiles, airplanes, and power plants. Biological oxidation in the cell provides the energy to fuel the multitude of chemical processes going on in plant and animal organisms. Natural oxidative processes in the atmosphere and oceans regularly remove the myriad mountains of pollutants released to them by man and animals. In the chemical industry today it is estimated that more than half of all production involves, at one point or another, oxidative steps. Thus it is not surprising to note that since at least the discovery of fire, the mechanism and control of oxidation have attracted the attention of scientists, engineers, and politicians.

The overall process of oxidation of a typical fossil fuel can be represented by the thermochemical equation:



The overall reaction is enormously exothermic, liberating about 156 kcal/mol of $>\text{CH}_2$ groups (11 kcal/g of $>\text{CH}_2$). If allowed to proceed adiabatically to form gases from a stoichiometric mixture, the final temperature would be about 4500 K.¹ Very few chemical reactions can boast such a high energy density. One consequence of such exothermic reactions is the related

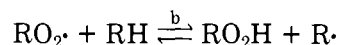
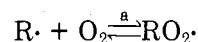
phenomena (and hazards) of flames and explosions.

In the conversion of chemical energy in a heat engine to mechanical or electrical energy, one is limited by the Carnot efficiency of the heat engine. Today's power plants run at about 35% Carnot efficiency, limited by the temperatures at which gas turbines can operate. In chemical synthesis or a biochemical process, one is not interested in the overall reaction represented by eq 1 but in the multitude of intermediate stages each involving lesser amounts of energy releases at ambient temperatures. And in current efforts to master photosynthesis one is concerned with the reverse process to eq 1, the conversion of heat or light energy into high energy chemicals via water and carbon dioxide.

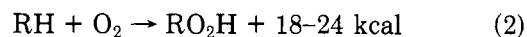
Modern chemical investigations of the molecular mechanism of oxidation started in the early part of this century and reached a peak during the middle 1960s. The current renewed interest in energy problems, air pollution, and stratospheric chemistry has sparked a revival of activity in the subject of oxidation. In our own laboratories we have recently started reexploring some of the problems which have remained unresolved.

Free-Radical Mechanisms

At temperatures below 200 °C, it is generally agreed that the oxidation of "easily oxidized" organic compounds involves a free-radical chain² (eq 2). Easily chain cycle:



net reaction:



oxidized species are those with relatively weak C-H bonds. Aldehydes (C-H = 87 kcal), allylic or benzylic C-H (85 kcal), and compounds with tertiary C-H (92 kcal) bonds seem to fit this category. The chain cycle

(1) Normal flame temperatures such as produced from gas + air are appreciably lower than this (2000-2400 K) because of the diluent effect of the inert N₂ present in air.

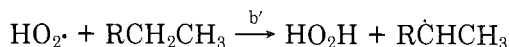
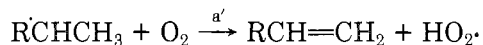
(2) For general information on this and related points the reader is referred to V. Ya. Shtern, "The Gas Phase Oxidation of Hydrocarbons" (translated by B. P. Mullin), Butterworths, 1962, and to the discussions in ref 4 below.

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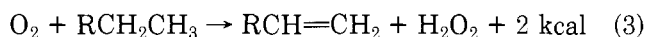
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is very slow, step b appearing to require a fairly high activation energy.³

Above 250 °C, the mechanism appears to change to:⁴ chain cycle:

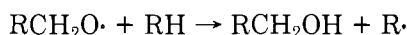
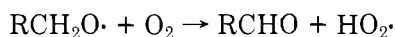
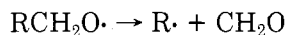


net reaction:



Whereas the low-temperature mechanism is reasonably exothermic and hence potentially autocatalytic, the high-temperature mechanism is nearly thermo-neutral and has a relatively small free energy change ($\Delta G^\circ_{300} \sim -4$ kcal/mol).

In both of these temperature regions, the systems are complicated by secondary reactions of the products which are usually more reactive than the starting materials.² The hydroperoxides undergo radical-induced decomposition even at 100 °C and are unstable to unimolecular bond fission above 150 °C because of the relative weak RO-OH bond ($DH^\circ \sim 43$ kcal). By way of contrast, H_2O_2 is much more stable than RO_2H and does not decompose significantly in the gas phase below 450 °C; $DH^\circ(\text{HO}-\text{OH}) = 51$ kcal/mol. The induced decomposition of the RO_2H produces alkoxy radicals, $\text{RO}\cdot$, which can produce aldehydes and alcohols by subsequent radical reactions.



All of these steps are relatively fast at 300 K or above.

