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# Cooxidation of Hydrocarbons in Liquid Phase. VI. Reactivities of Hydrocarbons and Peroxy Radicals

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Cooxidation of all the combinations of two hydrocarbons among styrene, α-methylstyrene, tetralin and cumene was studied at 70°C in the presence of azobisisobutyronitrile as a thermal initiator. The reactivity ratios for each binary mixture were determined by several appropriate methods. The relative reactivities of styrene, α-methylstyrene, tetralin and cumene toward the peroxy radicals were approximately in the ratio 15 : 10 : 5 : 1. It was also concluded that the secondary peroxy radicals were more reactive than the tertiary peroxy radicals and that the polymeric peroxy radicals were more reactive than the normal alkylperoxy radicals.

The cooxidation of the binary mixtures of styrene, α-methylstyrene, tetralin and cumene was studied and the reactivity ratios were determined by several methods in order to obtain an information on the reactivities of the hydrocarbons and of the peroxy radicals toward each other.

## Results

The rates of cooxidations of 6 systems are shown in Fig. 1. In all cases, the observed rates of oxygen absorption were corrected for nitrogen evolved by the decomposition of AIBN, oxygen absorbed by the dimethylcyanomethyl radical, and oxygen evolved in the termination step.1) The reactivity ratios, $r$, were determined by several methods discussed in a previous paper.1)

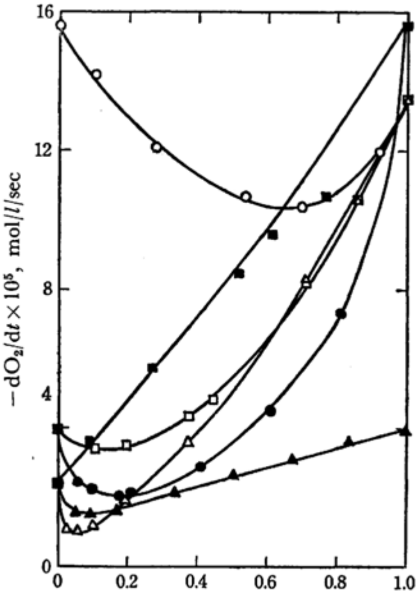

Fig. 1. Cooxidation of hydrocarbons.
70°C, oxygen pressure = 760 mmHg,
AIBN = $1.00 \times 10^{-2}$ M
- ○: Styrene (I) - α-methylstyrene (II)
- □: Styrene (I) - tetralin (II)
- △: Styrene (I) - cumene (II)
- ●: α-Methylstyrene (I) - tetralin (II)
- ■: α-Methylstyrene (I) - cumene (II)
- ▲: Tetralin (I) - cumene (II)

**Styrene (S) and α-Methylstyrene (M).** The reactivity ratios were determined from the rates of cooxidations by our rate method1,2) and the values of 1.6 and 0.71 were obtained for $r_S$ and $r_M$ respectively. The product of the two reactivity ratios is 1.1.

**Styrene (S) and Tetralin (T).** This system was studied previously.1) Our rate method gave the values of $r_S = 2.7$ and $r_T = 0.49$, while the Fineman-Ross method gave the values of $r_S = 3.0$ and $r_T = 0.45$.1)

**Styrene (S) and Cumene (C).** The reactivity ratios were determined by measuring the oxygen uptake and hydroperoxide formed, which was first employed by Mayo and his co-workers.3) The results are summarized in Table 1. Hydroperoxide was determined by the Wibaut method.4) The oxidation of styrene gives mostly styrene polyperoxide with small amounts of benzaldehyde and formaldehyde.5) The Wibaut method4) gives little titer for the oxidation of styrene,1) while cumyl hydroperoxide can be determined quantitatively by this method (Table 1). The slightly greater yield of cumyl hydroperoxide than expected in the oxidation of cumene may be ascribed to the oxidation which proceeds after the absorption measurement is completed, while the product is being removed from the reaction vessel for analysis. It was demonstrated that the titrable hydroperoxide was unstable in the oxidizing styrene.6) In order to minimize this complication, the conversions were kept very low. Thus, the hydroperoxide determined by the Wibaut method was taken as the amount of cumene reacted, and styrene reacted was calculated from the difference between oxygen uptake and hydroperoxide formed. The reactivity ratios were determined by the Fineman-

