Oxidation of Organic Compounds II

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Oxidation of Organic Compounds

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Frank R. Mayo
General Chairman

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Oxidation of Organic Compounds

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Ozone Chemistry, Photo and
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Oxidations

Gas–Phase Oxidations

JOHN H. KNOX
Session Chairman

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Rate Constants in the Gas-Phase Oxidation of Alkanes and Alkyl Radicals

JOHN H. KNOX

The University of Edinburgh, Edinburgh, Scotland

Data on alkyl radical oxidation between 300° and 800°K. have been studied to establish which of the many elementary reactions proposed for systems containing alkyl radicals and oxygen remain valid when considered in a broad framework, and the rate constants of the most likely major reactions have been estimated. It now seems that olefin formation in autocatalytic oxidations at about 600°K. occurs largely by decomposition of peroxy radicals rather than by direct abstraction of H from an alkyl radical by oxygen. This unimolecular decomposition apparently competes with H abstraction by peroxy radicals and mutual reaction of peroxy radicals. The position regarding other peroxy radical isomerization and decomposition reactions remains obscured by the uncertain effects of reaction vessel surface in oxidations of higher alkanes at 500°–600°K.

The oxidation of hydrocarbons in the gas phase has been studied intensively for over 70 years, yet the mechanism of the process is still poorly understood. Free radicals are certainly involved, but the identity of the elementary steps and their rate constants are in many cases uncertain. The papers in this section were chosen to cover the oxidation of alkyl and other simple organic radicals over a wide range of conditions in order that areas of agreement and divergence of views could be exposed and in the hope that a self-consistent mechanism for gas phase oxidations might emerge.

Two quotations from recent reviews are particularly relevant to any discussion of oxidation mechanisms:

"It is as easy to derive a rate constant for a chemical reaction which does not occur as for one which does occur" (*41*).

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"If there are more than two free radical intermediates, the mechanism (of a reaction) cannot be deduced by a kinetic study based upon analysis of all products and reactants" (32)—the uncertainty principle of reaction mechanism.

Kineticists interested in oxidation have too often failed to appreciate the importance of the second statement and have claimed validity for mechanisms on the grounds that they explain the products and certain basic features of the over-all kinetics of the reactions: they have thus fallen into the trap described in the first quotation. There are indeed few reactions in oxidation about whose importance we can be certain, and even fewer whose rate constants can be stated with any conviction. Nevertheless, the papers presented here, along with other relevant information, allow one to make first some qualitative, and later some quantitative statements about the elementary reactions occurring in oxidation systems.

Probable Reactions in Gas-Phase Oxidations

When alkyl radicals are generated in oxygen, there are only a few primary reactions, but the radical products of these reactions evidently undergo many reactions. The elementary steps 0 to 11 are thought to include most of those which are plausible at temperatures between 25° and 600°C. We denote an unspecified radical by X, an alkyl radical by R, an olefin by A, a carbonyl compound by AO, and an oxygen-containing heterocyclic compound by $\overset{O}{\boxed{\quad\quad}}$. Primes on symbols denote species with fewer (usually one fewer) C atoms than the parent alkane or alkyl radical. Reaction 11 is the intramolecular abstraction of H from some point in the peroxy radical.

$$X + RH = R + XH \qquad (0)$$

$$R = R' + A' \qquad (1)$$

$$R + O_2 = ROO \qquad (2)(-2)$$

$$R + O_2 = A + HO_2 \qquad (3)$$

$$RO_2 + RO_2 = RO + RO + O_2 \qquad (4)$$

$$RO_2 + HO_2 = ROOH + O_2 \qquad (5)$$

$$HO_2 + HO_2 = HOOH + O_2 \qquad (5')$$

$$RO_2 + RO = ROOH + AO \qquad (6)$$

$$RO_2 + RH = ROOH + R \qquad (7)$$

$$RO_2 = A + HO_2 \qquad (8)$$

$$RO_2 = \overset{O}{\boxed{\qquad\quad}} + OH \qquad (9)$$

$$RO_2 = \text{fragmentation products} + X \qquad (10)$$

$$RO_2 = QOOH \qquad (11)$$

Although Reactions 8 to 10 have been written as distinct unimolecular processes, it is possible that they may occur *via* Reaction 11, followed by decomposition of the QOOH radical. Reactions 9 to 11 are to be regarded as reaction types rather than as single reactions—*i.e.*, each represents several distinct elementary processes.

