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The Cooxidation of Hydrocarbons in the Liquid Phase. V. Determination of the Reactivity Ratios

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The cooxidations of cumene (C) and tetralin (T) and of styrene (S) and tetralin were studied in the presence of azobisisobutyronitrile; the reactivity ratios, r, were obtained as $r_C=0.21$ and $r_T=5.0$ for the cumene-tetralin system at 80°C and as $r_S=2.7$ and $r_T=0.49$ for the styrene-tetralin system at 70°C. A new method for the determination of r values from the rates of cooxidation has been developed. The merits and demerits of several methods for the determination of r values are discussed. In cases where a large curvature, preferably a rate minimum, is obtained by plotting the rates against the reactant compositions, the determination from the rates of cooxidation may be most suitable. In other cases, the use of the copolymerization equation may be preferable by product analyses. The hydroperoxide method may be valid for some systems.

In the liquid-phase autoxidation of hydrocarbons, the peroxy radicals play an important role as chain carriers, and the bimolecular reaction of the peroxy radical and the hydrocarbon is the rate-determining step. The reactivities of the hydrocarbons toward the peroxy radicals, however, are hard to ascertain, although much data have been presented on the reactivities of the hydrocarbons toward other free radicals and atoms.[1] The difficulty in obtaining the reactivities toward the peroxy radicals comes mostly from the fact that there are no appropriate sources for the peroxy radicals. The other oxy radical, alkoxy radicals, can be produced by the thermal or photochemical decomposition of dialkyl peroxides,[2] alkyl hypohalites,[3] peroxy oxalates,[4]

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[1] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York (1966), Chap. 12; K. U. Ingold, International Symposium on Free Radicals in Solution, Ann Arbor, Mich,. Aug., 1966.

or hyponitrites.[5]

The absolute rate constants for the propagation step in the autoxidation of hydrocarbons, k_p, can be determined by either the rotating sector method[6] or the thermocouple method.[7] However, the reactivities of the hydrocarbons toward the peroxy radicals obtained from the absolute rate constants ate those toward the peroxy radicals derived from the hydrocarbons themselves, and the reactivities of the various hydrocarbons toward a specific peroxy radical can not be obtained.

Recently, the cooxidation method has been used in order to get information on this subject. By performing the cooxidations of binary mixtures of standard hydrocarbon and various hydrocarbons, relative reactivities can be obtained from the values of the reactivity ratios. Furthermore, the reactivities and selectivities of the various peroxy radicals may also be obtained from the reactivity ratios together with the knowledge of the absolute k_p values.

Thus, the reactivity ratios are understood to be very important, and several workers have tried to determine them. However, the precise determination of the reactivity ratios is very hard, and some of the values thus far reported are suspect. This paper will present an improved method for the determination of the reactivity ratios from the rates of cooxidation and will discuss the several methods thus far reported.

Results

Cooxidation of Cumene and Tetralin. When this work was started, the reactivity ratios, r, in the cooxidation of cumene (C) and tetralin (T) had been reported to be $r_c=0.043$ and $r_T=16$ at 90°C by Russell,[8] $r_T=10$ at 60°C by Alagy *et al.*,[9] and $r_C=0$ and $r_T=2.5$ at 60°C in a benzene solution by Russell and Williamson.[10] These values seemed inconsistent, and so the cooxidation of this binary system was reinvestigated in order to obtain reliable r values from the rates of cooxidation.[11]

In the oxidation of the binary mixtures of cumene and tetralin, the following six propagation steps and three termination steps are involved:

$$\begin{array}{lll}
\text{Propagation:} & C\cdot + O_2 \rightarrow CO_2\cdot & \\
 & T\cdot + O_2 \rightarrow TO_2\cdot & \\
 & CO_2\cdot + CH \rightarrow COOH + C\cdot & k_{CC} \\
 & CO_2\cdot + TH \rightarrow COOH + T\cdot & k_{CT} \\
 & TO_2\cdot + TH \rightarrow TOOH + T\cdot & k_{TT} \\
 & TO_2\cdot + CH \rightarrow TOOH + C\cdot & k_{TC} \\
\text{Termination:} & \left.\begin{array}{l} CO_2\cdot + CO_2\cdot \rightarrow \\ CO_2\cdot + TO_2\cdot \rightarrow \\ TO_2\cdot + TO_2\cdot \rightarrow \end{array}\right\} \begin{array}{l}\text{non-radical} \\ \text{products} + O_2\end{array} & \begin{array}{l} k_{tCC} \\ 2k_{tCT} \\ k_{tTT} \end{array}
\end{array}$$

The steady-state treatment gives the following rate equation:[14]

$$-\frac{dO_2}{dt}=\frac{(r_C[C]^2+2[C][T]+r_T[T]^2)R_i^{1/2}}{(r_C^2\delta_C^2[C]^2+2\phi r_C r_T\delta_C\delta_T[C][T]+r_T^2\delta_T^2[T]^2)^{1/2}} \tag{1}$$

where: $r_c = k_{CC}/k_{CT}$, $r_T = k_{TT}/k_{TC}$, $\delta_C = (2k_{tCC})^{1/2}/k_{CC}$,
$\delta_T = (2k_{tTT})^{1/2}/k_{TT}$, $\phi = k_{tCT}/(k_{tCC}k_{tTT})^{1/2}$.

It was confirmed that the rates of the cooxidation of cumene and tetralin were independent of the oxygen pressure above 150 mmHg and were proportional to the square root of the initiator concentrations; this demonstrates that only peroxy radicals are involved in the termination reactions and that Eq. (1) is obeyed under the reaction conditions employed.

