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Oxidation of Hydrocarbons in the Presence of Added Hydroperoxide. On the Determination of Rate Constants by the Hydroperoxide Method

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Abstract

Oxidation of tetralin in the presence of tert-butyl hydroperoxide and tetralyl hydroperoxide, initiated with azobisisobutyronitrile, was studied at 60°C in order to examine the complications involved in the hydroperoxide method devised by Howard and Ingold. From literature data on absolute rate constants and our rates of oxidation, cross termination rate constants and contributions of each elementary propagation and termination step were computed. It was confirmed that this method was quite useful in determining the cross propagation rate constant, but it was also demonstrated that the rate of oxidation should be measured at very low conversion and with quite high concentrations of hydroperoxide, especially when the peroxy radical derived from the added hydroperoxide has a much lower termination rate constant than that from the oxidizing substrate.

1. Introduction

Oxidation of organic compounds by molecular oxygen at relatively low temperature proceeds by a radical chain mechanism where the important rate determining steps are the propagation reaction of the chain-carrying peroxy radical with the stubstrate and the bimolecular termination reaction of peroxy radicals [1, 2]. The absolute rate constants for the propagation reaction have been measured for various substrates by several investigators, most extensively by Howard, Ingold, and their coworkers [3]. Howard, Schwalm, and Ingold [4] devised a new technique where a substrate was oxidized in the presence of an added hydroperoxide. Then all the peroxy radicals derived from the substrate undergo a fast hydrogen atom transfer reaction with hydroperoxide, and with sufficient hydroperoxide only peroxy radicals from the added hydroperoxide are involved in the rate-controlling propagation and termination reactions.

Thus with the absolute termination rate constant determined separately, the rate constant for the cross propagation reaction can be determined and the relative reactivities of various substrates and peroxy radicals toward each other

are obtained. Numerous cross propagation rate constants have been determined by this hydroperoxide method [4–6].

Among the hydroperoxides, tert-butyl hydroperoxide is most widely used. Howard and coworkers [5] claim that this hydroperoxide is ideally suited because it is commercially available, easily purified, and, above all, addition of this hydroperoxide allows many unreactive substrates to be oxidized at reasonable chain lengths since the rate constant for chain termination by tert-butylperoxy radicals is lower than for any other known alkylperoxy radical. However, as discussed later, this in turn may cause complications since the complete exchange of the chain-carrying peroxy radical from substrate peroxy radical to tert-butylperoxy radical is difficult. Howard et al. measured the absolute termination rate constant in the oxidation with sufficient concentration of added hydroperoxide and by comparing it with the termination rate constant determined in the oxidations of the parent hydrocarbon of the hydroperoxide. They confirmed the complete transfer of the chain-carrying peroxy radical. However, we have previously pointed out [7] that the peroxy radical from the substrate might possibly participate in the termination, even with rather high concentrations of hydroperoxide.

The objective of this paper is to examine the complications involved in this hydroperoxide method by calculating the rates of each elementary reaction involved in the propagation and termination steps and by comparing the relative importance of these reactions. The principal conclusion may be obvious qualitatively, but we would like to supply the supporting numbers.

2. Results and Discussion

The oxidation of tetralin (TH) with added tert-butyl hydroperoxide (BOOH) initiated with azobisisobutyronitrile (AIBN) proceeds by the following elementary reactions:

Initiation:

$$\text{AIBN} + \text{O}_2 \longrightarrow (\text{CN})(\text{CH}_3)_2\text{COO}\cdot \tag{1}$$

$$(\text{CN})(\text{CH}_3)_2\text{COO}\cdot + \text{TH, BOOH} + \text{O}_2 \rightarrow \text{TOO}\cdot, \text{BOO}\cdot \tag{1'}$$