Oxidations will be chain reactions when one or more of Reactions 7 to 10 are faster than Reactions 4 to 6 combined. They will be autocatalytic when products such as ROOH and HOOH pyrolyze to give new free radicals by reactions such as 12 and 12′, or when products such as aldehydes and olefins react with oxygen to give new free radicals by reactions such as 13.

$$ROOH = RO + OH \qquad (12)$$

$$HOOH + M = OH + OH + M \qquad (12')$$

$$CH_2O + O_2 = CHO + HO_2 \qquad (13)$$

Effect of Temperature on Dominant Reactions

At 25° to 50°C. At ambient temperatures Reactions 7 to 10 are slow compared with Reactions 4 to 6 because of their relatively high activation energies, and the alkyl radicals to be oxidized must be generated photochemically or by some other external agency. The oxidations proceed essentially by nonchain free radical processes—*i.e.*, by Reactions 2 and 4 to 6. Typical of such studies are those of Calvert and co-workers (*18, 19, 51, 52*) on the photo-oxidation of azoalkanes, and of Nalbandyan and co-workers (*43*) on the mercury-photosensitized oxidation of alkanes. The important reactions are probably represented by Schemes A and B shown in Figure 1. Although Nalbandyan has suggested that the Hg-photosensitized oxidations are chain reactions at room temperature, this seems unlikely in view of the relative unreactivity of peroxy radicals in abstraction reactions. Although the main product at 25°C. is the alkyl hydroperoxide, which presumably arises from Reaction 5, other minor products occur, and other mutual reactions of radicals ought to be added as minor reactions in Scheme B.

In Schemes A and B and those following, the symbols in boxes represent reactive intermediates, starting materials, termination products (T), or branching intermediates (B); single arrows represent elementary reactions consuming one molecule of intermediate; double arrows represent elementary reactions consuming two molecules of intermediate;

—②→ represents a reaction producing two molecules of intermediate. The descriptions on the arrows give the type of reaction involved: phot = photolysis, Hg phot = mercury-photosensitized decomposition, ox = reaction with oxygen, abs = H atom abstraction from the substrate, pyr = pyrolysis, and wall = reaction on wall.

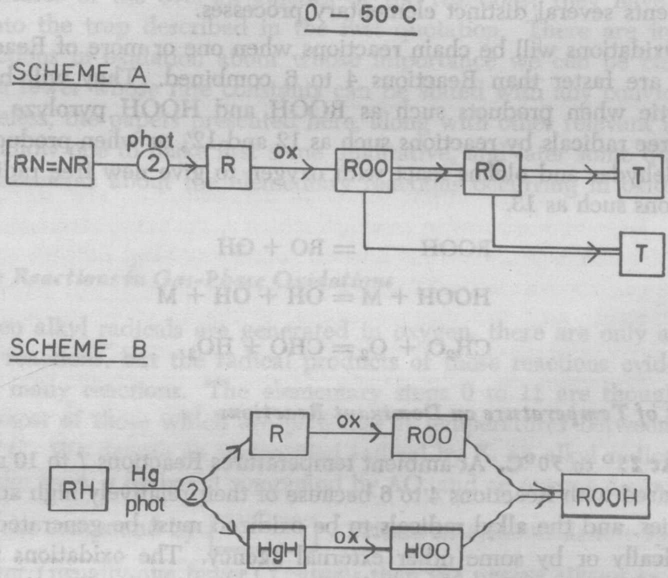

Figure 1. Photo-oxidation of azoalkanes and mercury-photosensitized oxidation of alkanes

The mechanisms for ambient temperature oxidations become more complex as the alkyl radical R becomes more complex and as the reactions proceed. Thus, with azo-2-methylpropane (52) the pyrolysis of the *tert*-butoxy radical must be included, and in all but the initial stages, reactions of alkoxy radicals with products containing weak C—H bonds must be included. Numerous tertiary reactions can then occur. As with most free radical systems, useful information can be obtained only if the degree of conversion of the starting material is kept low.

