Limiting Rates of Hydrocarbon Autoxidations[1]

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Abstract: A kinetic analysis of hydrocarbon autoxidation initiated by thermal or catalyzed hydroperoxide decomposition and involving the rate-determining steps (2) $ROO\cdot + RH \rightarrow ROOH + R\cdot$ (k_p) and (3) $2ROO\cdot \rightarrow$ inert products (k_t) predicts a maximum rate $-d[RH]/dt = nk_p2[RH]^2/2fk_t$, where n/f is determined by the stoichiometry and details of the initiation process. Under these conditions chains are near unity and much RH is consumed by alkoxy- or other nonperoxide radical attack. Application of the analysis to cooxidations, involving either added cooxidants or intermediate oxidation products, shows that great increases in rate of oxidation of an unreactive component, which would not be observed in long-chain reactions, are possible under limiting rate conditions. While literature data indicate that some metal-catalyzed autoxidations reach these limiting rate conditions, others are even faster and follow kinetics which do not agree with this analysis. Under these conditions, not only must (2) be unimportant in the consumption of RH, but additional propagation steps, *e.g.*. peroxy radical–metal ion reactions, must be taken into account.

The autoxidation of hydrocarbons under conditions where kinetic chains are long and hydroperoxides are major products has had extensive and rewarding investigation.[2] Here chains propagate *via* the sequence

$$R\cdot + O_2 \xrightarrow{k_a} RO_2\cdot \qquad (1)$$

$$RO_2\cdot + RH \xrightarrow{k_p} ROOH + R\cdot \qquad (2)$$

Since $k_a \gg k_p$, termination at usual oxygen pressures is *via* bimolecular interaction of peroxy radicals[3]

$$2RO_2\cdot \xrightarrow{k_t} \text{inert products} + O_2 \qquad (3)$$

Under these conditions

$$\frac{-d[O_2]}{dt} = \frac{-d[RH]}{dt} = k_p[RH](R_i/2k_t)^{1/2} \qquad (4)$$

where R_i represents the rate of chain initiation, frequently achieved by adding an initiator with a known decomposition rate and efficiency. Not only do many systems obey eq 4, but, by using nonsteady-state methods, k_p's and k_t's have been determined and correlated. In particular, (2) proves to be a relative slow process, with a rate somewhat dependent on $ROO\cdot$, but highly sensitive to R–H bond strength and the presence of electron-supplying or -withdrawing groups.

It is quite possible, and technically often desirable, to autoxidize hydrocarbons under conditions quite different from those under which the above data are obtained. At high temperatures, or in the presence of metal catalysts, or both, negligible hydroperoxide accumulates, autoxidation rates are high, and a number of anomalies occur that are not immediately accommodated by the simple kinetic scheme given. As examples, actual autoxidation rates may be considerably higher than would be predicted by (4) and may be further increased by cooxidation of relatively small amounts of more easily oxidized substrate (typically aldehydes or 2-butanone); further some autoxidations take a much longer time to reach a maximum rate than that expected to build up a small steady-state concentration of hydroperoxide. The first of these difficulties was pointed out at the Oxidation Symposium in 1967,[4] and some have been considered by other investigators in specific systems. Here an attempt is made for general analysis of the problem, considering first a model system involving initiation by thermal decomposition of hydroperoxide, then a generalization of the kinetic treatment, and finally some of the characteristics of metal-catalyzed systems and a comparison with examples of literature data.

Although the models employed are simplified, they do account for the sorts of anomalies observed and, I believe, provide a basis for understanding the factors ultimately limiting rates in autoxidation processes. Further, they show that, under these limiting conditions, many, and sometimes substantially all, of the attacks on the hydrocarbon being oxidized must be *via* species other than peroxy radicals.