Propagation:

$$\text{TOO}\cdot + \text{TH} \xrightarrow{k_{\text{TT}}} \text{TOOH} + \text{T}\cdot \tag{2}$$

$$\text{TOO}\cdot + \text{BOOH} \xrightarrow{k_{\text{TBOOH}}} \text{TOOH} + \text{BOO}\cdot \tag{3}$$

$$\text{BOO}\cdot + \text{TH} \xrightarrow{k_{\text{BT}}} \text{BOOH} + \text{T}\cdot \tag{4}$$

$$\text{T}\cdot + \text{O}_2 \longrightarrow \text{TOO}\cdot \tag{5}$$

Termination:

$$\left.\begin{array}{ll} \text{(6)} & \text{TOO}\cdot + \text{TOO}\cdot \xrightarrow{k_{t\text{TT}}} \\ \text{(7)} & \text{TOO}\cdot + \text{BOO}\cdot \xrightarrow{k_{t\text{TB}}} \\ \text{(8)} & \text{BOO}\cdot + \text{BOO}\cdot \xrightarrow{k_{t\text{BB}}} \end{array}\right\} \text{nonradical products} + \text{O}_2$$

In the presence of hydroperoxide, the termination reaction by tert-butylperoxy radicals is by the direct interaction to form di-tert-butyl peroxide and oxygen [6d].

The steady-state treatment for these elementary steps gives Eqs. (9) and (10) for the concentrations of two peroxy radicals,

$$\text{(9)} \quad [\text{TO}_2\cdot] = \{k_{\text{BT}}[\text{TH}]R_i^{1/2}\}/\{2k_{\text{BT}}^2k_{t\text{TT}}[\text{TH}]^2 + 4k_{\text{TBOOH}}k_{\text{BT}}k_{t\text{TB}}[\text{TH}][\text{BOOH}] + 2k_{\text{TBOOH}}^2k_{t\text{BB}}[\text{BOOH}]^2\}^{1/2}$$

$$= \{R_i/(2k_{t\text{TT}} + 4pk_{t\text{TB}} + 2p^2k_{t\text{BB}})\}^{1/2}$$

$$\text{(10)} \quad [\text{BO}_2\cdot] = k_{\text{TBOOH}}[\text{BOOH}][\text{TO}_2\cdot]/k_{\text{BT}}[\text{TH}] = p[\text{TO}_2\cdot]$$

where R_i is the rate of initiation and $p = k_{\text{TBOOH}}[\text{BOOH}]/k_{\text{BT}}[\text{TH}]$. The rate of oxidation is given by

$$\text{(11)} \quad -d[\text{O}_2]/dt = k_{\text{BT}}(k_{\text{TT}}[\text{TH}] + k_{\text{TBOOH}}[\text{BOOH}])[\text{TH}]R_i^{1/2}/\{2k_{\text{BT}}^2k_{t\text{TT}}[\text{TH}]^2 + 4k_{\text{TB}}k_{\text{BT}}k_{t\text{TB}}[\text{TH}][\text{BOOH}] + 2k_{\text{TBOOH}}^2k_{t\text{BB}}[\text{BOOH}]^2\}^{1/2}$$

$$= (k_{\text{TT}} + pk_{\text{BT}})[\text{TH}]R_i^{1/2}/(2k_{t\text{TT}} + 4pk_{t\text{TB}} + 2p^2k_{t\text{BB}})^{1/2}$$

The rate constant for hydrogen atom abstraction from hydroperoxide, k_{TBOOH}, can be calculated from Eq. (12):

$$\text{(12)} \quad k_{\text{TBOOH}} = [(k_{\text{TT}}k_{\text{BT}}^2[\text{TH}]^3 - 2k_{\text{BT}}k_{t\text{TB}}[\text{TH}]\text{Q}) \pm \{4k_{\text{BT}}^2[\text{TH}]^2Q^2(k_{t\text{TB}}^2 - k_{t\text{TT}}k_{t\text{BB}}) - 2k_{\text{BT}}^2[\text{TH}]^4Q(2k_{\text{TT}}k_{\text{BT}}k_{t\text{TB}} - k_{\text{TT}}^2k_{t\text{BB}} - k_{\text{BT}}^2k_{t\text{TT}})\}^{1/2}]/[\text{BOOH}](2k_{t\text{BB}}Q - k_{\text{BT}}^2[\text{TH}]^2)$$

where $Q = (-d[\text{O}_2]/dt)^2/R_i$.