At 100° to 150°C. In this range of temperature chain oxidation by Reactions 2 and 7 can occur. Conditions favoring chain reaction are (1) low rates of initiation, which give low radical concentrations and favor Reaction 7 relative to Reactions 4 to 6, (2) high pressures which favor Reaction 7, and (3) high temperatures which increase the rate of

Reaction 7 more than that of Reaction 4. Conditions 1 and 3 will, however, conflict if reactions are thermally initiated (*e.g.*, peroxide decomposition) since the rate of initiation will probably rise faster than the rate of Reaction 7, and the lower temperatures may be more conducive to chain reaction. These features are clearly brought out by the work of Allara, Mill, Hendry, and Mayo (*1*). The oxidation of 2-methylpropane was initiated by pyrolysis of azo-isobutyronitrile or di-*tert*-butyl peroxide. At 100°C. and high pressure the reaction proceeded by chains of moderate length (50 units at 22 atm.), the length increasing with pressure. At 155°C. when the initiation rate is much higher, the chain length measured as (rate of consumption of alkane)/(rate of generation of radicals by initiation) was around unity at 1 atm. pressure. At the lower temperature the major chain product was hydroperoxide, but at 155°C. the main products were derivable from the *tert*-butoxy radical, as shown in Figure 2. The yield of 2-methylpropene, an important product of the

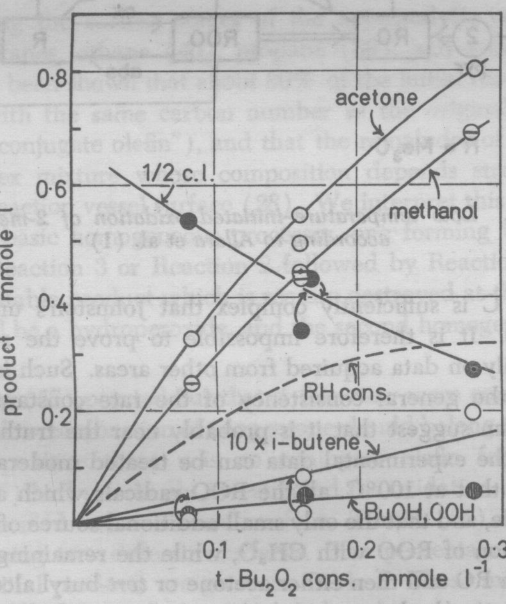

Figure 2. Product development in oxidation of 2-methylpropane at 155°C. initiated by di-tert-butyl peroxide

Data from Ref. 1 and private communication
BuOH,OOH represents sum of alcohol and peroxide
RH consumption calculated from products
c.l. represents chain length = [RH consumed]/ [2(Bu_2O_2) consumed]

autocatalytic oxidation above 270°C., was small and irreproducible, which suggests that it may have been formed heterogeneously. The oxidation of 2-methylpropane in this temperature range is represented to a good approximation by Scheme C of Figure 3.