Initiation by Thermal Decomposition of Hydroperoxides

In hydrocarbon systems containing no added catalysts, thermal decomposition of hydroperoxides provides the chief source of chain initiation as soon as more than traces are present. If the initiation involves simple unimolecular homolysis

$$ROOH \xrightarrow{k_d} RO\cdot + HO\cdot \qquad (5)$$

initial scission of the peroxide should be followed immediately by the steps

$$RO\cdot + RH \longrightarrow ROH + R\cdot \qquad (6a)$$

$$HO\cdot + RH \longrightarrow H_2O + R\cdot \qquad (6b)$$

since rate constants for these processes are very large, of the order of 10^4 and 10^8, respectively,[5,6] so that ter-

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[1] Support of this investigation by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

[2] Extensive reviews of this subject are available: *cf.* (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 9; (b) "Oxidation of Organic Compounds—I," Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968; (c) "Oxidation of Organic Compounds—II," Advances in Chemistry Series, No. 76, American Chemical Society, Washington, D. C., 1968; (d) F. R. Mayo, *Accounts Chem. Res.*, **1**, 193 (1968); (e) K. U. Ingold, *ibid.*, **2**, 1 (1969).

[3] Reaction 3 is actually complex and involves the sequence $2RO\cdot \rightleftharpoons RO_4R \rightarrow$ products. Further, with *t*-peroxy radicals only a fraction of the interactions leads to termination, while in olefin autoxidation, some double-bond addition occurs in competition with (2). Neither point is critical in the subsequent discussion which is concerned primarily with the autoxidation of paraffins and alkyl aromatics yielding primary and secondary hydroperoxide products.

[4] C. Walling, ref 2c, p 431.

mination steps involving these species are highly improbable. Beyond this point, it is assumed that the autoxidation continues *via* reactions 1–3 leading to the usual steady-state expression for total radicals

$$2k_d[\mathrm{ROOH}] = 2k_t[\mathrm{ROO\cdot}]^2 \qquad (7)$$

However, if the reaction is conducted under conditions (*e.g.*, high temperature) where hydroperoxide does not accumulate, it too reaches a low steady state.

$$\frac{d[\mathrm{ROOH}]}{dt} = k_p[\mathrm{ROO\cdot}][\mathrm{RH}] - k_d[\mathrm{ROOH}] = 0 \qquad (8)$$

From (7) and (8)

$$[\mathrm{ROO\cdot}] = k_p[\mathrm{RH}]/k_t \qquad (9)$$

$$[\mathrm{ROOH}] = k_p^2[\mathrm{RH}]^2/k_tk_d \qquad (10)$$

Hydrocarbon is consumed by two paths, *via* reaction with HO· and RO· (two molecules/molecule of hydroperoxide decomposed) and *via* reaction with ROO· (from (8), one molecule/molecule of hydroperoxide decomposed). Accordingly

$$-d[\mathrm{RH}]/dt = 3k_d[\mathrm{ROOH}] = 3k_p^2[\mathrm{RH}]^2/k_t \qquad (11)$$

The kinetic length of the hydroperoxide chain, defined as molecules of hydroperoxide formed per radical introduced into the system, is one-half, and only one-third of the hydrocarbon is actually being consumed by reaction with ROO· radicals. These conclusions—chain lengths near unity and substantial abstraction of hydrogen from RH by species other than ROO·—are the crux of the analysis, and, as shown in the next section, are not restricted to the rather specific model chosen here. While the first has been recognized in previous analyses, the second has never received adequate attention.

Returning to eq 11 we see that, since k_d and [ROOH] are inversely proportional, both disappear from the rate expression. The actual rate constant for hydroperoxide decomposition is unimportant providing that it is large enough to ensure that hydroperoxide reaches a low steady-state concentration early in the reaction. Before this point the autoxidation is autocatalytic; afterwards (11) is obeyed. If we assume E_p = 12–15 kcal/mole and E_t = 4 kcal, reasonable values for relatively unreactive hydrocarbons and secondary peroxy radicals, $E_{\text{over-all}}$ = (24–30) − 4 = 20–26 kcal, about the same as that predicted for a long-chain process with E_i = 30–40 kcal.