When the concentration of added hydroperoxide is high enough and only BOO· peroxy radicals are involved, both in chain propagation and termination reactions, then the oxidation proceeds substantially by steps (1), (1′), (3), (4), (5), and (8). Under these circumstances, the rate of oxidation can be expressed as Eq. (13):

$$\text{(13)} \quad -d[\text{O}_2]/dt = k_{\text{BT}}(R_i/2k_{t\text{BB}})^{1/2}[\text{TH}]$$

For Eq. (13) to hold, it is necessary and sufficient that for reaction rates reaction (2) $\ll$ reaction (3) in the propagation step and that reactions ((6) + (7)) $\ll$ reaction (8) in the termination steps; that is, Eqs. (14) and (15) should be satisfied:

$$k_{TT}[TH] \ll k_{TBOOH}[BOOH] \tag{14}$$

$$2k_{BT}^2k_{tTT}[TH]^2 + 4k_{TBOOH}k_{BT}k_{tTB}[TH][BOOH] \ll 2k_{TBOOH}^2k_{tBB}[BOOH^2] \tag{15}$$

When Eqs. (14) and (15) are satisfied, Eq. (11) is virtually consistent with Eq. (13).

Figure 1 shows the rates of oxidation of tetralin and cumene in the presence of added tert-butyl and tetralyl hydroperoxides, respectively. In the cumene–tetralyl hydroperoxide system, the rate of oxidation became constant with higher than 0.1 *M* tetralyl hydroperoxide, and as shown in Figures 2 and 3 the computation with the rate constants compiled from the literature [3, 6d] indicates that both Eqs. (14) and (15) are satisfied. However, in the oxidation of tetralin with added tert-butyl hydroperoxide, the rate of oxidation increased with increasing tert-butyl hydroperoxide. In Table I are summarized the rate constant for the reaction of tetralylperoxy radical with tert-butyl hydroperoxide calculated from

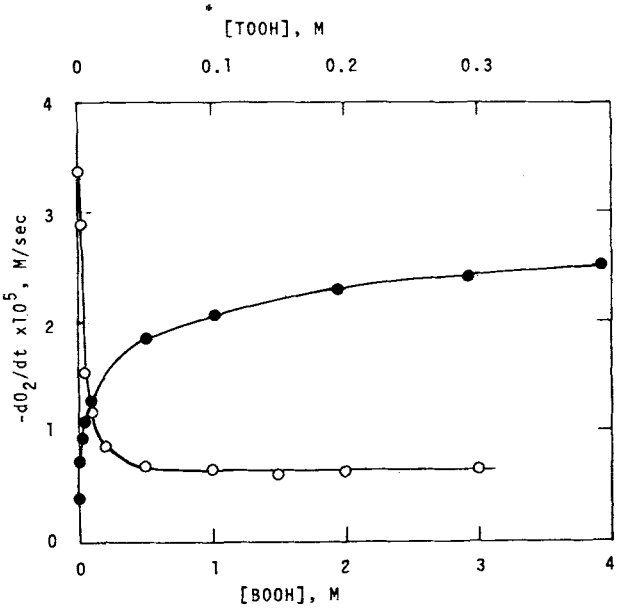

Figure 1. Rates of oxidations of cumene (○) and tetralin (●) with added tetralyl and tert-butyl hydroperoxides, respectively. ○—70°C, [AIBN] = 1.66×10^{-2} *M*, [cumene] = 7.20*M*. ●—60°C, [AIBN] = 1.20×10^{-2} *M*, [tetralin] = 1.47*M* in PhCl.

TABLE I. Rate of oxidation of tetralin in the presence of tert-butyl hydroperoxide and calculated rate constant for reaction of tetralylperoxy radical with tert-butyl hydroperoxide. 60°C, [TH] = 1.47 M in PhCl, [AIBN] = 0.0120M.

[BOOH] M	$(-d[O_2]/dt)_{prop}$[a] x10^5, M/sec	k_{TBOOH}[b] x10^{-3}, $M^{-1}sec^{-1}$	k_{TBOOH}[c] x10^{-3}, $M^{-1}sec^{-1}$
0	0.40		
0.0103	0.73	10.6	4.33
0.0307	0.94	6.85	2.41
0.0534	1.11	6.02	1.89
0.0950	1.26	4.71	1.34
0.522	1.85	2.71	0.49
1.02	2.06	2.12	0.31
1.95	2.29	1.90	0.20
2.93	2.42	1.83	0.14
3.93	2.51	1.88	0.12

[a] Observed rate of oxidation was corrected for nitrogen evolution from AIBN and oxygen absorption and evolution associated with initiation and termination. Since the kinetic chain length was long, the correction was always less than 2.5% of the observed value.