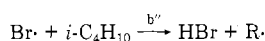
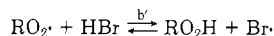
One of the perplexing problems which appear to have been solved 15 years ago^{5,6} was the reason for the turnover in mechanism with temperature. Reaction a in the low-temperature mechanism is reversible, the R-O₂· bond being only about 28 kcal/mol. A steady-state treatment for the rate of this chain reaction gives eq 4 and 5. Here $K_a = k_a/k_{-a}$ is the equilibrium

$$\frac{d(\text{RO}_2\text{H})}{dt} = \frac{k_b k_a (\text{R}\cdot)(\text{O}_2)(\text{RH})}{k_{-a} + k_b(\text{RH})} \xrightarrow{T < 100^\circ\text{C}} k_a (\text{R}\cdot)(\text{O}_2) \quad (4)$$

$$\frac{d[\text{RO}_2\text{H}]}{dt} = \xrightarrow{T > 160^\circ\text{C}} K_a K_b (\text{R}\cdot)(\text{O}_2)(\text{RH}) \quad (5)$$

constant for step a.

(3) A commercial process for the production of *t*-BuOOH involves the oxidation of isobutane by O_2 at $T < 100$ °C. The spontaneous oxidation has a half-life of ~ 2 days in liquid or gas phase at 100 °C.¹⁰ For the commercial production HBr is used as a catalyst (1–2 mol %). It replaces the slow step b by the much faster steps:



See: F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, 41, 2595 (1949); U.S. Patent 2 403 771 (July 1946); F. F. Rust et al., *Ind. Eng. Chem.*, 41, 2612, 2597, 2609 (1949). The catalyzed chain is about 1000-fold faster than the spontaneous reaction. RO_2H is a major product below 100 °C only for C-H bond weaker than 90 kcal. For tertiary and secondary compounds where the half-life can be days, peroxides and alcohols are produced.

(4) S. W. Benson, Symposium on the Mechanisms of Pyrolysis, Oxidation and Burning of Organic Materials, *NBS Spec. Publ.*, 357, 121 (1972). See also J. H. Knox, *Comb. Flame*, 9, 297 (1965). Knox appears to have been the first to call attention to the fact that $\text{HO}_2 + \text{RH}$ (step b') could not possibly account for the observed rates of oxidation of C_2H_6 and C_3H_8 .

(5) S. W. Benson, *J. Am. Chem. Soc.*, 87, 972 (1965).

(6) S. W. Benson, *Adv. Chem. Ser.*, No. 76 II, 143 (1968).

Below 100 °C where eq 4 describes the rate, step a is essentially irreversible and rate determining for the chain cycle. k_a has been measured in gas-phase reactions^{7,8} for CH_3 and larger radicals, has no activation energy, and is about $10^{9.3} \text{ M}^{-1} \text{ s}^{-1}$, a value typical of radical recombinations. With increasing temperature, step a becomes reversible and the very slow step b becomes rate determining with a chain rate described by eq 5. Since step a is exothermic by about 28 kcal, K_a has a negative temperature coefficient of this amount. This is much larger than the activation energy of step b (~ 14 kcal), so that the chain activation energy which is equal to $(\Delta H_a + E_b)$ is negative (~ -14 kcal). This explains the decreasing rate of peroxide formation at temperatures in excess of 300 °C and the turnover to the high-temperature mechanism.

The rate of formation of olefins is given by eq 6.

$$\frac{d(\text{olefin})}{dt} = k_a' (\text{R}\cdot)(\text{O}_2) \quad (6)$$

Above 200 °C for most saturated hydrocarbons, this rate (eq 6) exceeds that given by eq 5. Thus the mechanism turns over from RO_2H production to olefin production above 200 °C.

A large amount of experimental work has been done on the kinetics of oxidation of liquid hydrocarbons at $T \leq 120$ °C.⁹ The oxidations of even the most weakly bound C-H bonds in alkanes turn out to be very slow, and even though the chain is properly predicted by eq 4, the activation energy for step b lies in the range of 14 ± 2 kcal¹⁰ for tertiary C-H bonds. This unexpectedly high activation energy implies an even higher activation energy for hydrogen abstraction from secondary CH_2 or primary CH_3 groups, one consequence of which is that it is not plausible to expect HO_2 to be the propagating radical in high-temperature oxidation as shown in mechanism 3.⁴ This is certainly the case in C_2H_6 oxidation at 600 K and is very likely the case in C_3H_8 and the other alkane oxidations as well. How then can H_2O_2 be the major product of high-temperature oxidations if step b' is too slow to produce it? We shall return to this point later.