This analysis produces striking results when applied to cooxidations. Let R_1H and R_2H represent the two hydrocarbons and RH total hydrocarbon with similar subscripts for other reactants and constants. Further, to simplify the analysis assume that HO·, R_1O·, and R_2O· show the same selectivity k_{61}/k_{62} between R_1H and R_2H, that R_1OO· and R_2OO· show the same selectivity k_{p1}/k_{p2} between R_1H and R_2H, and that k_t is the same for all combinations of ROO·'s. The first two of these assumptions are quite plausible. A characteristic of RO· and HO radicals is that they are relatively unselective compared to ROO·, so differences between them will be small; further, cooxidation studies under long-chain conditions show only small differences in ROO· selectivities. The assumption that k_t is invariant with ROO· structure is not generally valid, although the greatest difference is between tertiary and nontertiary peroxy radicals, and this treatment is concerned primarily with the latter. Variations in k_t would distort, for example, the curves of Figure 1, but not the general conclusions reached. Under these conditions (11) becomes

$$-d([R_1H] + [R_2H])/dt = 3(k_{p1}[R_1H] + k_{p2}[R_2H])^2/k_t \qquad (12)$$

and one-third of total RH consumption is still *via* ROO· attack. However, the partitioning between R_1H and R_1H becomes complicated. Now

$$\frac{-d[R_1H]}{dt} = \frac{(k_{p1}[R_1H] + k_{p2}[R_2H])^2}{k_t} \times \left(\frac{2k_{61}[R_1H]}{k_{61}[R_1H] + k_{62}[R_2H]} + \frac{k_{p1}[R_1H]}{k_{p1}[R_1H] + k_{p2}[R_2H]}\right) \qquad (13)$$

where the first term in the large parentheses represents consumption by HO· and RO· and the second by ROO·.

If we let $k_{62}k_{p1}/k_{61}k_{p2} = \alpha$ and $k_{p2}[R_2H]/k_{p1}[R_1H] = r$, where α is a ratio of relative reactivities toward alkoxy and toward peroxy radicals and r the relative rate of reaction of the two hydrocarbons toward peroxy radicals, we obtain

$$\frac{-d[R_1H]}{dt} = \frac{k_{p1}^2[R_1H]^2}{k_t}(1 + r)^2\left(\frac{2}{1 + \alpha r} + \frac{1}{1 + r}\right) \qquad (14)$$

$$\frac{d[R_2H]}{d[R_1H]} = \frac{(2\alpha + 1)r + 3\alpha r^2}{3 + (2 + \alpha)r} \qquad (15)$$

The most interesting case arises when R_2H is a very easily autoxidized material. As an example, consider the cooxidation of benzaldehyde and cyclohexane. Here k_p's near room temperature have been reported as k_{p1} = 0.11,[7] k_{p2} = 1910,[8] while, toward *t*-butoxy radicals k_{62}/k_{61} = 3.4.[9] Although the value of k_{p2}/k_{p1} from the above figures may be in considerable doubt because different ROO· radicals were involved in the two measurements, it is plain that r approaches unity at a very low $[R_2H]/[R_1H]$ ratio and hydroxy and alkoxy radicals may be much less selective than peroxy radicals, so that α may have values as small as 0.01. Qualitatively, the result of a small α is evident from (14). Even at low concentrations the reactive R_2H is rapidly autoxidized, providing hydroperoxide to maintain the chain. However, the alkoxy radicals react predominantly with R_1H present in large excess and thus carry it along in the reaction.[10] The magnitude of the predicted effect is shown in Figure 1, where relative rates of oxidation of R_1H are plotted against relative rates of comsumption of R_2H and R_1H for various values of α. The contrast with long-chain kinetics is striking since in this case

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(5) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 4885, 4891 (1967); C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967).

(6) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc.*, *B*, 742 (1966).

(7) L. Sajus, ref 2b, p 59.