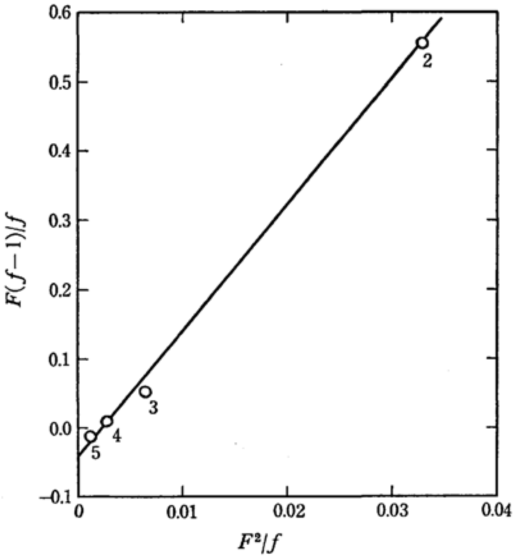

Fig. 2. Fineman-Ross plot for the cooxidation of styrene and cumene.
70°C, oxygen pressure = 760 mmHg

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1) E. Niki, Y. Kamiya and N. Ohta, This Bulletin, **42**, 512 (1969).

2) E. Niki, M. Kuwata, Y. Kamiya and N. Ohta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 1679 (1967).

3) F. R. Mayo, M. G. Syz, T. Mill and J. K. Castleman, "Advances in Chemistry Series," Vol. 75, Am. Chem. Soc., Washington D. C. (1968), p. 38.

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

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

6) R. Hiatt, C. W. Gould and F. R. Mayo, *J. Org. Chem.*, **29**, 3461 (1964).

TABLE 1. COOXIDATIONS OF STYRENE (S) AND CUMENE (C) AT 70°C

| Run No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $[S]_0$, M | 0.00 | 2.92 | 0.730 | 0.398 | 0.208 |
| $[C]_0$, M | 7.20 | 4.80 | 6.60 | 6.87 | 7.02 |
| S, molar fraction | 0.000 | 0.378 | 0.0995 | 0.0548 | 0.0288 |
| Time, min | 30 | 24 | 45 | 36 | 33 |
| $(-O_2)_{observed}$, mM | 42.5 | 46.1 | 30.5 | 22.4 | 19.7 |
| $(-O_2)_{corrected}$, mM[a] | 42.8 | 46.3 | 30.9 | 22.7 | 20.0 |
| Conversion, %[b] | 0.59 | 0.60 | 0.43 | 0.30 | 0.28 |
| $(hpo)_{observed}$, mM | 46.4 | 3.78 | 10.8 | 10.1 | 11.7 |
| $(hpo)_{corrected} = \Delta C$, mM[c] | 46.4 | 3.76 | 10.7 | 10.1 | 11.7 |
| $\Delta S$, mM[d] |  | 42.54 | 20.2 | 12.6 | 8.3 |
| $(hpo)/(-O_2)$ | 1.08 | 0.0811 | 0.346 | 0.445 | 0.585 |
| $F = [S]_0/[C]_0$ |  | 0.609 | 0.111 | 0.0580 | 0.0296 |
| $f = \Delta S/\Delta C$ |  | 11.3 | 1.89 | 1.25 | 0.710 |

a) $(-O_2)_{corrected} = (-O_2)_{observed} + R_i(1/e - 1)/2$. $R_i$ and $e$ represent the rate of initiation and the efficiency of the radical production from initiator respectively. The correction was made for nitrogen evolved in the initiation step, and for oxygen absorbed and evolved in the initiation and termination steps.

b) (Initial hydrocarbon concentration)/$(-O_2)$.

c) $(hpo)_{corrected} = (hpo)_{observed} - (hpo\text{ from AIBN})$, where hpo represents hydroperoxide. $\Delta C$ means cumene reacted.

d) $\Delta S$ = Styrene reacted.