The reactivity ratios were determined from the rates of cooxidation. Equation (1) has three unknown factors, r_c, r_T and ϕ. The expression:

$$F(r_C, r_T, \phi) = Ar_C^2 + Br_C r_T\phi + Cr_C r_T + Dr_T^2 + Er_C + Fr_T + G = 0 \tag{2}$$

where: $A = V\delta_C^2[C]^2-[C]^4$, $B = 2V\delta_C\delta_T[C][T]$,
$C = -2[C]^2[T]^2$, $D = V\delta_T^2[T]^2-[T]^4$,
$E = -4[C]^3[T]$, $F = -4[C][T]^3$,
$G = -4[C]^2[T]^2$, $V = (-dO_2/dt)^2/R_i$,

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2) E. G. E. Hawkins, "Organic Peroxides," Spon Ltd., London (1961).

3) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960), and the subsequent papers.

4) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1762 (1960).

5) H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, **1966**, 6163; *J. Am. Chem. Soc.*, **89**, 6667 (1967).

6) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2729 (1965).

7) J. A. Howard and J. C. Robb, *Trans. Faraday Soc.*, **59**, 1590 (1963).

8) G. A. Russell, *J. Am. Chem. Soc.*, **77**, 4583 (1955).

9) J. Alagy, G. Clement and J. C. Balaceanu, *Bull. Soc. Chim. France*, 1495 (1960).

10) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2364 (1964).

11) Recently, Mayo *et al.*[12] and Howard *et al.*[13] presented reasonable values for this system using different methods from ours: $r_C=0.13$ and $r_T=4.6$ at 60°C; $r_C=0.18$ and $r_T=4.5$ at 56°C, and $r_C=0.11$ and $r_T=8.3$ at 30°C, respectively.

12) F. R. Mayo, M. G. Syz, T. Mill and J. K. Castleman, International Oxidation Symposium, San Francisco, Calif., Aug., 1967.

13) J. A. Howard, W. J. Schwalm and K. U. Ingold, *ibid.*

14) E. Niki, Y. Kamiya and N. Ohta, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 42, 1679 (1967). A statistical factor of 2 is included in the cross termination rate constant, k_{tCT}. The definition of $\phi=k_{tCT}/2(k_{tCC}k_{tTT})^{1/2}$ instead based on the treatment of Flory gives the same rate equation.

can be derived from Eq. (1). The runs performed with various initial mixture compositions all give Eq. (2) with various values for each coefficient, A to G. The three unknowns can be calculated from each combination of the three equations, F_1, F_2, and F_3. By eliminating the term $r_{\mathrm{C}}r_{\mathrm{T}}\phi$ and then the term r_{T}^2, r_{T} can be expressed with r_{C} (Eq. (3)):

$$r_{\mathrm{T}} = (u_1 r_{\mathrm{T}}^2 + u_2 r_{\mathrm{T}} + u_3)/(u_4 r_{\mathrm{T}} + u_5) \tag{3}$$

where:
$$\begin{aligned}
u_1 &= a(D_1B_3-D_3B_1)-d(A_1B_3-A_3B_1),\\
u_2 &= e(D_1B_3-D_3B_1)-d(E_1B_3-E_3B_1),\\
u_3 &= g(D_1B_3-D_3B_1)-d(E_1B_3-E_3B_1),\\
u_4 &= -c(D_1B_3-D_3B_1)+d(C_1B_3-C_3B_1),\\
u_5 &= -f(D_1B_3-D_3B_1)+d(F_1B_3-F_3B_1),\\
a &= A_1B_2-A_2B_1, \quad c = C_1B_2-C_2B_1,\\
d &= D_1B_2-D_2B_1, \quad e = E_1B_2-E_2B_1,\\
f &= F_1B_2-F_2B_1, \quad g = G_1B_2-G_2B_1.
\end{aligned}$$

The substitution of r_{T} thus obtained into the equation obtained by eliminating the term $r_{\mathrm{C}}r_{\mathrm{T}}\phi$ yields the fourth-degree equation of r_{C} (Eq. (4)), which can be solved by substitution or by Newton's method:

$$G(r_{\mathrm{C}}) = v_1 r_{\mathrm{C}}^4 + v_2 r_{\mathrm{C}}^3 + v_3 r_{\mathrm{C}}^2 + v_4 r_{\mathrm{C}} + v_5 \tag{4}$$

where:
$$\begin{aligned}
v_1 &= au_4^2 + cu_1u_4 + du_1^2,\\
v_2 &= 2au_4u_5 + cu_2u_4 + cu_1u_5 + 2du_1u_2 + eu_4^2\\
&\quad + fu_1u_4,\\
v_3 &= au_5^2 + cu_3u_4 + cu_2u_5 + du_2^2 + 2du_1u_3\\
&\quad + 2eu_4u_5 + fu_2u_4 + fu_1u_5 + gu_4^2,\\
v_4 &= cu_3u_5 + 2du_2u_3 + eu_5^2 + fu_3u_4 + fu_2u_5\\
&\quad + 2gu_4u_5,\\
v_5 &= du_3^2 + fu_3u_5 + gu_5^2.
\end{aligned}$$

The values of u_i and v_i are functions of [C], [T], δ_{C}, δ_{T}, R_i and the rates of oxygen absorption. The substitution of r_{C} obtained from Eq. (3) gives r_{T}. Thus, from each of the combination of the three runs performed, r_{C} and r_{T} are obtained. The values for r_{C} and r_{T} numbering, ${}_nC_3$, can be obtained by performing the cooxidations with n different compositions.[15]