(8) T. A. Ingles and H. W. Melville, *Proc. Roy. Soc.* (London), **A218**, 175 (1952).

(9) C. Walling and M. J. Mintz, *J. Am. Chem. Soc.*, **89**, 1515 (1967).

(10) In any practical autoxidation, R_2H would have to be added continuously to maintain an effective low concentration.

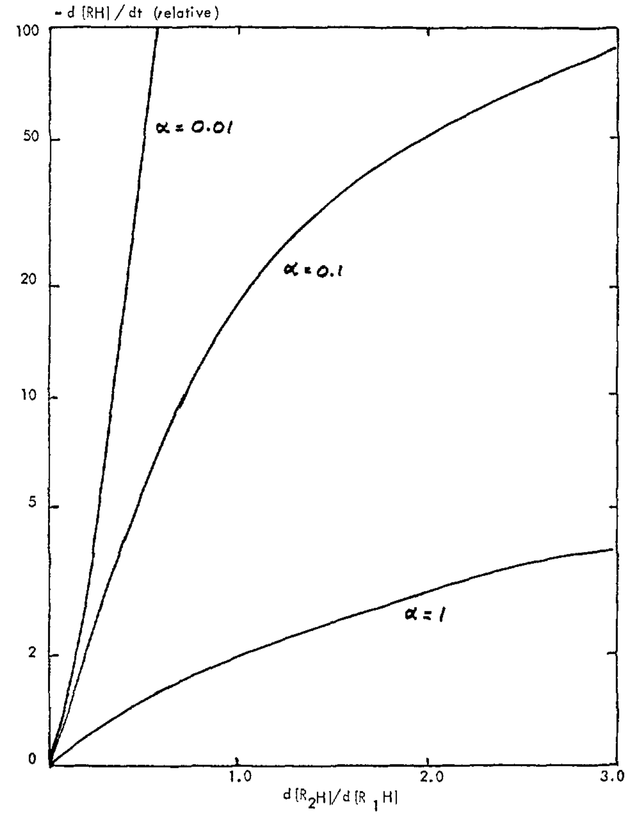

Figure 1. Effect of cooxidation on relative rates of R_1H oxidation from eq 14 and 15.

$d[R_2H]/d[R_1H] = r$ and, with an external initiator and the assumption of constant k_t, $-d[R_1H]/dt$ is not affected by added $[R_2H]$.

A cooxidant may not actually have to be added to a system since the autoxidations of many hydrocarbons yield oxygenated intermediates which may play the role of R_2H. For simplicity imagine that a single such product is formed in a yield of x moles/mole of R_1H oxidized. Its concentration will rise until its own rate of oxidation relative to that of R_1H equals x, *i.e.*, until $x = d[R_2H]/[R_1H]$ in (15). If $x = 0.5$ and $\alpha = 0.1$, from Figure 1 the rate of oxidation of R_1H will have increased eightfold and the over-all reaction will show marked over-all autocatalysis. This sort of behavior is a typical branching chain phenomenon as has been discussed previously in connection with gas-phase oxidations showing pronounced induction periods.

Generalization of the Limiting Rate Expression. Equation 11 may be easily generalized to any initiation scheme, assuming steps 1–3 and a low steady-state concentration of ROOH; details are given in the Appendix. If n is the average number of initiating radicals produced (by any means) per ROOH decomposed and f is the fraction of RH consumed which disappears by ROO· attack, the general expression is

$$-d[RH]/dt = nk_p^2[RH]^2/2fk_t \qquad (16)$$

As an example, if initiation were a bimolecular process as has been proposed for some systems[11]

$$2ROOH \longrightarrow RO\cdot + ROO\cdot + H_2O \qquad (17)$$

$n = 1$ and $f = {}^2/_3$, whence

$$-d[RH]/dt = 3k_p^2[RH]^2/4k_t \qquad (18)$$

If some hydroperoxide decomposes without yielding initiating radicals, n will decrease, while if β scission of alkoxy radicals occurs (certainly an important side reaction in high-temperature paraffin oxidations), it will be followed by reaction of the resulting fragments with oxygen, *e.g.*

$$R_2'CHO \longrightarrow R'CHO + R'\cdot \xrightarrow{O_2} R'OO\cdot \qquad (19)$$

with a consequent increase in f. All of these phenomena serve only to change the numerical coefficients in (16).