The Negative Temperature Coefficient

Oxidation has been notorious for its idiosyncrasies—what we might term phenomena. One of these we have already briefly mentioned is that of negative temperature coefficient. Above 300 °C initial rates of oxidation of hydrocarbons begin to decrease. If we pass an equimolar mixture of, for example, *n*-pentane and O_2 gases at 1 atm total pressure through a hot glass tube (residence time of 5 to 20 s) we find slow rates, increasing above 250 °C and reaching a maxima about 350 °C where they decrease to nearly zero at about 380 °C.¹¹ In the region between 450 and 500 °C the rate picks up again and explosion (“hot ignition”) can occur. A remarkable phenomenon known as “cool flames” characterizes this behavior in static systems. A 1:1 mixture of most hydrocarbons and O_2

(7) D. A. Parkes, *Int. J. Chem. Kin.*, 9, 451 (1977).

(8) N. Basco, D. G. L. James, and F. C. James, *Int. J. Chem. Kin.*, 4, 129 (1972).

(9) *Adv. Chem. Ser.*, No. 76 (I, II, and III) (1968) (Proceedings of the International Oxidation Symposium).

(10) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, ref 2, Vol. II, p 40.

(11) K. C. Salooja, *Comb. Flame*, 6, 275 (1962); 8, 311 (1964); 9, 219 (1965); Y. H. Chung and S. Sandler, *ibid.*, 6, 295 (1962).

when placed in a glass vessel at 300 °C and 1 atm pressure may not react measurably for periods of time of anywhere from 10 to 800 s. These induction periods vary with the nature of the hydrocarbon and are sensitive to the walls of the vessel and its geometry.² Reaction is then manifested by a blue flame which flashes through the vessel and disappears. After an interval which can be as long as the initial induction period another flame may occur. Up to 11 such repeating flames have been reported for some systems,¹² and it is found that from 5 to 10% reaction may occur during each recurrence. From direct measurements it is now known that these cool flames are actually hot, temperature increases of up to 200 °C having been observed.

These cool flames represent another instance of the negative temperature coefficient of oxidation. They must correspond to an exothermic reaction which turns itself off when it gets too hot! The induction periods imply the buildup of some catalytic material in the initial stages of the reaction which catalyzes the exothermic reaction. It is now generally agreed that hydroperoxides RO₂H are the autocatalytic precursors of the cool flames and possibly all lower temperature oxidations. Direct measurements in the flow experiments¹¹ have shown that as little as 0.1 mol % of hydroperoxide can eliminate the induction periods and diminish the negative temperature effect. We have already seen that the low-temperature mechanism produces hydroperoxides exothermally as the first product and that this production decreases with increasing temperature, being replaced by the nearly thermoneutral olefin formation. If the vessel geometry permits rapid heat conduction, the cool flames can be inhibited. If on the contrary heat flow from the mixture is too slow, the cool flame can accelerate to a hot ignition and violent explosion.

Thus the general outlines of oxidation seem well characterized. They include a very slow exothermic production of hydroperoxides during an induction period. If the temperature is high enough, secondary decomposition of the hydroperoxides¹³ provides a rapid source of free radicals which both replenishes the RO₂H and accelerates the reaction by raising the temperature. If the latter exceeds 350–450 °C the RO₂H production is decreased and is replaced by H₂O₂ production. The latter, H₂O₂, can play the same role as RO₂H in providing a secondary radical source, only above 480 °C.

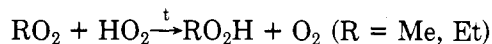
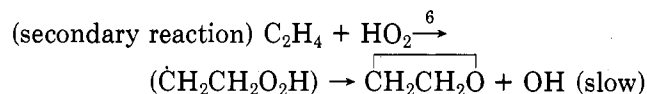
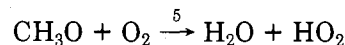
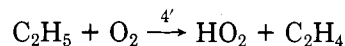
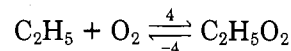
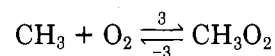
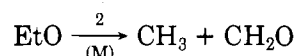
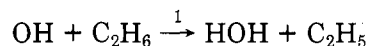
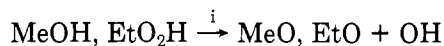
Independent measurements of the rate of decomposition of RO₂H have verified their short half-lives above 300 °C¹⁴ and their ability to thus act as degenerate chain branchers, as originally proposed by Semenov.¹⁵ This fission of RO₂H into RO + OH provides two active free radicals from what would at temperatures below 150 °C be considered a stable product, hence their role as chain branchers at higher temperatures.

We are still uncertain of the mechanism whereby these hydroperoxides are formed and the nature of the

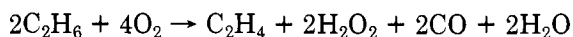
reactions that occur during the induction period. We can offer some reasonable speculation about the former, using the case of C₂H₆ oxidation as an example.