The values of δ were calculated from the rate equation for the oxidation of neat hydrocarbon, RH (Eq. (5)):

$$-\mathrm{dO_2/d}t = k_p(2k_t)^{-1/2}[\mathrm{RH}]R_i^{1/2} + R_i(1/e-1)/2 \tag{5}$$

The second term on the right hand of Eq. (5) is the correction for the nitrogen and oxygen evolved and is absorbed in the initiation and termination steps, e being the efficiency of the initiator. The values of $1.52\times10^{-4}\,\mathrm{sec}^{-1}$ and 0.65 were taken for k_i and e respectively at 80°C. The rates of the oxidation of pure cumene and tetralin at 80°C in the presence of 1.00×10^{-2} M of AIBN were 6.00×10^{-5} and 1.09×10^{-4} M/sec respectively, while values of 166 and 94.5 $(\mathrm{M\,sec})^{-1/2}$ were obtained for δ_{C} and δ_{T} respectively. The rates of the cooxidation of cumene and tetralin at 80°C are shown in Table 1.

Table 1. Rates of cooxidations of cumene and tetralin[a)]

Cumene M	Tetralin M	$-\mathrm{dO_2/d}t \times 10^5$ M/sec	ϕ[b)]
0.00	7.35	10.9	
2.40	4.90	7.72	4.12
3.60	3.68	6.13	4.38
4.80	2.45	4.69	4.39
6.00	1.23	3.49	4.40
6.55	0.668	3.17	4.41
7.20	0.00	6.00	

a) 80°C, [AIBN] = 1.00×10^{-2}M.
b) See text.

Examples of the solution of Eqs. (4) and (3) are shown in Fig. 1. Thus, the reactivity ratios were obtained as 0.21±0.01 and 5.0±0.1 for r_{C}

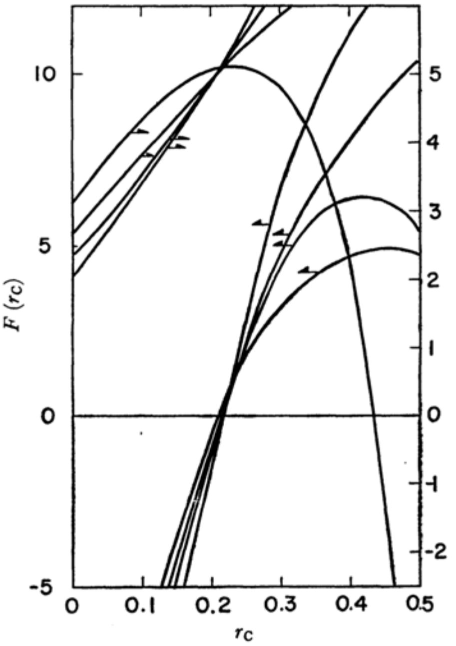

Fig. 1. Determination of r values in the cooxidation of cumene (C) and tetralin (T), 80°C.

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[15] Alagy *et al.*[9)] determined r values from the rates of cooxidation for the first time. They eliminated the term $r_{\mathrm{C}}r_{\mathrm{T}}\phi$ alone to obtain a group of quadratic equations of r_{C} *vs.* r_{T}, whose positive intersections being the solution. However, the drawing of the conics is troublesome. On the contrary, in the procedures presented in this paper, the values of two reactivity ratios can be obtained directly from the computer, more easily and more accurately.

and r_T respectively. These values seem reasonable compared with those of Mayo *et al.*[12] and Howard *et al.*[13] reported recently. Equation (1) can be solved for ϕ from a knowledge of the values of r_C and r_T, the two hydrocarbon concentrations, the rate of initiation, and the rate of oxidation. The results are shown in Table 1. A weighed average of 4.3 was taken as the value of ϕ.[16]

Cooxidation of Styrene and Tetralin. The cooxidation of styrene (S) and tetralin (T) was performed at 70°C under an atmospheric pressure of oxygen. This system was employed in order to establish the validity of our rate method for determining the reactivity ratios. Styrene[17] and tetralin are useful hydrocarbons since both of them produce secondary peroxy radicals whose termination reactions are simple compared with those of tertiary peroxy radicals; moreover, as will be discussed below, this system is suitable for the determination of the reactivity ratios by means of product analyses.

TABLE 2. RATES OF COOXIDATION OF STYRENE AND TETRALIN[a)]

Styrene M	Tetralin M	$-dO_2/dt$ $\times 10^5$ M/sec	Kinetic chain length	$(\text{M sec})^{-1/2}$	ϕ[b)]
8.75	0.00	14.0	272	44.8	
7.30	1.23	10.6	206		3.08
5.83	2.45	8.26	160		2.84
3.50	4.41	4.82	93.5		3.95
2.92	4.90	4.35	84.5		3.95
1.46	6.13	3.54	68.8		3.94
0.795	6.68	3.42	66.5		3.96
0.00	7.35	3.95	76.7	130	

a) 70°C, [AIBN] = 1.00×10^{-2}M.
b) Calculated assuming $r_S = 2.7$ and $r_T = 0.49$.

The rates of the cooxidations of styrene and tetralin are summarized in Table 2. A rate minimum is again observed in this system. The values of 2.7 and 0.49 were obtained for r_S and r_T respectively from the results in Table 2 by a treatment similar to that used for the system of cumene and tetralin. The value of ϕ was obtained as 3.9.