General expressions analogous to eq 14 and 15 can also be written down for cooxidations. With the same assumptions and definitions of terms, they are

$$\frac{-d[R_1H]}{dt} = \frac{nk_{p1}^2[R_1H]^2}{2k_t}(1+r)^2\left(\frac{(1-f)}{f(1+\alpha r)} + \frac{1}{1+r}\right) \qquad (20)$$

$$\frac{d[R_2H]}{d[R_1H]} = r\frac{f(1-\alpha)+\alpha(1+r)}{1+r+fr(\alpha-1)} \qquad (21)$$

In (20) the first term in the parentheses again represents consumption of R_1H by the nonperoxidic radicals and the second by ROO·. For a given value of r, its rate of oxidation increases with decreasing f and α, *i.e.*, as the fraction of its reaction going through nonperoxidic radicals is increased, and curves similar to Figure 1 can be calculated for any model system.

Metal-Catalyzed Reactions. Technically the most important autoxidations operated at high and presumably limiting rates are those catalyzed by transition metal salts, most commonly cobalt. Since such salts are powerful catalysts for hydroperoxide decomposition and are partially oxidized to higher valence states, a commonly accepted scheme for their action is *via* a redox cycle such as

$$ROOH + Co^{II} \longrightarrow RO\cdot + OH^- + Co^{III} \qquad (22a)$$

$$ROOH + Co^{III} \longrightarrow ROO\cdot + H^+ + Co^{II} \qquad (22b)$$

Since this scheme has the same stoichiometry as (17), it leads immediately to the rate expression 18 with both hydroperoxide and metal ion concentrations vanishing. In fact, this result, except for the numerical coefficient of ${}^3/_4$, was first derived for this case by Woodward and Mesrobian in 1953,[12,13] who further showed that the cobalt-catalyzed autoxidation of tetralin in acetic acid in fact obeyed (18) with a value for k_p^2/k_t in good agreement with that predicted from long-chain initiated systems. Qualitatively an independence of metal ion concentration above a rather low level (0.02–0.5%) and rather similar results with several different transition metals have been observed in a variety of other systems.[2]

Trivalent cobalt is a strong oxidizing agent which directly attacks many organic molecules including alkyl-

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(11) J. L. Bolland, *Proc. Roy. Soc.* (London), **A186**, 218 (1946); L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

(12) A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 6189 (1953). These authors, however, did not point out the short-chain nature of the reaction under these conditions, nor the important role of alkoxy radicals.

(13) For simplicity all metal ion reactions are written here as first order in metal, although evidence exists for higher order terms. However, since the metal ion does not appear in the final rate expression this has no effect upon the analysis.

aromatics,[14] and it has been frequently suggested that such attack is important in producing initiating radicals in autoxidations.[2] A possible limiting case is one in which all Co^{III} reduction occurs by such a path, with reoxidation of Co^{II} by hydroperoxide, to give the initiating cycle

$$Co^{III} + RH \longrightarrow Co^{II} + H^+ + R\cdot \xrightarrow{O_2} ROO\cdot \qquad (23a)$$

$$Co^{II} + ROOH \longrightarrow Co^{III} + RO\cdot + OH^- \qquad (23b)$$

Here $n = 2, f = {}^1/_3$, identical with the thermal initiation scheme (5) and accordingly, yielding the same rate expression (11). In short, the effect of changing from initiation scheme 22 to 23 is merely an increase in the limiting rate by a factor of 4, but no change in kinetic form.