Knox¹⁶ has studied the oxidation of C₂H₆ at 600 K and shown that C₂H₄ + H₂O + H₂O₂ are the major products of the early stages. The reaction starts out slowly, accelerates to a maximum rate, and then slowly declines as reactants are consumed. While we do not know how the reaction starts, let us see how it might continue once a small, critical concentration of EtO₂H has been formed. This EtO₂H would now act as an initiator, providing free radicals to permit the chain to proceed (Scheme I).

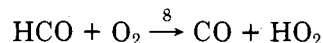
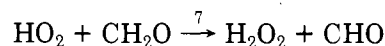
Scheme I



A steady-state treatment of this system will show that, once formed, EtO₂H will maintain HO at a level sufficiently high to yield the observed maximum rate. Since the termination step t replenishes the EtO₂H lost in the initiation, once the critical concentration is attained, (EtO₂H)/(C₂H₆) ~ 10⁻³, the rate is likewise maintained.¹⁷ If one adds up all the steps in the above chain cycle so as to use up all the radicals then one finds an overall stoichiometry of (neglecting the secondary ethylene oxide production):



in approximate agreement with the observed data. To attain this stoichiometry one needs to add the fast secondary reactions:



In the above C₂H₆ stoichiometry two aldehyde molecules are produced and consumed. They appear to play an essential role in all oxidations by providing a relatively easily abstractable H atom from the RCO-H group. The activation energy for abstraction of the aldehydic C-H by HO₂ or RO₂ is about 8 kcal.¹⁸

(12) L. R. Sochet, J. P. Sawyersyn, and M. Lucquin, ref 2, p 111; J. C. Dechoux, J. L. Flament, and M. Lucquin, *Comb. Flame*, 17, 205 (1971).

(13) S. W. Benson, *J. Chem. Phys.*, 40, 1007 (1964); R. Hiatt and K. C. Irwin, *J. Org. Chem.*, 33, 1416 (1968).

(14) S. W. Benson and G. N. Spokes, *J. Phys. Chem.*, 72, 1182 (1968).

(15) N. N. Semenov, "Photochemistry and Reaction Kinetics", P. G. Ashmore and F. S. Dainton, Ed., The University Press, Cambridge, England, 1967, p 229.

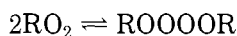
(16) J. H. Knox, *Comb. Flame*, 9, 297 (1965).

(17) S. W. Benson and P. S. Nangia, paper in preparation.

(18) R. R. Baldwin, D. H. Langford, and R. W. Walker, *Trans. Faraday Soc.*, 65, 729, 806(1969).

Thermochemistry

The secondary reactions involved in oxidation introduce so many complexities into the overall scheme that it becomes very difficult to identify the major pathways without some guidance from thermochemistry. In 1947, Foner and Hudson¹⁹ made measurements of the appearance potential of HO₂⁺ ions from both HO₂ radicals and H₂O₂ molecules. This allowed them to obtain the bond dissociation energy of HO₂ as 47 ± 2 kcal, from which one can deduce $DH^\circ(\text{HO}_2\text{-H}) = 89.6 \pm 2$ kcal. More recent measurements have supported this value,²⁰ but still more recent ones²¹ revised $D(\text{H-O}_2)$ to 52 ± 2 kcal/mol, making $DH^\circ(\text{HO}_2\text{-H}) = 84.5 \pm 2$ kcal. The senior author some time ago²² suggested that $DH^\circ(\text{HO}_2\text{-H}) = DH^\circ(\text{RO}_2\text{-H})$, where R = alkyl. Since then chemical evidence²³ has favored $DH^\circ(\text{RO}_2\text{-H}) = 89.6 \pm 2$ kcal, which we shall continue to adopt here. This gives $DH^\circ(\text{R-O}_2) = 28.5 \pm 2$ kcal. Further measurements in solution on the reversible equilibria:

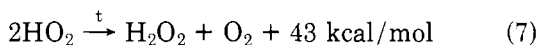


have yielded $\Delta H^\circ_r = -8.5 \pm 1$ kcal ($T \sim -130$ °C). Using these values corrected to gas phase have then permitted, with the use of group additivity rules,²⁴ the estimation of bond dissociation energies and heats of formation of molecules of the type RO_nR' and the related radicals RO_n.^{22,23} It is from estimates such as these and related thermochemical data on stable molecules and radicals that we have been able to make some of the preceding analyses. We shall make use of them subsequently.

Because of the major role played by HO₂ and RO₂ radicals in almost all oxidative processes, the task of fixing their thermochemistry with greater accuracy than the foregoing is of considerable interest, and we are currently engaged in attempting to measure them with the technique known as "the very low pressure reactor" (VLPR).²⁵ If successful, the same measurements will make possible direct measurements of the rates of self-reactions of RO₂ radicals.