The reactivity ratios in this styrene-tetralin system were also determined by product analyses. In order to avoid high conversions of the oxidants, the oxygen uptake and the hydroperoxide formation were measured by the use of a gas buret and by the iodometric titration of the Wibaut method[18] respectively. The amount of styrene reacted was taken as the difference between the oxygen uptake and the hydroperoxide formed, the latter corre-

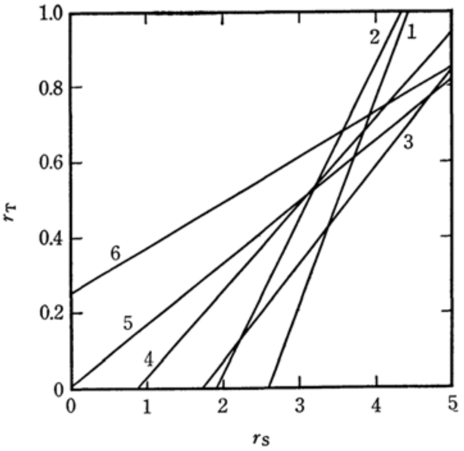

Fig. 2. Determination of r values in the cooxidation of styrene (S) and tetralin (T), 80°C; Mayo-Lewis method.

TABLE 3. COOXIDATIONS OF STYRENE (S) AND TETRALIN (T)[a)]

Run No.	1	2	3	4	5	6	7	8
$[S]_0$	17.50	0.00	10.50	8.76	7.00	5.84	4.36	2.92
$[T]_0$	0.00	15.70	5.88	7.36	8.82	9.80	11.02	12.26
Time, min	44	80	70	95	110	130	140	150
$-O_2$[b)]	0.698	0.386	0.606	0.638	0.636	0.606	0.562	0.592
conv., %	3.99	2.62	3.70	3.96	4.01	3.87	3.66	3.90
hpo[c)] $= \Delta T$	0.0036	0.370	0.0914	0.144	0.185	0.234	0.276	0.390
ΔS[d)]			0.5146	0.494	0.451	0.372	0.286	0.202
$[S]_f$			9.986	8.266	6.549	5.468	4.074	2.718
$[T]_f$			5.788	7.216	8.635	9.566	10.744	12.87

a) 70°C, 760 mmHg of oxygen pressure and 1.00×10^{-2}M of AIBN. Quantities in millimoles. The subscripts o and f represent the initial and final concentrations respectively.
b) After correction.
c) Hydroperoxide determined by the Wibaut method.[18] After correction for hydroperoxide from AIBN.
d) $S = (-O_2) - \Delta T$.

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16) Howard *et al.* reported the values of 5.9 and 4.8 for ϕ at 30°C and 56°C respectively.[13]

17) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956); F. R. Mayo, *ibid.*, **80**, 2465 (1958).

18) J. P. Wibaut, H. B. van Leeuwen and B. Van der Wal, *Rec. Trav. Chim.*, **73**, 1033 (1954).

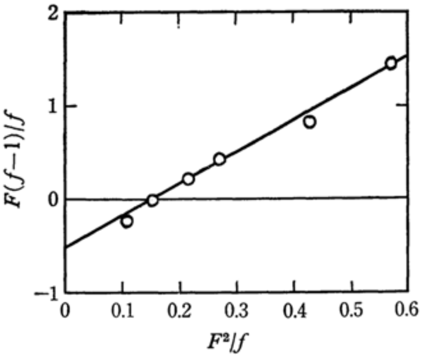


Fig. 3. Determination of r values in the cooxidation of styrene (S) and tetralin (T), 70°C; Fineman-Ross method.
The solid line corresponds to $r_S=3.3$ and $r_T=0.49$.
$F=[S]_0/[T]_0, f=\Delta S/\Delta T$

sponding to the disappearance of tetralin. The oxidation products of styrene are mostly styrene polyperoxide, plus small amounts of benzaldehyde and formaldehyde, under an atmospheric pressure of oxygen and with a long kinetic chain length.[17] The Wibaut method[18] gave little titer for polyperoxide, while the tetralyl hydroperoxide could be determined quantitatively (Table 3). This procedure was first employed by Mayo and his coworkers for the cooxidation of styrene and cumene.[12] The results are summarized in Table 3. The oxidations were performed up to a conversion of approximately 4% based on the oxygen uptake, where 2—7% of the initial hydrocarbons were oxidized. The results in Table 3 were treated by means of the Mayo-Lewis method[19] and the Fineman-Ross method,[20] which are shown in Figs. 2 and 3.

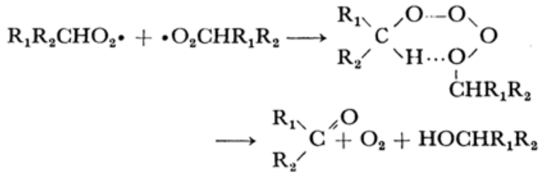
The r values obtained from the Mayo-Lewis method show considerable scatter. This must be mostly because the conversions of both hydrocarbons are very small where, as will be discussed later, a small error in the final concentrations of the hydrocarbons causes a large error in the r values. A Fineman-Ross plot gave the values of 3.3 and 0.49 for r_S and r_T respectively. These values are in reasonably good agreement with those obtained from the rates of cooxidation. Although the conversions were kept low, there still remains some possibility that some loss of precision is involved due to the complicated chain-transfer reaction of tetralyl hydroperoxide with the polystyrylperoxy radical.[21] On the other hand, the reactivity ratios can be determined from the rates of cooxidation at the initial stage of the oxidation.

Discussion

The merits and demerits of several methods for the determination of the reactivity ratios will be discussed in this section.