TABLE 2. COOXIDATIONS OF $\alpha$-METHYLSTYRENE (M) AND TETRALIN (T) AT 70°C

| Run No. | 6 | 7 | 8 | 9 |
|---|---|---|---|---|
| $[M]_0$, M | 2.56 | 1.78 | 0.905 | 0.700 |
| $[T]_0$, M | 4.90 | 5.65 | 6.50 | 6.68 |
| M, molar fraction | 0.344 | 0.240 | 0.122 | 0.0948 |
| Time, min | 70 | 80 | 60 | 50 |
| $(-O_2)_{observed}$, mM | 104 | 103 | 76.1 | 68.0 |
| $(-O_2)_{corrected}$, mM | 105 | 104 | 76.6 | 68.4 |
| Conversion, % | 1.41 | 1.40 | 1.03 | 0.93 |
| $(hpo)_{observed}$, mM | 32.6 | 46.9 | 57.1 | 55.5 |
| $(hpo)_{corrected} = \Delta T$, mM[a] | 31.4 | 44.8 | 53.5 | 51.0 |
| $\Delta M$, mM[b] | 73.6 | 59.2 | 23.1 | 17.4 |
| $F = [M]_0/[T]_0$ | 0.522 | 0.315 | 0.139 | 0.105 |
| $f = \Delta M/\Delta T$ | 2.34 | 1.32 | 0.432 | 0.341 |

a) $\Delta T$ = tetralin reacted. b) $\Delta M$ = $\alpha$-methylstyrene reacted.

Ross method:[7]

$$\frac{F}{f}(f-1) = r_S\frac{F^2}{f} - r_C\,, \qquad (1)$$

where $F = [S]_0/[C]_0$ and $f = \Delta S/\Delta C$. Figure 2 gives the values of 18 and 0.045 for $r_S$ and $r_C$ respectively. These values are reasonably in agreement with the values of $r_S = 20$ and $r_C = 0.05$ at 60°C obtained by Mayo and his co-workers.[3]

**$\alpha$-Methylstyrene (M) and Tetralin (T).** Previously, we obtained the values $r_M = 5.5$ and $r_T = 0.70$ by our rate method.[2] Since the product of these two reactivity ratios exceeds unity considerably, the reactivity ratios for this binary mixture were determined by two other methods.

The amounts of oxygen uptake and hydroperoxide formation determined by the Wibaut method in the cooxidations of $\alpha$-methylstyrene and tetralin are shown in Table 2. This method is the same as that employed in the cooxidations of styrene and cumene. The Fineman-Ross plot obtained by the results in Table 2 is shown in Fig. 3, which gives the values of 6.1 and 0.41 for $r_M$ and $r_T$ respectively. The product of the two reactivity ratios is 2.5.

The $r_T$ value was determined separately by the hydroperoxide method which was first employed

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

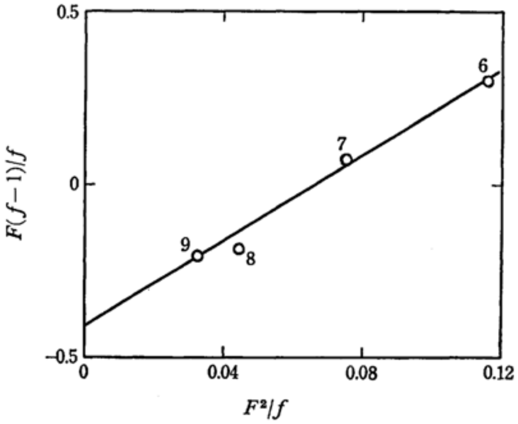

Fig. 3. Fineman-Ross plot for the cooxidation of α-methylstyrene and tetralin.
70°C, oxygen pressure = 760 mmHg

by Howard, Schwalm and Ingold.[8] This method was devised on the basis that the peroxy radicals abstract the hydrogen atom from hydroperoxides much faster than they abstract the hydrogen atom from the hydrocarbons or add to the double bond.