From the available literature, two recent studies of metal-catalyzed autoxidations involving either intermediates or added materials as cooxidants illustrate the powers and limitations of this treatment of limiting rates. Brill[15] has shown that the cobalt-catalyzed autoxidation of toluene or *p*-xylene in acetic acid at 90° is markedly accelerated by 2-butanone. With 1 *M* *p*-xylene a maximum rate of approximately 25%/hr is attained, corresponding to $-d[RH]/dt = 5.6 \times 10^{-5}$ mole/(l. sec). At this temperature,[16] $k_p^2/2k_t \cong 2.8 \times 10^{-7}$, and, simply applying (16), $n/f \cong 200$.[17] In a more detailed study of toluene autoxidation under the same conditions, but without added cooxidant, Morimoto and Ogata[18] have reported a maximum rate of 5×10^{-5} mole/(l. sec). They also clearly implicate benzaldehyde as a critical cooxidant, since they show that it is present at a constant level (4.5% based on toluene) during most of the reaction, that the autoxidation does not reach its maximum rate until this level is reached, and that addition of benzaldehyde greatly decreases the initial induction period. For toluene at 90°[16] $k_p^2/2k_t \cong 4 \times 10^{-8}$, whence $n/f \cong 1250$.

These large values of n/f lead to the inescapable conclusion that negligible peroxy radical attack on parent hydrocarbon is occurring at these high rates in these systems. However, in both, autoxidation rates appear to be first rather than second order in parent hydrocarbon and still somewhat dependent on cobalt concentration in spite of its high level (~0.1 *M*). Although this finding does not vitiate the conclusion that peroxy radical attack on parent hydrocarbon must be unimportant, it poses a dilemma from which there are two possible escapes. Either the limiting rate has not yet been reached, or reactions between peroxy *radicals* and cobalt are taking place which were not taken into account in the kinetic scheme. These could be either bimolecular redox steps or termolecular processes involving metal ion, peroxy radical (perhaps *via* a complex), and hydrocarbon, but it seems improbable that their nature can be unscrambled equivocally from over-all kinetics.[19]

Finally, still higher rates of cobalt- (or cobalt–manganese-) catalyzed autoxidations in acetic acid can be achieved by adding bromide ion in various forms, and this system provides the basis for important technical oxidations of alkyl aromatics. The process has been studied by several investigators.[20–23] It shows complex kinetics, and the acceleration has been ascribed both to a change in the redox potential of cobalt altering the rate of chain initiation[22] and to participation of a bromine atom[20,21] or other chain carrier.[23] This analysis shows that the former cannot be important *per se*, but only if attack on the hydrocarbon involves some faster step than hydrogen abstraction by peroxy radicals, while Fields and Meyerson's observation[22] that the bromide-catalyzed autoxidation of toluene can give substantial yields of benzyl alcohol and benzaldehyde, compared with the limiting 4.5% yield of the latter in the absence of bromide,[18] certainly suggests that some new chain carrier is involved. For *p*-toluic acid, Ravens[20] has reported a rate law

$$d[O_2]/dt = k[Co^{II}][HBr]^{1/2}[O_2]^{1/2} \qquad (24)$$

and proposed a kinetic scheme involving

$$O_2 + HBr \longrightarrow Br' + HO_2\cdot \qquad (25)$$

and the redox step

$$Co^{II} + RCH_2O_2\cdot \longrightarrow Co^{III} + OH^- + RCHO \qquad (26)$$

However, since addition of sodium acetate does not retard the rate in similar systems,[21,23] it seems unlikely that this scheme is correct.

Conclusions

The analysis and discussion which have been presented predict the limiting rates of autoxidation which can be anticipated for the "classical" hydroperoxide chain autoxidation of hydrocarbons under different conditions of chain initiation employing values of $k_p^2/2k_t$ obtained under conditions of slow reaction and long kinetic chains. At these limiting rates substantial attack on hydrocarbon occurs *via* alkoxy or hydroxy radicals, and this explains the large increases in rate which may arise in cooxidations involving intermediate oxygenated products or added easily autoxidized materials. While some metal-catalyzed autoxidations proceed near the predicted maximum rates, others are notably faster but show kinetics inconsistent with this analysis. Under these conditions it becomes likely that hydrogen abstraction by peroxy radicals from *any* substrate becomes unimportant, and either peroxy *radicals* participate in redox cycles with the metal or some entirely new chain carriers are involved.