Determination from the Rates of Cooxidation. The merits of this method are, first, the rates of oxygen absorption can be measured quite easily and accurately, and secondly, they can be obtained at the initial stage of the oxidation. In the present work, the conversions of both hydrocarbons are about only 1% or less. These merits will become more obvious hereafter.

One of the difficulties comes from the complicated termination reactions. The chain termination reactions by secondary and primary peroxy radicals are now fairly well understood to proceed *via* the following cyclic transition state:[22]



The bimolecular interactions of tertiary peroxy radicals, lacking α-hydrogen, are complicated and have been studied intensively by many investigators recently.[23] As for the interaction between cumylperoxy radicals, it is assumed to produce oxygen and two cumyloxy radicals, a minor portion of which recombines in the cage to form dicumyl peroxide, while the rest undergoes cleavage reaction to give acetophenone and methyl radical. The methylperoxy radical produced from the methyl radical participates in the terminating reaction. This method of determining r values assumes that ϕ is a constant. However, as has been pointed out by Mayo,[12] the ϕ concept is an arbitrary one, and if the methylperoxy radical plays a significant part in the chain termination reaction, the three termination steps listed above may not be enough in themselves and so this method may be unreliable.

The absolute rate constants in the oxidations of cumene[7,13,23–26] and tetralin[27,28] have been de-

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[19] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

[20] M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).

[21] R. Hiatt, C. W. Gould and F. R. Mayo, *J. Org. Chem.*, **29**, 3461 (1964). See also discussion in the present text.

[22] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957); J. A. Howard and K. U. Ingold, *ibid.*, **90**, 1056 (1968).

[23] D. G. Hendry, *ibid.*, **89**, 5433 (1967), and papers cited therein.

[24] H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954). The values were corrected by a factor of 1.0/0.65 since Melville and Richards assumed that e was equal to 1.0.

[25] J. R. Thomas and C. A. Tolman, *J. Am. Chem. Soc.*, **84**, 2079 (1962).

termined and the extrapolated values of $k_{CC}=1.4$, $k_{tCC}=2.8\times10^4$, $k_{TT}=41$, and $k_{tTT}=9.8\times10^6\ \text{M}^{-1}\ \text{sec}^{-1}$ are obtained at 80°C. The other rate constants in the cooxidation of cumene and tetralin can be calculated by the use of these absolute rate constants, the two reactivity ratios, and the ϕ value. They are $k_{CT}=6.7$, $k_{TC}=8.2$, and $k_{tCT}=2.3\times10^6\ \text{M}^{-1}\ \text{sec}^{-1}$. From the four propagation rate constants, $k_{TC}/k_{CC}=5.9$ and $k_{TT}/k_{CT}=6.1$; this implies that the tetralylperoxy radical is approximately 6 times as reactive as the cumylperoxy radical toward cumene and tetralin.[29] The steady state concentrations of cumylperoxy and tetralylperoxy radicals can be calculated from Eqs. (6) and (7):

$$[\text{CO}_2\cdot] = k_{TC}[\text{C}]R_i^{1/2}/(2k_{tCC}k_{TC}^2[\text{C}]^2 + 4k_{tCT}k_{CT}k_{TC}[\text{C}][\text{T}] + 2k_{tTT}k_{CT}^2[\text{T}]^2)^{1/2} \tag{6}$$

$$[\text{TO}_2\cdot] = k_{CT}[\text{T}][\text{CO}_2\cdot]/k_{TC}[\text{C}] \tag{7}$$

In Fig. 4, the calculated concentrations are plotted against the hydrocarbon compositions, while Fig. 5 shows the rates of each of the four propagation steps. The rates of the individual termination reaction can be computed using the values of the peroxy radical concentrations and the absolute rate constants. The results are shown in Fig. 6. These figures show that the contribution of the bimolecular interaction of cumylperoxy radicals in the chain termination is small even when the concentration of the cumylperoxy radicals is much larger than that of the tetralylperoxy radical; for example, at the 0.90 molar fraction of cumene, the cumylperoxy radical is richer than the tetralylperoxy radical by a factor of 12, but the relative importance of the interaction of cumylperoxy radicals is only 5%, and 80% of the termination is performed by the reaction between cumylperoxy and tetralylperoxy radicals. The crossed interaction between cumylperoxy and tetralylperoxy radicals is assumed to proceed as follows to really terminate chains without any cleavage reaction to form the methyl radical.[31] Thus, the ϕ value may well be assumed to be constant when the concentration of tetralin is more than 10%.

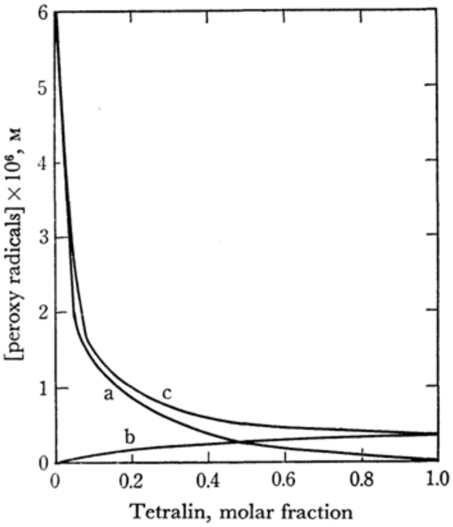
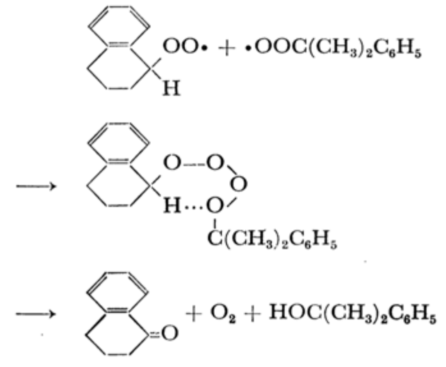