When enough tetralyl hydroperoxide is added in the oxidation of α-methylstyrene, the tetralylperoxy radical contributes as a chain carrier, and the rate of oxidation is given by

$$-\mathrm{d}O_2/\mathrm{d}t = k_{\mathrm{TM}}[\mathrm{M}]R_i^{1/2}/(2k_{\mathrm{tTT}})^{1/2} = k_{\mathrm{TM}}[\mathrm{M}](ek_i[\mathrm{AIBN}]/k_{\mathrm{tTT}})^{1/2}, \quad (2)$$

where $R_i$ is the rate of initiation, $e$ the efficiency of the radical production, and $k_{\mathrm{TM}}$ and $k_{\mathrm{tTT}}$ the rate constants of the following reactions:

$$\mathrm{TO_2}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{TM}}} \mathrm{TOOM}\cdot\ ,$$

$$\mathrm{TO_2}\cdot + \mathrm{TO_2}\cdot \xrightarrow{k_{\mathrm{tTT}}} \text{tetralone} + \text{tetralol} + \mathrm{O_2}\,.$$

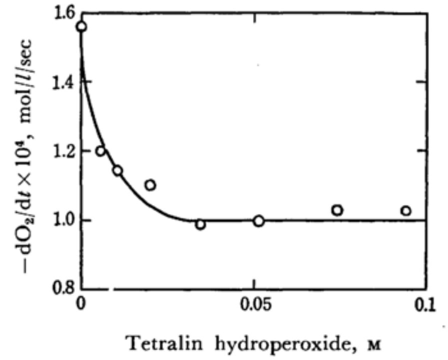

Fig. 4. Oxidation of α-methylstyrene in the presence of tetralin hydroperoxide.
70°C, oxygen pressure = 760 mmHg,
AIBN = $1.00\times10^{-2}$ M

The rates of the oxidation of α-methylstyrene in the presence of tetralyl hydroperoxide are shown in Fig. 4 as a function of the concentration of tetralyl hydroperoxide. The rates of the oxidation of α-methylstyrene decrease with an increase in the concentration of tetralyl hydroperoxide; this is because the rapid termination by the two secondary tetralylperoxy radicals replaces the slower termination by the tertiary α-methylstyrylperoxy radicals. But when the concentration of tetralyl hydroperoxide exceeds $3.5\times10^{-2}$ mol/$l$, the rates of the oxidation of α-methylstyrene are virtually constant, $1.00\times10^{-4}$ mol/$l$/sec. The rate constants for the individual step in the oxidation of tetraline were determined by several investigators,[9-11] and the compilation and extrapolation to 70°C of the reported data give the values 30 and $8.0\times10^6$ $l$/mol/sec for $k_p$ and $k_t$ respectively. Substitution of the values $1.00\times10^{-4}$ mol/$l$/sec, 7.70 mol/$l$, 0.65, $3.96\times10^{-5}$ sec$^{-1}$, $1.00\times10^{-2}$ mol/$l$, and $8.0\times10^6$ $l$/mol/sec for the rate of oxidation, [M], $e$, $k_i$, [AIBN], and $k_{\mathrm{tTT}}$, respectively, into the Eq. (2) gives $k_{\mathrm{TM}}$ to be 72. Therefore, the $r_{\mathrm{T}}$ is calculated to be 30/72 = 0.42.

**α-Methylstyrene (M) and Cumene (C).** In a previous paper[12] of this series, we have obtained the reactivity ratios for this system as $r_{\mathrm{M}}=9.3$ and $r_{\mathrm{C}}=0.10$ by using Mayo-Lewis method.[13]