Self-Reactions of RO₂

One of the most puzzling features of the free-radical mechanism has been the self-reactions of RO₂ radicals. Much work has been done in liquid phase on the tertiary alkyl peroxy radicals *t*-RO₂, the most stable of this class.^{26,27} The least stable (or most reactive) have been the HO₂ radicals for which there seems to be almost universal agreement that one in every 100 gas-phase collisions leads to termination.²⁸



$$k_t \sim 2 \times 10^9 \text{ L/(mol}\cdot\text{s)} \quad (E_t = 0)$$

(19) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **23**, 1364 (1955).

(20) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962).

(21) D. D. Wagman, *NBS Spec. Publ.*, **513** (1978).

(22) S. W. Benson, *J. Chem. Phys.*, **33**, 306 (1960); *J. Am. Chem. Soc.*, **86**, 5055 (1964); S. W. Benson and R. Shaw, "Organic Peroxides", D. Swern, Ed., Vol. I, Wiley-Interscience, New York, 1970, p 105.

(23) P. S. Nangia and S. W. Benson, paper submitted for publication.

(24) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

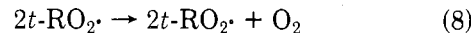
(25) M. B. Vayjooee, A. J. Colussi, and S. W. Benson, *J. Am. Chem. Soc.*, **100**, 3214 (1978); *Int. J. Chem. Kin.*, **11**, 147 (1979).

(26) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **47**, 3797 (1969).

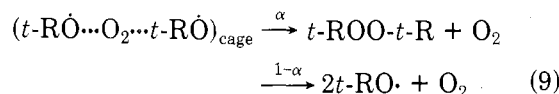
(27) K. U. Ingold, *Acc. Chem. Res.*, **2**, 1 (1969).

The reaction is exothermic enough to produce electronically excited O₂ (¹Δ or ¹Σ), and the literature is rife with observations of chemiluminescence from oxidative systems possibly arising from this or related reactions.

For the tertiary radicals *t*-RO₂, there is equally good agreement that the nearly thermoneutral reaction, eq 8, is very slow with a rate constant of about 10³ L/

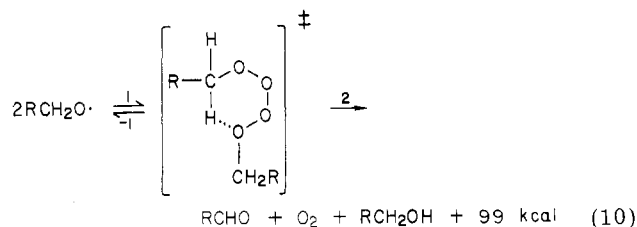


(mol·s) in solution at 300 K and an activation energy of about 8 kcal.^{23,26} In solution the two *t*-RO₂ radicals are generated in a solvent cage in close proximity (along with the O₂), and there is a probability, α, that they recombine before diffusing apart (eq 9). α decreases



with increasing temperature, becoming <0.1 at 100 °C for *t*-RO₂ ≡ *t*-Bu.¹⁰

However, when we consider peroxy radicals with α H atoms such as CH₃O₂, RCH₂O₂, and R₂CHO₂, the evidence points to rapid termination processes in solution, with k_t going from about 10⁹ (for CH₃O₂) to 10^{8.5} (*i*-PrO₂) in units of L/(mol·s).²⁷ The mechanism for these rapid terminations which appears to lead mainly to disproportionation products RCH₂OH + RCHO + O₂ has been suggested by Russell²⁹ as:



The reaction is sufficiently exothermic to produce electronically or vibrationally excited products and has been proposed as the source of (¹Δ)O₂ or electrically excited aldehydes seen in oxidation reactions.^{30,31} The concerted mechanism suggested by eq 10 has always presented a puzzle since it would require an activation energy for step 2 of $E_2 \leq 2$ kcal/mol,⁴ a unique and unreasonably low value for such concerted processes. Recent gas-phase measurements on the self-termination of CH₃O₂ radicals^{32,33} have given $k_t(\text{MeO}_2) = 3 \times 10^8$ L/(mol·s), suggesting that there is no significant effect of solvent on such reactions.

Some time ago the senior author proposed, as an escape from the above mechanistic dilemma, a more complex path³⁴ involving the production of the Criegee zwitterion:

(28) (a) C. J. Hochanadel, J. A. Ghormley, and P. J. Ogren, *J. Chem. Phys.*, **56**, 4426 (1972); (b) S. N. Foner and R. L. Hudson, *Adv. Chem. Ser.*, **No. 36**, 34 (1962); (c) T. T. Paukert and H. S. Johnston, *J. Chem. Phys.*, **56**, 2824 (1972); (d) J. Troe, *Ber. Bunsenges. Phys. Chem.*, **73**, 946 (1969).