Fig. 4. Concentrations of peroxy radicals in the cooxidation of cumene (C) and tetralin (T), 80°C, [AIBN] = 1.0×10^{-2}.
a: $[\text{CO}_2\cdot]$, b: $[\text{TO}_2\cdot]$, c: $[\text{CO}_2\cdot]+[\text{TO}_2\cdot]$



The effects of error in the determination of the reactivity ratios from the rates of cooxidation were examined. Table 4 shows how a 10% error in r values affects the rates of cooxidation. It was confirmed that every group of the calculated rates of cooxidation in Table 4 gave the assumed r values. Since the plots of the oxygen uptake against the time gave an excellent straight line at the initial stage of the oxidation with satisfactory reproducibility, and since it is not difficult to obtain the rates of oxidation within an experimental error of 10%, accurate r values are expected to be obtained from the rates of cooxidation.

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26) A. A. Vichutinskii, *Dokl. Akad. Nauk SSSR*, **157**, 150 (1964).

27) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1119 (1966).

28) C. H. Bamford and M. J. S. Dewar, *Proc. Royal Soc.*, **A198**, 252 (1949).

29) If the reactivities of the peroxy radicals, ROO·, are independent of the structure of R, the product of two reactivity ratios is unity. However, it must be noteworthy that the product of two r values being unity does not always imply the identical reactivities of the peroxy radicals independent of their nature. Even if the reactivities are different, the product of two r values can be unity when the *relative* reactivities of the peroxy radicals are same toward the hydrocarbons. Ingold and his collaborators[27,30] suggest that the differences in the reactivities of the peroxy radicals are due to steric factors. But the difference in the electron affinity of the peroxy radicals may be responsible in part.

30) B. S. Middleton and K. U. Ingold, *Can. J. Chem.*, **45**, 191 (1967).

31) A large value of ϕ may also support this concept.

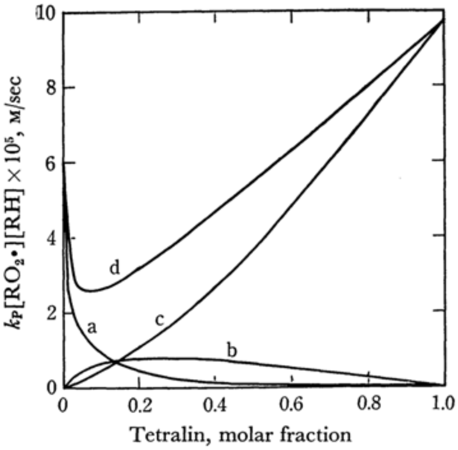

Fig. 5. Rates of propagation steps in the cooxidation of cumene (C) and tetralin (T), 80°C, [AIBN] = 1.0×10^{-2}M.
a: $k_{CC}[CO_2\cdot][CH]$, b: $k_{CT}[CO_2\cdot][TH]=k_{TC}[TO_2\cdot][CH]$, c: $k_{TT}[TO_2\cdot][TH]$, d: a+2b+c

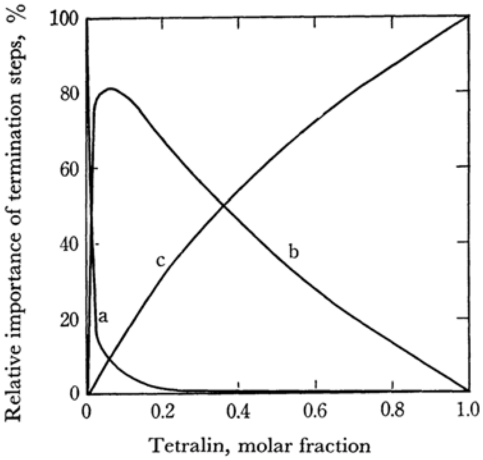

Fig. 6. Relative importance of the termination steps in the cooxidation of cumene (C) and tetralin (T), 80°C, [AIBN] = 1.0×10^{-2}.

$$\left.\begin{array}{l}\text{a: COO}\cdot+\text{COO}\cdot\\ \text{b: COO}\cdot+\text{TOO}\cdot\\ \text{c: TOO}\cdot+\text{TOO}\cdot\end{array}\right\}\rightarrow\text{non-radical products}+O_2$$

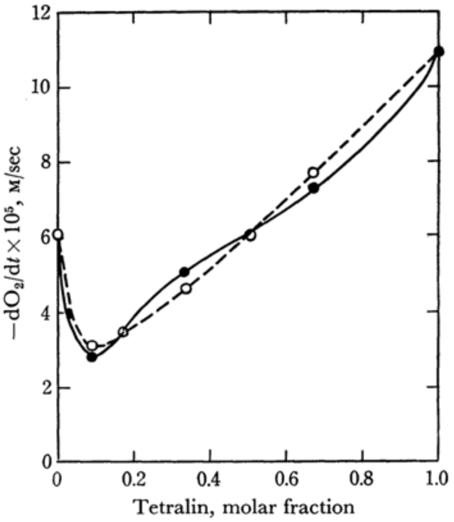

Fig. 7. Rates of cooxidation of cumene and tetralin, 80°C, [AIBN] = 1.0×10^{-2}.
○: observed, ●: assumed (see text)

It was found, however, that when the curve obtained by plotting the rates of oxidation against the hydrocarbon compositions is uneven, a small error in the rate will produce a large error in the reactivity ratios. Figure 7 shows a plot obtained by assuming that Nos. 1,3, and 5 in Table 4 have −10%, +10% and −5% errors respectively in the rates of oxidation. The curve, as may be seen, is uneven. The calculation of the reactivity ratios from Eqs. (4) and (3) using these values gave poor results. For example, Nos. 1, 2 and 4 gave the values of 0.06 and 2.0 for r_C and r_T respectively, while Nos. 1, 3, and 4 gave 0.0 and 0.6. It was also found that the smaller the curvature of the plot, the larger the effects of error in the rate of oxidation on the reactivity ratios (see No. 5 in Table 4).