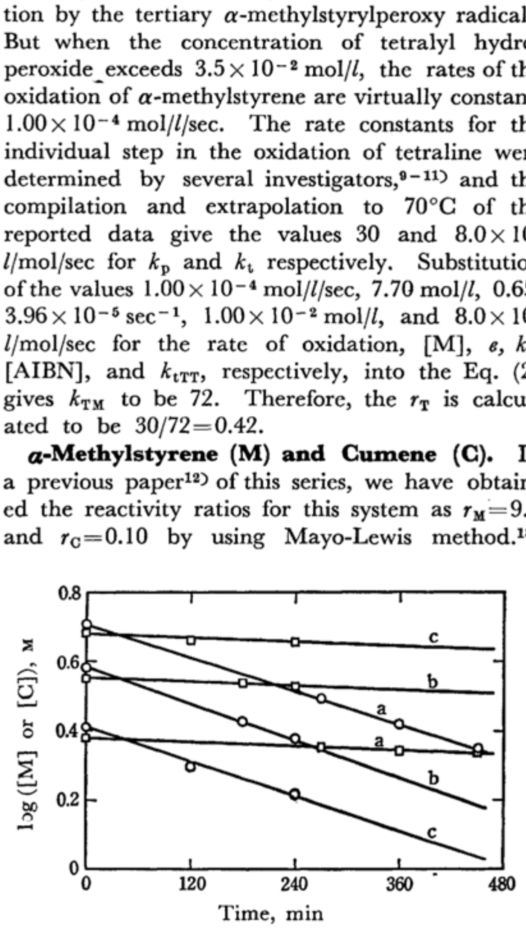

Fig. 5. Cooxidation of α-methylstyrene and cumene.
70°C, oxygen pressure = 760 mmHg,
AIBN = $1.00\times10^{-2}$ M
○: α-Methylstyrene, □: cumene
a : $[\mathrm{M}]_0=5.13$, $[\mathrm{C}]_0=2.40$
b : $[\mathrm{M}]_0=3.85$, $[\mathrm{C}]_0=3.60$
c : $[\mathrm{M}]_0=2.57$, $[\mathrm{C}]_0=4.80$

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[8] J. A. Howard, W. J. Schwalm and K. U. Ingold, "Advances in Chemistry Series," Vol. 75, Am. Chem. Soc., Washington D. C. (1968), p. 6.

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

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

[11] H. Berger, A. M. W. Blaauw, M. M. Al and P. Smael, "Advances in Chemistry Series," Vol. 75, Am. Chem. Soc., Washington D. C. (1968), p. 346.

[12] E. Niki and Y. Kamiya, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 42 (1967).

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

Table 3. The rates of oxidations of $\alpha$-methylstyrene and cumene in their cooxidations
70°C, oxygen pressure=760 mmHg, [AIBN]=$1.00\times10^{-2}$ M

| $[\mathrm{M}]_0$ M | $[\mathrm{C}]_0$ M | $-\mathrm{d}M/\mathrm{d}t\times10^4$ mol/$l$/sec | $-\mathrm{d}C/\mathrm{d}t\times10^5$ mol/$l$/sec | $F=[\mathrm{M}]_0/[\mathrm{C}]_0$ | $f=\frac{(-\mathrm{d}M/\mathrm{d}t)}{(-\mathrm{d}C/\mathrm{d}t)}$ |
|---|---|---|---|---|---|
| 5.13 | 2.40 | 1.58 | 0.815 | 2.14 | 19.4 |
| 3.85 | 3.60 | 1.26 | 1.26 | 1.07 | 10.0 |
| 2.57 | 4.80 | 0.872 | 1.77 | 0.535 | 4.92 |

The rates of disappearance of $\alpha$-methylstyrene and cumene were followed by gas-liquid chromatography, and as a result the conversion of the hydrocarbons, especially that of $\alpha$-methylstyrene, was rather high. In order to avoid the complicated effects of the oxidation products and of the variation of the medium, the $r$ values were determined using the rates of oxidation of both hydrocarbons at the initial stage. The concentrations of the two hydrocarbons were measured periodically and the in logarithm was plotted against time as shown in Fig. 5. The calculated rates of oxidations of $\alpha$-methylstyrene and cumene are given in Table 3, and the Fineman-Ross plot obtained from these data are shown in Fig. 6. The solid line in Fig. 6 corresponds to $r_M=9.3$ and $r_C=0.10$.