[b] Calculated with $k_{BT} = 3.1$.

[c] Calculated with $k_{BT} = 12.4$.

Eq. (12) with the rate of oxidation and following rate constants[1,2] at 60°C, k_{TT} = 20 [3], k_{BT} = 3.1 and 12.4, $k_{tBB} = 2.1 \times 10^3$ [5], $k_{tTT} = 6.5 \times 10^6$ [3], and $k_{tTB} = 4.7 \times 10^5/M$ sec.

Table II summarizes the concentration of the two peroxy radicals and the rates of individual propagation and termination steps. It shows that when the concentration of tert-butyl hydroperoxide is higher than 0.5M, more than 97%

[1] Korcek et al. [5] reported $k_{BT} = 12.4\ M^{-1}\ sec^{-1}$ at 60°C, but accompanying discussion is made mostly with $k_{BT} = 3.1$ calculated from the extrapolated rate of oxidation of tetralin, $(-d[O_2]/dt)_{BOOH\to\infty} = 2.8 \times 10^{-5}\ M$/sec (see Fig. 1). A referee has pointed out that the rate of oxidation of tetralin in the presence of tert-butyl hydroperoxide may not be directly proportional to the concentration of the substrate because the rate of oxidation is so high that the solution becomes depleted of oxygen and some termination may occur via T· + BOO·. This point is also argued in [5]. We have since carried out some additional experiments and found that the rates of oxidation of 1.47M tetralin with 3.95M added BOOH under air and under 1 atmosphere of pure oxygen agreed well and that the rate of oxidation of 0.73M tetralin with 3.95M BOOH was half as large as that of 1.47M tetralin with the same concentration of added BOOH.

[2] The rate constant k_{tTB} was calculated with $\phi = k_{tTB}/(k_{tTT}k_{tBB})^{1/2} = 4$ [8].

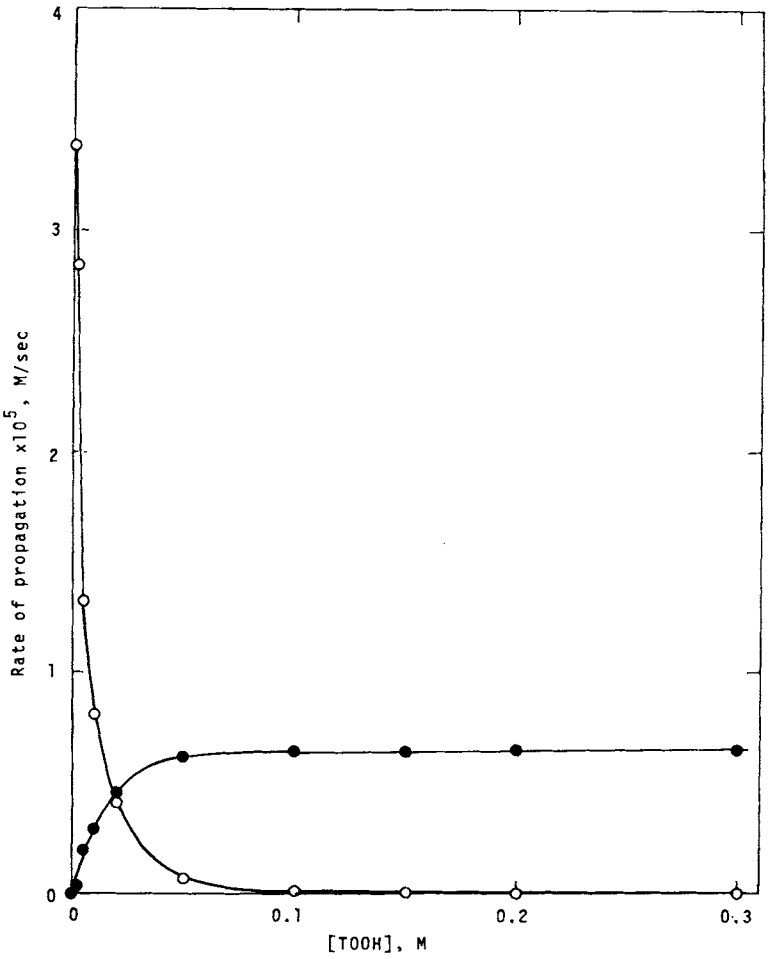

Figure 2. Rates of propagation reactions in the oxidation of cumene (CH) with tetralyl hydroperoxide (TOOH) at 70°C, [AIBN] = 1.66×10^{-2} M. ○—$CO_2\cdot$ + CH; ●—$TO_2\cdot$ + CH.