The above discussion suggests that the determination of the reactivity ratios from the rates of cooxidation is reliable and useful if a smooth plot is obtained between the rates of cooxidation and hydrocarbon compositions and if the curvature is

TABLE 4. EFFECTS OF ERROR IN THF REACTIVITY RATIOS ON THE RATES OF COOXIDATION OF CUMENE AND TETRALIN[a)]

No.	Cumene M	Tetralin M	$(-dO_2/dt)_{obs.}$ $\times10^5$ M/sec	$(-dO_2/dt)\times10^5$ in M/sec calculated by assuming[b)]:								
				r_C=0.21	0.21	0.21	0.19	0.19	0.19	0.23	0.23	0.23
				r_T=5.0	4.5	5.5	5.0	4.5	5.5	5.0	4.5	5.5
1	6.55	0.668	3.17	3.20	3.35	3.08	3.21	3.36	3.08	3.20	3.34	3.08
2	6.00	1.23	3.49	3.52	3.65	3.41	3.57	3.71	3.46	3.48	3.61	3.36
3	4.80	2.45	4.69	4.72	4.82	4.63	4.81	4.92	4.72	4.63	4.73	4.55
4	3.60	3.68	6.13	6.15	6.22	6.09	6.25	6.33	6.18	6.06	6.12	6.00
5	2.40	4.90	7.72	7.68	7.72	7.65	7.76	7.82	7.72	7.60	7.64	7.57

a) 80°C, [AIBN] = 1.00×10^{-2}M.
b) $\delta_C=166$, $\delta_T=94.5$, $R_i=1.98\times10^{-6}$ M/sec, and $\phi=4.3$.

large, preferably when the rate minimum is observed.

Mayo-Lewis Method.[19] This method was derived from the copolymerization equation[32] and was first applied to the cooxidations of benzaldehydes by Walling and McElhill.[33] The initial and final concentrations of both hydrocarbons must be known. The two initial concentrations can be calculated, and the final concentrations are measured experimentally either by analyzing them directly by means, for example, of gas-liquid chromatography or by analyzing the products. Russell and Williamson[10] determined the reactivity ratios for many systems by making use of this method. However, in most cases employed, the reactivity ratios show considerable scatter. The best results were obtained for the system of cumene and *cis*-decalin. Table 5 shows their results and also some values calculated assuming that the errors indicated in the eighth column are involved. The solutions of the results in Table 5 by using the integrated form of the Mayo-Lewis method are shown in Fig. 8, which indicates that a small error will produce a large error in *r* values. Experimentally, the values of $r_C=0.58$ and $r_D=1.56$ are obtained, but when one of the three concentrations contains an error of 5%, the values of r_C and r_D are 0.70 and 1.7 (Nos. 1, 2, 6); 0.69 and 1.4 (1, 3, 5); 0.48 and 1.3 (2, 3, 4), and 0.39 and 1.4 (1,2,7) respectively. Thus an error of only 5% in one of the three systems will produce a 10—30% error in the reactivity ratios. Furthermore, analyses by gas-liquid chromatography are usually apt to involve a greater error. When the conversions of the hydrocarbons are small, this analytical error may be more critical.

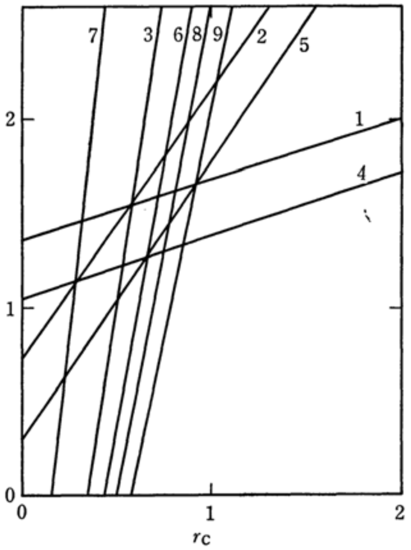

Fig. 8. Cooxidations of cumene (C) and *cis*-decalin (D), 60°C.

On the other hand, if the oxidation advances and hydroperoxides are built up considerably, the following cross induced decomposition of hydroperoxides by the peroxy radicals complicates the kinetic scheme. The work by Thomas and Tolman[25] and by Howard, Schwalm, and Ingold[13] indicates the possibilities of these reactions:

$$\text{AOOH} + \text{BOO}\cdot \longrightarrow \text{AOO}\cdot + \text{BOOH}$$
$$\text{BOOH} + \text{AOO}\cdot \longrightarrow \text{BOO}\cdot + \text{AOOH}$$

In order to reduce this difficulty, Hendry[34] devised a new technique in which the consumption of the more reactive hydrocarbon and the oxygen uptake are measured. This procedure is especially attractive in cases where reactants have large differences in reactivity. However, even in this procedure, the conversion of the more reactive hydrocarbon is more than 10%, generally between 20—25%.[34]

TABLE 5. COOXIDATIONS OF CUMENE (C) AND *cis*-DECALIN (D)