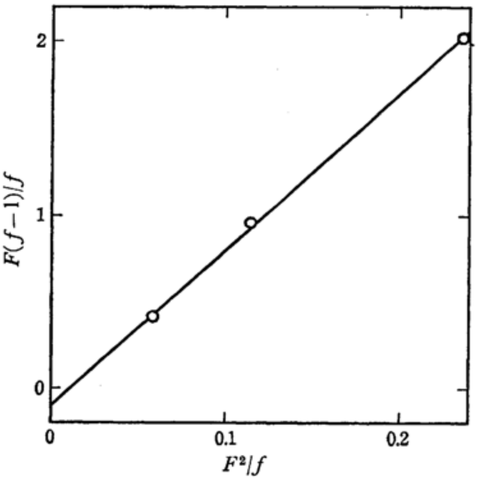

Fig. 6. Fineman-Ross plot for the cooxidation of $\alpha$-methylstyrene and cumene.
The solid line corresponds to $r_M=9.3$ and $r_C=0.10$.
70°C, oxygen pressure=760 mmHg

**Tetralin (T) and Cumene (C).** The values 4.2 and 0.19 were obtained for $r_T$ and $r_C$ respectively at 70°C from the rates of cooxidations using our rate method.[14]

## Discussion

In the past, it was generally accepted that the peroxy radicals derived from the hydrocarbons had approximately the same reactivities independent of their structures, and the rates of the reactions of peroxy radicals with hydrocarbons were determined solely by the hydrocarbons. If the reactivities of the peroxy radicals are really independent of their nature, the product of the two reactivity ratios is necessarily unity, since, in the cooxidations of the binary mixture of the hydrocarbons A and B,

$$k_{AA}=k_{BA},\ k_{BB}=k_{AB}$$

hence,

$$r_Ar_B=(k_{AA}/k_{AB})(k_{BB}/k_{BA})=(k_{AA}/k_{BA})(k_{BB}/k_{AB})=1$$

Alagy *et al.* determined the reactivity ratios for several systems and concluded that the reactivities of the peroxy radicals were dependent on the structure on the basis that the products of the two reactivity ratios deviated from unity.[15] On the contrary, Russell and Willamson[16] concluded that the reactivities of the peroxy radicals are fairly independent of their nature. Recently, this problem has received much attention. Howard and Ingold demonstrated by determining the absolute rate constants for hydrocarbon oxidations that the reactivities of the peroxy radicals are dependent on their structure, and that the primary peroxy radicals are more reactive than the secondary peroxy radicals and in turn the secondary peroxy radicals are more reactive than the tertiary ones.[10,17-19] They attributed the differences in the reactivities of the peroxy radicals to the steric effect. On the other hand, Mayo and his coworkers reported that the relative reactivities of the hydrocarbons toward various peroxy radicals were nearly independent of the alkylperoxy radicals involved.[3]

It is worth pointing out that the fact that the product of two reactivity ratios is unity does not always imply the same reactivities of the various peroxy radicals. Even if the absolute reactivities

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[14] E. Niki, Y. Kamiya and N. Ohta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 859 (1968).

[15] J. Alagy, G. Clement and J. C. Balaceanu, *Bull. Soc. Chim. France*, **1960**, 1495; **1961**, 1303, 1792.

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

[17] K. U. Ingold, Intern. Symp. Free Radicals in Solution, Univ. of Michigan, Ann Arbor, Mich., 1966.

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

[19] J. A. Howard and K. U. Ingold, *ibid.*, **46**, 2655, 2661 (1968).

of the peroxy radicals are different, the product of two reactivity ratios can be unity. For example, when the peroxy radical $AO_2\cdot$ is more reactive than the peroxy radical $BO_2\cdot$ by a factor of $p$ toward both hydrocarbons A and B, the product of $r_A$ and $r_B$ is:

$$r_A \times r_B = (k_{AA}/k_{AB})(k_{BB}/k_{BA})$$
$$= (k_{AA}/k_{BA})(k_{BB}/k_{AB}) = p/p = 1$$

Another problem is the error involved in the reactivity ratios. It is extremely difficult to obtain accurate $r$ values in the cooxidation of the hydrocarbons. If it is assumed that the reactivity ratios contain 10, 20, 30, and 50% of error, then the product of two $r$ values lies in the range of 0.81—1.2, 0.64—1.4, 0.49—1.7, and 0.25—2.3, respectively. Thus, it would be risky to estimate whether the reactivities of the different peroxy radicals are the same or not from the product of two reactivity ratios.

After all, the reactivities of the peroxy radicals may be evaluated from the absolute propagation rate constants and the reactivity ratios. In Table 4 are summarized the reactivity ratios obtained for the cooxidation of styrene, α-methylstyrene, tetralin and cumene at 70°C.