of tetralylperoxy radicals react with tert-butyl hydroperoxide and Eq. (14) is satisfied. However, the cross interaction of tetralyl and tert-butyl peroxy radicals contributes about 20% of the termination reaction, even with 3.93 M tert-butyl hydroperoxide. The plot of relative importance of reaction (8) in the total termination reactions as a function of tert-butyl hydroperoxide concentration implies that tetralin should be oxidized in neat tert-butyl hydroperoxide in order to satisfy Eq. (15).

Table I indicates that the rate constant k_{TBOOH} calculated with both k_{BT} = 3.1 and 12.4 M^{-1} sec^{-1} decreases markedly with an increase in tert-butyl hydro-

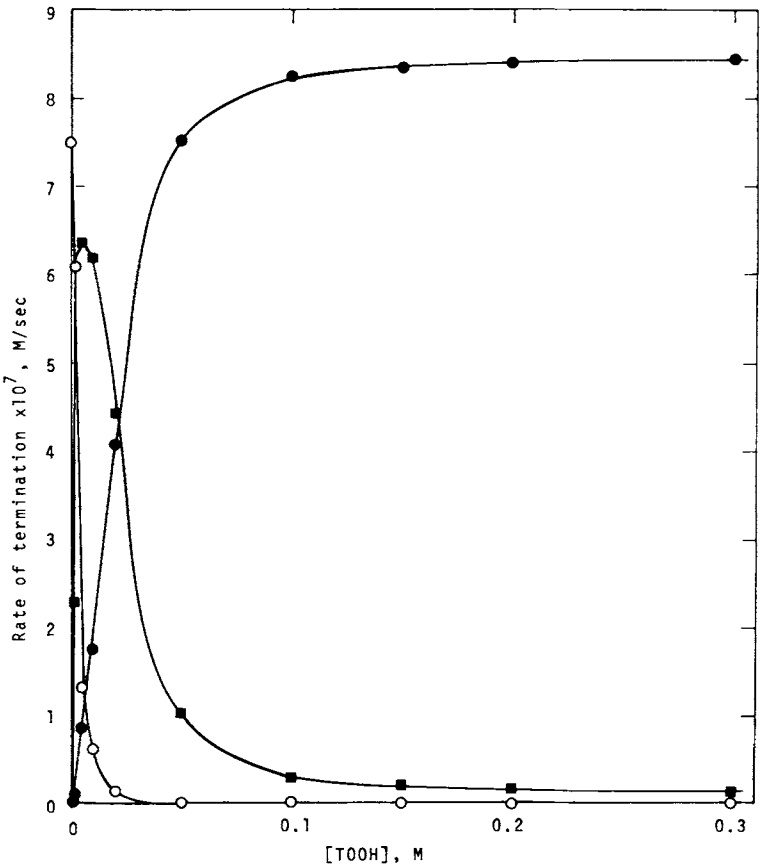

Figure 3. Rates of termination reactions in the oxidation of cumene (CH) with tetralyl hydroperoxide (TOOH) at 70°C, [AIBN] = 1.66×10^{-2} M, $R_i = 8.54 \times 10^{-7}$ M/sec. ○—$CO_2\cdot$ + $CO_2\cdot$; ■—$CO_2\cdot$ + $TO_2\cdot$; ●—$TO_2\cdot$ + TO_2.

peroxide concentration.[3] Howard et al. [4] also observed this phenomenon for cumyl hydroperoxide and argued that the decrease in this rate constant was due to the formation of hydroperoxide dimer at its high concentration. Walling and Heaton [9] studied the formation of tert-butyl hydroperoxide dimer in various

[3] On the contrary, the rate constant for the attack of the cumylperoxy radical to tetralyl hyperperoxide, k_{CTOOH}, calculated from the data in Figure 1, increases with an increase in tetralyl hydroperoxide concentration. The calculation of k_{CTOOH} from the data of Howard et al. [4] also showed a similar trend. At present it is not clear whether this is real or experimental uncertainty.