No.	$[C]_0$ M	$[D]_0$ M	$[C]_f$ M	$[D]_f$ M	Conv., % C	Conv., % D	Error %[b]
1	0.200	0.800	0.192	0.750	4.0	6.2	
2	0.500	0.500	0.466	0.446	6.8	10.8	
3	0.800	0.200	0.726	0.170	9.2	15.0	
4	0.200	0.800	0.183	0.713			− 5
5	0.500	0.500	0.443	0.424			− 5
6	0.800	0.200	0.690	0.162			− 5
7	0.800	0.200	0.762	0.178			+ 5
8	0.800	0.200	0.654	0.153			−10
9	0.800	0.200	0.581	0.136			−20

a) The values of Nos. 1, 2, and 3 are the results of Russell and Williamson at 60°C in benzene.[10]

b) Assumed.

Fineman-Ross Method.[20] This method was also derived from the copolymerization equation. A limitation of this method is that this can be used only when the conversions of both oxidants are small enough so that the decrease in the concentrations is negligible compared with their initial concentrations. The determination of the variation in the reactants at the very initial stage is very difficult.

Hydroperoxide Method. Recently, Howard, Schwalm, and Ingold[13] proposed a new method for the determination of the reactivity ratios. They

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[32] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[33] C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, **73**, 2927 (1951).

[34] D. G. Hendry, International Oxidation Symposium, San Francisco, Calif., Aug., 1967.

have oxidized one hydrocarbon in the presence of hydroperoxide derived from another hydrocarbon. In the oxidation of the system of AH plus BOOH, the following elementary steps are involved:[13)]

$$\begin{array}{lll}
\mathrm{AH} \longrightarrow \mathrm{A}\cdot & & R_i = \text{Rate of initiation} \\
\mathrm{A}\cdot + \mathrm{O_2} \longrightarrow \mathrm{AOO}\cdot & & \\
\mathrm{AOO}\cdot + \mathrm{BOOH} \longrightarrow & & \\
\quad \mathrm{AOOH} + \mathrm{BOO}\cdot & & k_{\mathrm{ABOOH}} \\
\mathrm{BOO}\cdot + \mathrm{AH} \longrightarrow \mathrm{BOOH} + \mathrm{A}\cdot & & k_{\mathrm{BA}}\ (\ll k_{\mathrm{ABOOH}}) \\
2\,\mathrm{BOO}\cdot \longrightarrow \text{non-radical products} & & k_{t\mathrm{BB}}
\end{array}$$

A steady state treatment gives the following rate equation:

$$-\mathrm{dO_2}/\mathrm{d}t = k_{\mathrm{BA}}[\mathrm{AH}]R_i^{1/2}/(2k_{t\mathrm{BB}})^{1/2} \qquad (8)$$

Since [AH], R_i, and $k_{t\mathrm{BB}}$ are known, k_{BA} can be calculated by measuring the rate of oxidation. If k_{BA} is known, r_{B} can be calculated with the value of k_{BB}, which can be measured separately.

Howard *et al.*[13)] assumed that the termination reaction is solely by the interaction of the peroxy radicals which were derived from the hydroperoxide. However, there remains some possibility that a cross termination reaction by AOO· and BOO· radicals as well as the bimolecular interaction of BOO· radicals may also be important, especially when the latter is much slower than the former. Actually, in a mixture of tetralin and cumyl hydroperoxide, the cross termination between cumylperoxy and tetralylperoxy radicals is calculated, from the concentrations of both peroxy radicals and the absolute rate constants, to compose up to 30% of the total. Another limitation is that this method is applicable only for the peroxy radicals whose incipient hydroperoxides can be isolated.

In conclusion, the method for the determination of the reactivity ratios must be carefully chosen depending on the systems. When the rates of cooxidation are plotted against the reactant compositions, three types of lines are obtained: a large curvature, a gently-sloping curve, and a straight line. In cases where a large curvature, preferably a rate minimum, is observed and a smooth line is obtained, the determination from the rates of cooxidation may be most suitable. In other cases, the use of the copolymerization equation may be preferable. A direct determination of the reactants by gas-liquid chromatography is not appropriate, and the measurements of the oxygen uptake and/or hydroperoxide formed, and the analyses of hydroperoxides are more suitable when the copolymerization equation is used. The hydroperoxide method may be valid for some systems.

Experimental

Cumene and tetralin were shaken successively with sulfuric acid, water, alkali, and water, dried with calcium chloride, and then distilled under reduced pressure of nitrogen. Styrene was washed with alkali and then with water, dried, and distilled under reduced pressure of nitrogen. All the hydrocarbons were passed down the activated alumina column immediately before use. Azobisisobutyronitrile was recrystallized from methanol several times. Oxygen was used without further purification.

The rate of oxygen absorption was measured by a manometer in a constant pressure closed system. Stirring was accomplished by means of a magnetic stirrer with a Teflon-coated stirring bar. The volume of oxygen absorbed was read periodically, every one or two minutes, depending on the rate, and was plotted against the time. In every run, more than fifteen points were plotted. No induction period was observed, and a straight line was obtained. The slope was read and was taken as the rate of oxidation. The cell was cleaned by washing successively with a solution of $K_2Cr_2O_7$ plus concentrated sulfuric acid, ammonia, water, acetone, and methanol, and then dried. Hydroperoxide was determined by iodometric titration, the Wibaut method,[18)] where hydroperoxide was treated with KI in 80% acetic acid at room temperature.

The calculation was done at the Data Processing Center of the University of Tokyo using a OKITAC 5090 computer.