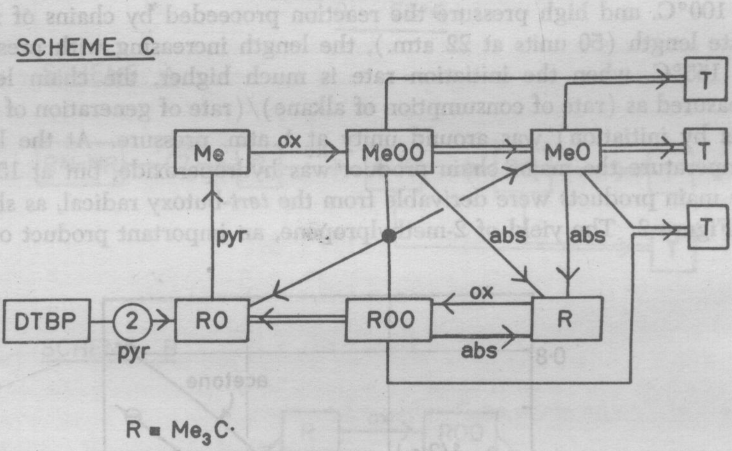

Figure 3. Low temperature–initiated oxidation of 2-methylpropane according to Allara et al. (1)

Scheme C is sufficiently complex that Johnston's uncertainty principle applies. It is therefore impossible to prove the scheme without relying heavily on data acquired from other areas. Such information and particularly the general consistency of the rate constants required by the mechanism suggest that it is probably near the truth. Assuming its correctness, the experimental data can be treated moderately rigorously if it is noted that at 100°C. all the ROO radicals which abstract H give hydroperoxide, and that the only small additional source of hydroperoxide will be reaction of ROO with CH_3O, while the remaining ROO radicals will first form RO and then either acetone or *tert*-butyl alcohol. Measurement of the ratio (hydroperoxide)/(acetone + *tert*-butyl alcohol)$^{1/2}$ will then give $k_7/k_4^{1/2}$.

At 250° to 400°C. There is a serious gap in our information about alkane or alkyl radical oxidations between 150° and 250°C. Above about 250°C. the oxidations of organic substances and alkanes in particular become autocatalytic (*42*). The autocatalysis must arise from reactions such as 12, 12′, and 13, and below 350°C. Reaction 12 seems by far the most likely. Around 400°C. Reaction 13 may become important and at about 450°C. Reaction 12′. It is not, however, the purpose of this paper to discuss the nature of the branching reactions in alkane combustion. These have been given more than their due share of attention elsewhere.

It is in the region 250° to 400°C. that Johnston's uncertainty principle has so often been ignored. Although Reactions 8 to 11 can explain the formation of the observed products, this is no guarantee that they in fact occur, and there is a great need for careful independent experiments in this area.

Until recently the major problems in the study of combustion have been analytical since it is essential to determine products in the earliest stages of reaction when secondary reactions involving products can be shown to be unimportant. Generally this implies reactant consumptions below 0.1 or 1%. Only gas chromatography is capable of adequate sensitivity, selectivity, and quantitative accuracy under these conditions. However, even gas chromatography has not been able to deal effectively with the analysis of peroxides, and there is need for more work in this field.

By studying the earliest stages of the autocatalytic combustion of the simpler alkanes, ethane (*40*), propane (*39*), and 2-methylpropane (*28, 58*), it has been shown that about 80% of the initial reaction product is the olefin with the same carbon number as the original alkane (we term this the "conjugate olefin"), and that the remainder of the products form a complex mixture whose composition depends strongly on the nature of the reaction vessel surface (*28*). We interpret this to mean that there are two basic homogeneous processes, one forming the conjugate olefin, either Reaction 3 or Reaction 2 followed by Reaction 8, and one forming an unstable product which is readily destroyed at the walls. The latter may well be a hydroperoxide, and the second homogeneous process Reaction 7.

Zeelenberg (*57*) pointed out that if this view were correct, all products from the slow combustion of neopentane should belong to the surface-sensitive group since there was no conjugate olefin for neopentane. Zeelenberg (*56*) had previously investigated the oxidation of neopentane using an unspecified reaction vessel surface. Turner (*55*) re-investigated the reaction using two different surfaces. The percentage yields of the three major initial products are given in Table I. These initial fractional yields clearly depend on the surface used and support our contention regarding the nature of the reaction. All the initial products from the neopentane oxidation at about 250°C. arise on the walls of the reaction vessel from some precursor probably formed homogeneously.

With hydrocarbons containing straight chains of five or more carbon atoms (and probably of four carbon atoms also), the initial products at

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