A referee suggested that Table I and accompanying discussion might be clearer if k_{TBOOH} were calculated from whatever value of k_{BT} gave the most constant values. However, a constant k_{TBOOH} could not be obtained by k_{BT} in the range of 1 to 12.4. (Considering $k_{TT} = 20$ at 60°C [3], k_{BT} should perhaps lie between 2 and 10.)

TABLE II. Concentration of peroxy radicals and rates of individual propagation and termination reactions in the oxidation of tetralin with added tert-butyl hydroperoxide.[a] 60°C, [TH] = 1.47M, [AIBN] = 1.20 × 10^{-2} M.

[BOOH]	$[TO_2\cdot]$	$[BO_2\cdot]$	V_2	$V_3=V_4$	$\frac{V_3}{V_2+V_3}$	V_6	V_7	V_8	$\frac{V_8}{V_6+V_7+V_8}$
M	x10^7, M		x10^5, M/sec			x10^7, M/sec			
0	1.36	0	0.40	0	0	1.60	0	0	0
0.0103	0.53	12.63	0.15	0.58	0.795	0.33	1.20	0.07	0.043
0.0307	0.39	18.10	0.12	0.82	0.872	0.18	1.28	0.14	0.088
0.0534	0.32	22.31	0.09	1.02	0.919	0.12	1.27	0.21	0.131
0.0950	0.26	25.94	0.08	1.18	0.937	0.08	1.24	0.28	0.175
0.522	0.13	39.76	0.04	1.81	0.978	0.02	0.92	0.66	0.413
1.02	0.09	44.59	0.03	2.03	0.985	0.01	0.75	0.84	0.525
1.95	0.06	49.87	0.02	2.27	0.991	0.00	0.55	1.05	0.656
2.93	0.04	52.79	0.01	2.41	0.996	0.00	0.43	1.17	0.731
3.93	0.03	54.86	0.01	2.50	0.996	0.00	0.33	1.27	0.794

[a] V_n represents the rate of reaction (n).

media by infrared spectroscopy and obtained ΔH = 5.95 kcal/mole and ΔS = 18.4 eu, which gives the equilibrium constant K = 0.8 at 60°C. Table III shows the calculated monomer and dimer concentrations, monomer ratio, rate constant k_{TBOOH} calculated assuming only monomer hydroperoxide hydrogen is abstracted by the tetralylperoxy radical, and calculated and observed rates of oxidation for each experiment. It gives the rate constant k_{TBOOH} = 5.3 × 10^3 M/sec as an average. The calculated and observed rates of oxidation agree fairly well, especially above [BOOH] = 0.09 M.

The correlation between the drift in k_{TBOOH} and hydroperoxide monomer concentration is not strictly quantitative. However, that the corrected k_{TBOOH} in Table III is substantially constant may imply that this explanation is passable. It may be noteworthy that the small error in the rate of oxidation gives a large error in k_{TBOOH}. For example, 10% error in the rate of oxidation gives 30% error in k_{TBOOH}. It may be also possible that the dimer is not really stable to the peroxy radical but has small reactivity. If so, the drift in k_{TBOOH} appears smaller at higher hydroperoxide concentration, although even in this case k_{TBOOH} should be a linear function with the monomer fraction (actually it is not). Another possible reason is that this drift is in part due to k_{tBB}: the rate constant k_{tBB} may vary with the concentration of added tert-butyl hydroperoxide. With sufficient hydroperoxide, the tert-butoxy radical produced in the nonterminating bimolecular interaction of tert-butylperoxy radicals abstracts hydrogen from hydroperoxide and the termination reaction is solely by two tert-butylperoxy radicals to yield di-tert-butyl peroxide. However, when added hydroperoxide

TABLE III. Formation of tert-butyl hydroperoxide dimer in the oxidation of tetralin with added tert-butyl hydroperoxide. 60°C, [TH] = 1.47M in PhCl, [AIBN] = 1.20 × 10^{-2} M.