TABLE 4. THE REACTIVITY RATIOS AT 70°C

| Hydrocarbon A | Hydrocarbon B | $r_A$ | $r_B$ | $r_Ar_B$ |
|---|---|---|---|---|
| Styrene | α-Methylstyrene | 1.6 | 0.71 | 1.1 |
| Styrene | Tetralin | 2.9 | 0.47 | 1.4 |
| Styrene | Cumene | 18 | 0.045 | 0.81 |
| α-Methylstyrene | Tetralin | 5.7 | 0.51 | 2.9 |
| α-Methylstyrene | Cumene | 9.3 | 0.10 | 0.93 |
| Tetralin | Cumene | 4.2 | 0.19 | 0.80 |

The calculated rate constants for the reactions of styryl, α-methylstyryl, tetralyl and cumyl peroxy radicals with these four hydrocarbons are shown in Table 5. The absolute rate constants at 70°C for styrene,[20] α-methylstyrene[10,21] tetralin,[9-11] and cumene[11,22-26] were calculated from the compilation of the values in literature. Table 5 indicates that the rate constants for the reactions of hydrocarbons with peroxy radicals are dependent on both of them. The relative reactivities of the hydrocarbons toward the peroxy radicals and *vice versa* calculated from Table 5 are shown in Tables 6 and 7 respectively. Table 6 indicates that the relative reactivities of styrene, α-methylstyrene, tetralin, and cumene are approximately in the ratio 15 : 10 : 5 : 1. On the other hand, Table 7 shows that the secondary peroxy radicals are more reactive than the tertiary peroxy radicals, and that the polymeric peroxy radicals are more reactive than the usual monomeric aralkylperoxy radicals.

The results and discussion given above suggest that the rates of the reactions between hydrocarbons and peroxy radicals depend not only on the hydrocarbons being attacked but also on the attacking peroxy radicals. The reactivities of the hydrocarbons may be determined mostly by the bond dissociation energy of the bond being broken and the degree of the resonance stabilization of the radical newly formed. Probably, both steric and polar effects may be responsible for the differences in the reactivities of the peroxy radicals. Howard and Ingold[10,18] emphasized the steric effects to explain the differences in the reactivities of the peroxy radicals. Indeed the relative reactivities of cumene and tetralin toward various free radicals and atoms suggest the considerable steric effects of the attacking species,[27] but it is not clear whether

TABLE 5. RATE CONSTANTS FOR THE REACTIONS OF PEROXY RADICALS WITH HYDROCARBONS AT 70°C

| Hydrocarbon | $(k_p/(2k_t)^{1/2})\times 10^3$ $(l/\text{mol/sec})^{1/2}$ | Rate constants in $l$/mol/sec[b] | | | |
|---|---|---|---|---|---|
| | | $SO_2\cdot$ | $MO_2\cdot$ | $TO_2\cdot$ | $CO_2\cdot$ |
| Styrene | 22.2 | 210[a] | 69 | 64 | 27 |
| α-Methylstyrene | 28.1 | 130 | 48[a] | 59 | 12 |
| Tetralin | 7.70 | 72 | 8.4 | 30[a] | 6.3 |
| Cumene | 4.63 | 12 | 5.2 | 7.1 | 1.2[a] |

a) Calculated by extrapolation from literature values; see text.
b) $SO_2\cdot$, $MO_2\cdot$, $TO_2\cdot$, and $CO_2\cdot$ represent styryl-, α-methylstyryl-, tetralyl-, and cumylperoxy radicals respectively.

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20) J. A. Howard and H. U. Ingold, *ibid.*, **43**, 2729, 2737 (1965).

21) J. A. Howard and K. U. Ingold, *ibid.*, **44**, 1113 (1966).

22) H. W. Melville and S. Richards, *J. Chem. Soc.*, **1954**, 944.

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

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

25) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 793 (1967).

26) D. G. Hendry, *J. Am. Chem. Soc.*, **89**, 5433 (1967).

27) E. Niki, Y. Kamiya and N. Ohta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 1187 (1968).