(29) G. A. Russell, *J. Am. Chem. Soc.*, **89**, 4799 (1967).

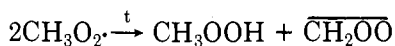
(30) D. Mendenhall, private communication.

(31) L. R. Sochet, J. P. Sawerysyn and M. Lucquin, ref 2, p 111.

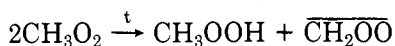
(32) D. A. Parkes, "Proceedings of the 15th Symposium on Combustion", The Combustion Institute, Pittsburgh, 1975.

(33) C. J. Hochanadel, J. A. Ghormley, J. W. Boyle, and P. J. Ogren, *J. Phys. Chem.*, **81**, 3 (1977).

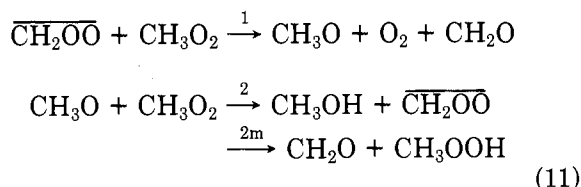
(34) Reference 6, p 151.



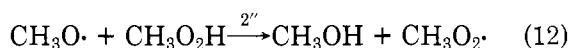
Unfortunately for such a suggestion it appeared to go to the wrong products. However we have recently revived it, using the more complex process:



chain cycle



If steps 1 and 2 are faster than step t, then they constitute a chain mechanism for the termination of CH_3O_2 with the net chain production of alcohol + O_2 + aldehyde. From various kinetic and thermochemical data³⁵ we have estimated that reaction t is about 28 kcal/mol exothermic, reaction 1 is about 45 kcal/mol exothermic, reaction 2 is 43 kcal/mol exothermic, and reaction 2' which would terminate the chain is about 67 kcal/mol exothermic. If hydroperoxide accumulated, then a competing reaction to 2 and 2' would become the fast, nonterminating:



The sequence t, 1, and 2'' would now constitute a more complex chain with the same products and a minor production of steady-state ROOH. To account for the overall rates we could set $k_t \leq 10^{9-2/\theta}$ L/(mol·s) ($\theta = 2.303RT$ in kcal/mol), a not unreasonable value. The A factors could decrease, the activation energy could increase slightly, or the effective chain length could decrease (or some combination of all three) as we went from $\text{CH}_3\text{O}_2\cdot$ to $\text{RCH}_2\text{O}_2\cdot$ to $\text{R}_2\text{CHO}_2\cdot$.

This more complex mechanism has a number of virtues in that it seems kinetically and structurally reasonable, gives the proper products, and accounts for the small amounts of hydroperoxides that have been observed in such termination systems. Since the Criegee intermediate $\text{RR}'\text{COO}$ is needed to account for ozone chemistry,⁹ its possible role in oxidation reaction presents a challenging problem for further exploration. It may become a very important intermediate in atmospheric chemistry (stratosphere and troposphere), and a study of its reactions with other active species would be of great interest.

Initiation Reactions

Perhaps the most elusive feature of the oxidation reaction has been the initiation reaction, the step by which the reaction gets started. Below 450 °C there is usually no homogeneous, radical reaction which can account for the initiation of the oxidative chain cycle. Above 450 °C reactions such as eq 13 begin to have fast

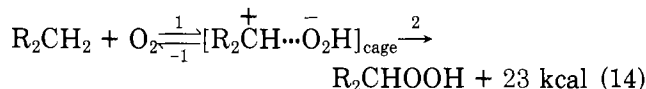


enough rates despite their endothermicity (40–50 kcal/mol) to provide a homogeneous radical source. At room temperature, at 150 °C and even at 300 °C,

(35) P. S. Nangia and S. W. Benson, paper in preparation.

however, such reactions are negligibly slow.³⁶ We must recall that at these lower temperatures the very variable induction periods which precede reaction are themselves very sensitive to small amounts of impurities (particularly transition metals in liquid phase) and to the nature of surfaces in gas reactions.