Although a number of such steps have been proposed in the past, *e.g.*, reaction 26, none have really been conclusively identified nor their rates established. The comprehensive data on the rates of individual steps in "classical" long-chain autoxidations may now make this possible, and lead to understanding of a series of reactions of unusual scientific interest and technical importance.

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(14) T. A. Cooper and W. A. Waters, *J. Chem. Soc., B*, 687 (1967).

(15) W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

(16) Obtained by extrapolating the data summarized by F. R. Mayo, M. G. Syz, T. Mill, and J. K. Castleman, ref 2b, p 56.

(17) Although we are actually dealing with a cooxidation of at least two components (see below), so that (16) applies strictly to the total rate of oxidation of all components, this total rate is even larger than that measured.

(18) T. Morimoto and Y. Ogata, *J. Chem. Soc., B*, 62, 1353 (1967).

(19) Some of these possibilities have been considered by Morimoto and Ogata.[18] However, their kinetic analysis is inconclusive, and, since they assume long kinetic chains, probably invalid.

(20) D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959).

(21) A. S. Hay and H. S. Blanchard, *Can. J. Chem.*, **43**, 1306 (1965).

(22) E. K. Fields and S. Meyerson, ref 2c, p 395.

(23) Y. Kamiya, ref 2c, p 193.

Appendix

Using the symbols employed previously, for a single-component system

$$-f\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = k_p[\mathrm{ROO}\cdot][\mathrm{RH}] \qquad (27)$$

and, since the rate of formation of hydroperoxide is $-n\mathrm{d}[\mathrm{RH}]/\mathrm{d}t$, at its steady state

$$-n\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = 2k_t[\mathrm{ROO}\cdot]^2 \qquad (28)$$

Eliminating [ROO·] gives

$$-\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = nk_p{}^2[\mathrm{RH}]^2/2fk_t \qquad (16)$$

For a cooxidation the same over-all expression applies and can conveniently be written as

$$\frac{-\mathrm{d}([\mathrm{R_1H}] + [\mathrm{R_2H}])}{\mathrm{d}t} = \frac{nk_{p1}{}^2[\mathrm{R_1H}]^2(1 + r)^2}{2fk_t} \qquad (29)$$

This rate expression may be partitioned into fractions $1 - f$ and f involving nonperoxy and peroxy radical paths, and expressed as

$$\frac{-\mathrm{d}([\mathrm{R_1H}] + [\mathrm{R_2H}])}{\mathrm{d}t} = \frac{nk_{p1}{}^2[\mathrm{R_1H}]^2(1 + r)^2}{2k_t}\left(\frac{1 - f}{f} + 1\right) \qquad (30)$$

The rate of disappearance of R_1H is obtained by multiplying each of the parts by the fraction of that radical attack which involves R_1H, *e.g.*, for peroxy radicals, $k_{p1}[\mathrm{R_1H}]/(k_{p1}[\mathrm{R_1H}] + k_{p2}[\mathrm{R_2H}])$, giving, in terms of r and α

$$\frac{-\mathrm{d}[\mathrm{R_1H}]}{\mathrm{d}t} = \frac{nk_{p1}{}^2[\mathrm{R_1H}]^2}{2k_t} \times (1 + r)^2\left(\frac{1 - f}{f}\,\frac{1}{1 + \alpha r} + \frac{1}{1 + r}\right) \qquad (20)$$

Similarly

$$\frac{-\mathrm{d}[\mathrm{R_2H}]}{\mathrm{d}t} = \frac{nk_p{}^2[\mathrm{R_1H}]^2}{2k_t} \times (1 + r)^2\frac{1 - f}{f}\,\frac{\alpha r}{1 + \alpha r} + \frac{r}{1 + r} \qquad (31)$$

Dividing (31) by (20) yields (21). Obviously the treatment may be easily generalized to any number of components or carrier radicals.