[BOOH] added	[BOOH] monomer[a]	[BOOH] dimer	BOOH monomer	k_{TBOOH} x10^{-3}	$(-dO_2/dt)$ obsd	$(-dO_2/dt)$ calcd
M	M	M	%	$M^{-1}sec^{-1}$	x10^5,M/sec	x10^5,M/sec
0.0103	0.0101	0.0001	98	10.8	0.73	0.56
0.0307	0.0293	0.0007	95	7.17	0.94	0.83
0.0534	0.0495	0.0019	93	6.49	1.11	1.02
0.0950	0.0840	0.0055	88	5.33	1.26	1.25
0.522	0.339	0.091	65	4.18	1.85	1.96
1.02	0.545	0.237	53	3.97	2.06	2.18
1.95	0.835	0.557	43	4.43	2.29	2.35
2.93	1.08	0.92	37	4.97	2.42	2.43
3.93	1.29	1.32	33	5.72	2.51	2.49

[a] Formation of complex between tert-butyl hydroperoxide with chlorobenzene and tetralin is neglected.

is not sufficient to convert all tert-butoxy radicals to tert-butylperoxy radicals, methylperoxy radicals produced by the β scission of tert-butoxy radicals may participate in the termination and increase the rate of termination.

The addition of 1.02M tert-butyl alcohol in the oxidation of tetralin with and without added tert-butyl hydroperoxide gave no effect on the rate of oxidation. On the other hand, the addition of 0.0528M water lowered the rate of oxidation of tetralin by a factor of three quarters in the presence of 0.501M tert-butyl hydroperoxide, but had no effect in the absence of tert-butyl hydroperoxide.

There is one more complication that must be taken into consideration. As the oxidation proceeds, hydroperoxide from the oxidizing substrate accumulates and another transfer reaction must also participate in the propagation step and complicate the kinetics:

$$\text{(16)} \qquad \text{BOO}\cdot + \text{TOOH} \xrightarrow{k_{\text{BTOOH}}} \text{BOOH} + \text{TOO}\cdot$$

The steady-state treatment for the steps from (1) to (8) and step (16) gives Eqs. (17), (18), and (19):

$$\text{(17)} \qquad [\text{TO}_2\cdot] = R_i^{1/2}/(2k_{t\text{TT}} + 4qk_{t\text{TB}} + 2q^2k_{t\text{BB}})^{1/2}$$

$$\text{(18)} \qquad [\text{BO}_2\cdot] = q[\text{TO}_2\cdot]$$

$$\text{(19)} \qquad -d[\text{O}_2]/dt = (k_{\text{TT}} + qk_{\text{BT}})[\text{TH}]R_i^{1/2}/(2k_{t\text{TT}} + 4qk_{t\text{TB}} + 2q^2k_{t\text{BB}})$$

where

$$q = k_{TBOOH}[BOOH]/(k_{BT}[TH] + k_{BTOOH}[TOOH]) \quad (20)$$

Equation (19) can be solved for q to yield Eq. (21):

$$q = \{M \pm (M^2 - LN)^{1/2}\}/L \quad (21)$$

where $L = 2k_{tBB}Q - k_{BT}^2[TH]^2$, $M = k_{TT}k_{BT}[TH]^2 - 2k_{tTB}Q$, $N = 2k_{tTT}Q - k_{TT}^2[TH]^2$, and $Q = (-d[O_2]/dt)^2/R_i$.

In order for Eq. (13) to hold, the following conditions must be met: reaction (2) $\ll$ reaction (3), reaction (16) $\ll$ reaction (4), and reactions ((6) + (7)) $\ll$ reaction (8).

The addition of $0.100M$ tetralyl hydroperoxide to tetralin gave no effect on the rate of oxidation in the absence of tert-butyl hydroperoxide. However, in the presence of tert-butyl hydroperoxide, the addition of tetralyl hydroperoxide decreased the rate of oxidation of tetralin. Table IV summarizes the pertinent results. The V values in Table IV show the rate of each elementary reaction. It shows that when $0.0501M$ tetralyl hydroperoxide is added initially the rate of oxidation is decreased by 20%, and about 50% of tert-butylperoxy radicals produced by the transfer reaction (3) react with tetralyl hydroperoxide before they attack tetralin ($V_{16}/(V_4 + V_{16})$), although 96% of tetralin is attacked by tert-butylperoxy radicals ($V_4/(V_2 + V_4)$). The contribution of tetralylperoxy radicals in the termination step ($(V_6 + V_7)/(V_6 + V_7 + V_8)$) increases, and this effect is quite significant when $0.101M$ tetralyl hydroperoxide is added initially. These results suggest that the rate of oxidation should be measured at quite low conversion, preferably well below 1%.