TABLE 6. RELATIVE REACTIVITIES OF HYDROCARBONS TOWARD PEROXY RADICALS AT 70°C

| Hydrocarbon | Peroxy radical | | | |
|---|---|---|---|---|
| | $SO_2\cdot$ | $MO_2\cdot$ | $TO_2\cdot$ | $CO_2\cdot$ |
| Styrene | 18 | 13 | 8.9 | 22 |
| $\alpha$-Methylstyrene | 11 | 9.3 | 8.2 | 10 |
| Tetralin | 6.2 | 1.6 | 4.2 | 5.3 |
| Cumene | 1 | 1 | 1 | 1 |

TABLE 7. RELATIVE REACTIVITIES OF PEROXY RADICALS TOWARD HYDROCARBONS AT 70°C

| Hydrocarbon | Peroxy radical | | | |
|---|---|---|---|---|
| | $SO_2\cdot$ | $MO_2\cdot$ | $TO_2\cdot$ | $CO_2\cdot$ |
| Styrene | 7.8 | 2.6 | 2.4 | 1 |
| $\alpha$-Methylstyrene | 11 | 4.0 | 4.9 | 1 |
| Tetralin | 11 | 1.3 | 4.8 | 1 |
| Cumene | 10 | 4.3 | 5.9 | 1 |

the volume of the hydrocarbon portion of the peroxy radicals is so important in determining the reactivities of the peroxy radicals. The thermodynamic data also throw doubt upon the importance of the steric effects of the peroxy radicals. Most alkyl-alkyloxy bond strengths are about 78 kcal.[28] But the bond strength of the *t*-butyl - *t*-butoxy bond is 69 kcal.[28] The 9 kcal lowering of the C–O bond dissociation energy observed in the *t*-butyl ether is attributed to the repulsion of closely bound bulky *t*-butyl groups.[28] On the other hand, the O–O bond dissociation energies of dimethyl, diethyl, dipropyl, and di-*t*-butyl peroxides are approximately the same.[28] These facts suggest that the volume of R in ROOR does not give a significant steric effect in contrast with ROR. Howard and Ingold related the differences in the reactivities of the primary, secondary and tetrtiary peroxy radicals to the chain termination reactions of these peroxy radicals.[10] However, the rates of chain terminating bimolecular interactions of the peroxy radicals may be dependent more on the mechanism of the reaction and statistical factors, *i. e.*, absence or presence of $\alpha$-hydrogen atoms and their number than on the steric effects.

If the steric effects of the attacking peroxy radicals are really important, the steric structure of the hydrocarbons being attacked may also have at least large effects. In this case, the product of two reactivity ratios is expected to deviate from unity. For example, if cumylperoxy radical is less reactive than tetralylperoxy radical due to the steric factors, then the steric effects may be more significant when the peroxy radicals abstract a hydrogen atom from cumene than from tetralin. That is

$$k_{TT}/k_{CT} < k_{TC}/k_{CC}\,.$$

Hence

$$r_T r_C = (k_{TT}/k_{TC})(k_{CC}/k_{CT}) < 1\,.$$

Thus, if the steric factors affect the reactivities of the hydrocarbons and the peroxy radicals, the product of the two reactivity ratios deviates from unity.

## Experimental

Styrene and $\alpha$-methylstyrene were washed with dilute alkali and water, dried, and distilled under reduced pressure of nitrogen. Tetralin and cumene were washed successively with sulfuric acid, water, alkali and water, dried, and then distilled under reduced pressure of nitrogen. All these four hydrocarbons were passed down the activated alumina column before use. Tetralyl hydroperoxide was prepared by the air oxidation of tetralin at 65°C for 50 hr in the presence of AIBN followed by the repeated recrystallization from *n*-hexane. Commercial AIBN was recrystallized from methanol.

The rate of cooxidation was measured by following the oxygen uptake periodically in a constant pressure closed system. The formation of hydroperoxide was measured by the iodometric titration employed by Wibaut *et al.*[4] In the cooxidation of $\alpha$-methylstyrene and cumene, the disappearance of the two hydrocarbons was determined by the gas - liquid chromatography using Apiezon-L column at 170°C. The calculation of the data was performed at the Data Processing Center of the University of Tokyo.

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[28] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).