This sensitive behavior has suggested to us the possibility that initiation may occur via ionic processes rather than radical processes. The recent accumulation of data on the thermochemistry of ions^{37,38} makes it possible to explain this proposal quantitatively. Let us consider the reaction 14 involving hydride ion transfer from a secondary position. We can represent ΔH°_1 , the



enthalpy change in step 1, which will be rate determining, as in eq 15. The first term on the right-hand

$$\Delta H^\circ_1 \text{ (kcal/mol)} = 48 + \text{IP}(\text{R}_2\text{CH}\cdot) - \text{EA}(\text{HO}_2\cdot) - \epsilon^2/r_i - \Delta H^\circ_{\text{solv}} \quad (15)$$

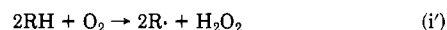
side of eq 15, 48 kcal, represents the difference in bond strengths of $\text{R}_2\text{CH-H}$ and H-O_2 .^{23,24} The second term is the ionization potential of the R_2CH radical (7.1 ~7.5 eV or about 168 kcal),³⁸ while the third term represents the electron affinity of the HO_2 radical which we have estimated at about 2.0 eV (46 kcal).³⁹ The fourth term, ϵ^2/r_i , represents E_c , the coulombic energy of the intimate ion pair, r_i being the distance between charge centers. If we use a reasonable value, $r_i = 2.75 \text{ \AA}$,⁴⁰ $E_c = 120 \text{ kcal/mol}$, so that these three ionic contributions IP, EA, and E_c nearly cancel, suggesting that the ionic pathway in the gas phase and the free-radical pathway might have nearly the same energy!

For the last term, $\Delta H^\circ_{\text{solv}}$, which would be of importance mainly in solution,⁴¹ we can estimate the enthalpy of solvation from a formula derived by Kirkwood for a point dipole μ in a spherical solvent cage of radius r_c ⁴² and dielectric constant D :

$$\Delta H_{\text{solv}} \sim -1.1 \frac{\mu^2}{r_c^3} \left(\frac{D-1}{2D+1} \right) \quad (16)$$

For the intimate ion pair this becomes

(36) Some authors (see ref 2) have proposed the termolecular reaction



to account for the initiation in liquid phase oxidation reactions. However, reaction i' is even more endothermic than the bimolecular reaction i given. From known data $\Delta H^\circ_{i'} = 48.5 \text{ kcal}$ for $\text{RH} = i\text{-C}_6\text{H}_{10}$, compared to $\Delta H^\circ_i = 45 \text{ kcal}$. Moreover, we can estimate (ref 24) the Arrhenius A factor for the termolecular reaction as $A_{i'} \leq 10^9 \text{ (L}^2\text{/mol}^2\text{-s)}$ compared to $A_i \sim 10^{10.5} \text{ (L/mol-s)}$. Thus the rate of (i') is orders of magnitude too small to be of significance compared to even the slow reaction i.

(37) P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).

(38) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, "Energetics of Gaseous Ions", *J. Phys. Chem. Ref. Data*, **6**, Suppl. 1 (1977).

(39) P. S. Nangia and S. W. Benson, calculations based on Born-Haber cycles involving pK of H_2O_2 in dilute aqueous solution. Our value is considerably lower than the 4.1 eV listed in ref 31 which we feel is in error.

(40) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963). Note that we have omitted a Born repulsion term in eq 15. This is based on the experience that the mutually induced polarization energy of the ions which we have also omitted very nearly cancels this term. Both are small (10% of the terms included).

(41) Gas-phase solvation by small, polar molecules can be appreciable (4–10 kcal).

(42) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

$$-\Delta H_{\text{solv}} \sim \frac{365 r_i^2}{r_c^3} \left(\frac{D-1}{2D+1} \right) \text{ kcal/mol}$$

$$\begin{aligned} (D=2) &\rightarrow 73r_i^2/r_c^3 \text{ kcal/mol} \\ (D=10) &\rightarrow 156r_i^2/r_c^3 \text{ kcal/mol} \end{aligned}$$

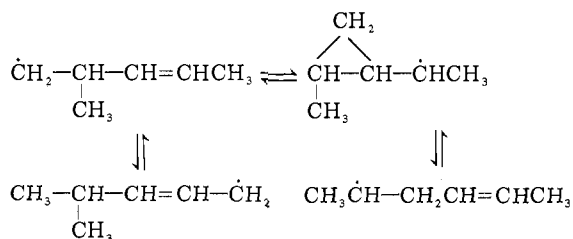
For $r_c = 4 \text{ \AA}$ these values become 8.6 ($D = 2$) and 18.5 ($D = 10$) kcal/mol, respectively, while for $r_c = 3.5 \text{ \AA}$ both these values increase by a further factor of about 1.5. For still higher dielectric constant solvents such as H_2O and alcohols, the numbers increase by only 15% above $D = 10$. Corrections to the idealized formula for extended dipole rather than a point dipole can increase these values by another 20–30%, so that the ΔH_{solv} term can range from about 12 to 35 kcal/mol, thereby lowering the effective endothermicity for step 1 from 36 to 13 kcal/mol. Weaker C–H bonds like tertiary or allylic could reduce these numbers by another 10–15 kcal due to the lower ionization potentials for the tertiary C–H radicals.⁴³

While these calculations are very crude, they are very convincing in suggesting that ion-pair pathways could provide the mechanisms for the induction periods and hydroperoxide buildup. Ionic or highly polar surfaces such as that found on silica or metal oxides could play the role of solvators in place of solvent. The phenomenon of spontaneous combustion may very well arise from such ionic pathways. The well-known phenomenon of spontaneous oxidation of n -alkyl ethers at room temperature could then be a consequence of a relatively weak bond, $DH^\circ(\text{C-H}) = 91 \text{ kcal}$, and a relatively high dielectric constant ($D = 4.3$).