The transfer rate constant k_{BTOOH} calculated from Eqs. (20) and (21) is also shown in Table IV, the average value being 120, which is smaller than k_{TBOOH} (Table III) by a factor of more than 10. It has been found that primary peroxy radicals are more reactive than secondary peroxy radicals and that the secondary peroxy radicals are in turn more reactive than the tertiary peroxy radicals in the hydrogen atom abstraction from hydrocarbons [3]. These ob-

TABLE IV. Oxidation of tetralin in the presence of tert-butyl and tetralyl hydroperoxides (in M and sec). 60°C, [TH] = $1.47M$ in PhCl, [AIBN] = 1.20×10^{-2} M.

[BOOH]	[TOOH]	$-dO_2/dt$ x10^5	k_{BTOOH}[a]	V_2 x10^5	V_3 x10^5	V_4 x10^5	V_{16} x10^5	$\frac{V_4}{V_2+V_4}$	V_6 x10^7	V_7 x10^7	V_8 x10^7	$\frac{V_8}{V_6+V_7+V_8}$
0.522	0	1.85		0.04	1.81	1.81	0	0.978	0.02	0.92	0.66	0.413
0.512	0.0101	1.76	95.3	0.04	2.08	1.72	0.36	0.977	0.02	1.00	0.58	0.363
0.505	0.0501	1.48	87.5	0.06	2.79	1.42	1.37	0.960	0.05	1.14	0.41	0.256
0.526	0.101	1.06	180	0.10	4.80	0.96	3.84	0.905	0.13	1.28	0.19	0.119

[a] Calculated from Eqs. (20) and (21).

servations have been ascribed to steric and polar effects. The bond dissociation energy of the hydroperoxidic O—H bond has been estimated to be 88–90 kcal/mole [10]. The two calculated transfer rate constants k_{TBOOH} and k_{BTOOH} are additional support for the relative reactivities of the peroxy radicals, but they might also imply the differences in the bond dissociation energies of the secondary and tertiary hydroperoxidic O—H bonds.

The above discussion suggests that the hydroperoxide method is most useful at very low conversions and with quite a high concentration of hydroperoxide, especially when the termination rate constant for the peroxy radical derived from the added hydroperoxide is much smaller than that from the substrate being oxidized.

3. Experimental

Tetralin, cumene, and chlorobenzene were washed successively with sulfuric acid, water, alkali, and water, dried, and distilled under reduced pressure of nitrogen. Tetralin and cumene were passed down the activated alumina column prior to be used to remove the hydroperoxide. Tetralyl hydroperoxide was prepared by air oxidation of tetralin at 50°C initiated with AIBN and purified by repeated recrystallization from *n*-hexane. Commercial tert-butyl hydroperoxide was distilled (41.3°C/25 mm Hg) and dried. AIBN was recrystallized from methanol.

The rate of oxygen absorption was measured by following either the volume change or pressure change using a mercury manometer and pressure transducer, respectively. Plots of oxygen uptake as a function of time gave satisfactory straight lines and the slope was taken as a rate of oxidation. It was measured below 1% conversion and used for calculation of the rate constants. The solutions were prepared by adding 2 ml tetralin, appropriate amounts of hydroperoxide and initiator, and finally chlorobenzene into a 10-ml volumetric flask. Oxidation of cumene was performed without diluent. All of the reactions were performed under 1 atmosphere of oxygen. The rate of initiation was determined by using the inhibitor, 2,6-di-tert-butyl-*p*-cresol [11]. Hydroperoxide may not be absolutely stable at 60–70°C, but may decompose thermally and contribute in the chain initiation. However, it was confirmed that the rate of initiation was independent of the amount of added tert-butyl hydroperoxide.

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