Oxidation of Dicarbanions by Electron Transfer to Aromatic Acceptors

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Abstract: Aromatic hydrocarbons may oxidize dimeric dicarbanions derived from 1,1-diphenylethylene (D) or α-methylstyrene (α). These dimers have similar structures, *viz.* $\mathrm{Na^+,\bar{C}(Ph)_2CH_2CH_2\bar{C}(Ph)_2,Na^+} = {}^-\mathrm{DD}^-$ and $\mathrm{K^+,\bar{C}(CH_3)(Ph)CH_2CH_2\bar{C}(CH_3)(Ph),K^+} = {}^-\alpha\alpha^-$. In our studies the oxidation was accomplished by the following electron acceptors: anthracene (A), dimethylanthracene (DMA), pyrene (π), benzpyrene (Bπ), and perylene radical anion ($\mathrm{Pe}\cdot^-$). The mechanism of oxidation shows some unifying features for all the investigated systems. The unimolecular dissociation of dimeric radical ions, namely, ${}^-\mathrm{DD}\cdot \rightarrow \mathrm{D}\cdot^- + \mathrm{D}$ (k_3) or ${}^-\alpha\alpha\cdot \rightarrow \alpha\cdot^- + \alpha$ ($k_{3'}$), is rate determining for all these processes and drives forward the over-all reaction. The dimeric radical ions are present in minute stationary concentrations maintained by the equilibria such as ${}^-\mathrm{DD}^- + \mathrm{A} \rightleftarrows {}^-\mathrm{DD}\cdot + \mathrm{A}\cdot^-$. This accounts for the autoinhibition of the oxidation. The above scheme accounts also for the exchange between ${}^-\mathrm{DD}^-$ and its monomer, D, although no bulk reaction takes place between these reagents. The formation of ${}^-\alpha\alpha\cdot$ is somewhat different from that of ${}^-\mathrm{DD}\cdot$. Instead of a direct electron transfer, *e.g.*, ${}^-\mathrm{DD}^- + \mathrm{A} \rightarrow {}^-\mathrm{DD}\cdot + \mathrm{A}\cdot^-$, the process occurs through the formation of an intermediate adduct, *i.e.*, ${}^-\alpha\alpha\text{–}\mathrm{A}^-$ followed by ${}^-\alpha\alpha\text{–}\mathrm{A}^- \rightarrow {}^-\alpha\alpha\cdot + \mathrm{A}\cdot^-$. The factors favoring the indirect electron transfer are discussed. Diadduct, *e.g.*, ${}^-\mathrm{A}\alpha\alpha\text{–}\mathrm{A}^-$, is formed as well as the monoadduct. The contribution of the latter to the over-all oxidation is negligible, and consequently its formation, favored by higher initial concentration of the acceptor, accounts for the most peculiar behavior of the system. Whereas the oxidation is accelerated by increase in the acceptor's concentration when its concentration is relatively low, the reaction is retarded by the acceptor when its initial concentration of the acceptor is sufficiently large.

Carbanions may be oxidized by suitable electron acceptors. For example, at the beginning of this century Schlenk described the reaction[1]

$$\mathrm{Ph_3C^-} + \text{anthracene (A)} \rightleftarrows \mathrm{Ph_3C}\cdot + \text{anthracene}\cdot^- \ (\mathrm{A}\cdot^-)$$

in which the electron-transfer process oxidizes a carbanion to its parent radical and reduces an aromatic hydrocarbon to its radical anion. In the following years similar reactions were reported by other investigators.

Quantitative studies of the kinetics of electron transfers from some dicarbanions to aromatic acceptors were carried out in our laboratory during the last

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(1) W. Schlenk and R. Ochs, *Ber.*, 49, 608 (1916).