Similar considerations to these, we have found, can account well for the low-temperature (-100°C) chemistry of ozone reactions with alcohols.³⁵ In these cases the stronger O–H bond formed in HO_3^- relative to HO_2^- reduces the activation energy by about 17 kcal. Also for O_3 the reaction is spin allowed.

Radical Isomerization Reactions

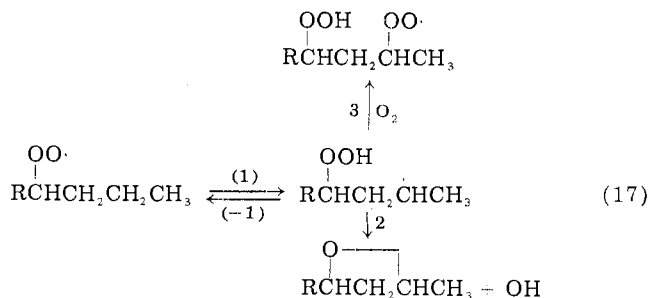
One of the important kinetic pathways available to larger free radicals is unimolecular isomerization. This is usually accomplished by internal H-atom metathesis or with unsaturated radicals by cyclization. We can illustrate these for hydrocarbon radicals:



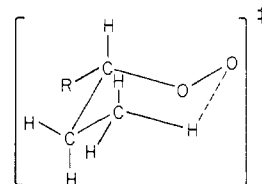
A recent review summarizes much of the observations on this subject.⁴⁴

(43) Note that reaction 1 as written involves a spin change. This suggests that the reaction may have a small activation energy in excess of its endothermicity, which would then make step 1 rather than step 2 rate determining. We can calculate with these formulas initiation rates which seem to account for the spontaneous rates observed on saturating hexadecane solutions with O_2 at 150°C .

Similar reactions occur for alkoxy and peroxy radicals, and they give rise to many of the diverse products seen in oxidation studies. It is now generally agreed that the cyclic oxides observed as products in hydrocarbon oxidation arise from such isomerization reactions.^{5,45} In the range $240\text{--}320^\circ\text{C}$ it is possible to obtain anywhere from 5 to 43% conversion of n -alkanes to cyclic oxides.⁴⁵ The mechanism of these reactions is given by eq 17. We have illustrated the case of γ -H



abstraction since it is kinetically the fastest, involving formation in the transition state of a strain-free six-membered ring. Abstraction from the α, β and other



positions can also occur, but their rates are expected to be less because of ring strain. Both reactions 2 and -1 will compete with external addition of O_2 to the free-radical site, and at low temperatures (100°C) this can dominate and give rise to disubstituted, oxygen-containing products. Thus in the case of 2,4-dimethylpentane at 117°C , one can obtain up to 95% yields of the 2,4-dihydroperoxy derivative $(\text{CH}_3)_2\text{C}(\text{OOH})\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}_2\text{H}$.⁴⁶

Despite the wealth of observations on such behavior there are almost no directly measured rate constants for such processes, so that experimental Arrhenius parameters are totally lacking.⁴⁷ Instead, all of the values to be found in the literature are estimated from models of transition states and related molecular reactions.²⁴ It would be a welcome change to be able to make some direct quantitative observations on these very important reactions. We are currently endeavoring to fill this void.

This research has been supported by grants from the Army Research Office, Durham, NC (Grant No. DAAG29-76-G-0195), and the National Science Foundation (Grant No. CHE-76-G-16787 A01).

(44) J. W. Wilt, "Free Radical Rearrangements", in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, Chapter 8.

(45) T. Berry, C. F. Cullis, M. Saeed, and D. L. Trimm, ref 2, p 86.

(46) F. F. Rust, *J. Am. Chem. Soc.*, **79**, 4000 (1957).

(47) Even the qualitative observations on product formation are open to some question since it is known that many products as well as radicals can undergo surface rearrangements on the walls of reaction vessels. See, for example, the discussion generated by the work of C. F. Cullis (ref 7, pp 111 and 117) involving the proposed unimolecular migration of CH_3 radicals in branched alkoxy and alkylperoxy radicals.