A Computer Simulation of the Oxidation Mechanism. The Liquid-phase Oxidation of Cumene Catalyzed by Triphenylsulfonium Chloride

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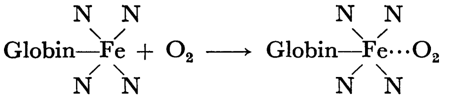
The mechanism of the liquid-phase oxidation of cumene (RH) catalyzed by triphenylsulfonium chloride was investigated by the computer simulation on the basis of the kinetic analysis. We will discuss particularly the initial short stage of the reaction through the time-conversions of the concentrations of components produced or consumed: R·, RO_2·, ROOH, a complex between the catalyst and O_2 (Cat.–O_2), *etc.* We determined the values of the rate constants appearing in the reaction steps with a good analytic fit to the experimental results, together with the activation energies of all the reaction steps. The following relationships were found between the initial rate of the component formation, r_i (component), and the initial concentration of reactants ((Cat.)$_i$, (RH)$_i$, and (O_2)$_i$):

$$r_i(\mathrm{Cat.{-}O_2}) \simeq 1.243 \times 10^{-2}(\mathrm{Cat.})_i^{0.970}(\mathrm{RH})_i^{0.0}(\mathrm{O_2})_i^{0.964} \quad \mathrm{mol}/l\cdot\mathrm{min}$$
$$r_i(\mathrm{R}\cdot) \simeq 4.705 \times 10^{-12}(\mathrm{Cat.})_i^{0.648}(\mathrm{RH})_i^{1.886}(\mathrm{O_2})_i^{-0.422} \quad \mathrm{mol}/l\cdot\mathrm{min}$$
$$r_i(\mathrm{RO_2}\cdot) \simeq 5.837 \times 10^{-12}(\mathrm{Cat.})_i^{0.316}(\mathrm{RH})_i^{0.509}(\mathrm{O_2})_i^{0.737} \quad \mathrm{mol}/l\cdot\mathrm{min}$$
$$r_i(\mathrm{ROOH}) \simeq 4.860 \times 10^{-4}(\mathrm{Cat.})_i^{0.436}(\mathrm{RH})_i^{1.842}(\mathrm{O_2})_i^{0.850} \quad \mathrm{mol}/l\cdot\mathrm{min}$$

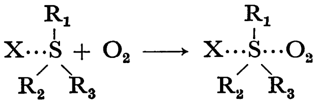
It is well known that, in the liquid-phase oxidation of hydrocarbons, some chelate compounds such as copper phthalocyanine[1] participate in the catalytic activation of the ground state, $^3\Sigma_g^-O_2$, as:

$$\text{Cu-pc} + O_2 \longrightarrow \text{Cu-pc}^{\delta+}\cdots O_2^{\delta-} \qquad (1)$$

where Cu-pc denotes copper phthalocyanine. With respect to the catalytic activation of the $^3\Sigma_g^-O_2$, other types of catalysts, such as hemoglobin[2] and sulfonium compounds,[3] can also activate the $^3\Sigma_g^-O_2$:



$$\text{Globin—Fe(N)}_4 + O_2 \longrightarrow \text{Globin—Fe(N)}_4\cdots O_2 \qquad (2)$$



$$\text{X}\cdots\text{S}(R_1)(R_2)(R_3) + O_2 \longrightarrow \text{X}\cdots\text{S}(R_1)(R_2)(R_3)\cdots O_2 \qquad (3)$$

(R_1, R_2, R_3 = alkyl or aryl group)

The complex expressed in Eq. (3) has been previously demonstrated in our kinetic study[4] of the mechanism of cumene oxidation catalyzed by triphenylsulfonium chloride. Such an interaction between sulfonium compounds and the $^3\Sigma_g^-O_2$ has also been confirmed by UV spectroscopic[5] and MO-theoretical studies.[6] Judging from the fact that a sulfonium catalyst plays an important role in the catalytic activation of the ground state $^3\Sigma_g^-O_2$, the first step can be said to consist of the formation of a complex, Cat.–O_2, as:

$$\text{Cat.} + O_2 \underset{k_i'}{\overset{k_i}{\rightleftarrows}} \text{Cat.–}O_2 \qquad (4a)$$

where Cat. denotes a sulfonium compound. Such a complex, Cat.–O_2, then abstracts an active hydrogen from hydrocarbon (RH) to produce an alkyl radical (R·):

$$\text{Cat.–}O_2 + \text{RH} \xrightarrow{k_1} \text{R}\cdot + \text{Cat.} + \cdot O_2H \qquad (4b)$$

This is followed by the usual propagation steps:

$$\text{R}\cdot + O_2 \xrightarrow{k_p} RO_2\cdot \qquad (4c)$$

$$RO_2\cdot + \text{RH} \xrightarrow{k_2} \text{ROOH} + \text{R}\cdot \qquad (4d)$$

The termination steps are:

$$2RO_2\cdot \xrightarrow{k_t} \text{inactive products} \qquad (4e)$$

$$\text{Cat.} \xrightarrow{k_d} \text{inactive form} \qquad (4f)$$

The deactivation of the catalyst is taken into consideration by Eq. (4f), and the possibility of the radical recombination of other types (R·+R· or R·+RO_2·) is discarded under the present reaction conditions, *i.e.*, an oxygen pressure above 200 mm of mercury.[7] In addition, the decomposition reaction of hydroperoxide is neglected in this paper, because the quantity of O_2 consumed by RH (mol) corresponds to that of hydroperoxide formed (mol) during the initial short stage of the reaction.

The present study has been undertaken in an attempt to elucidate the oxidation mechanism, especially that during the initial short stage of the reaction, by the use of a simulation analysis on a high-speed computer, with attention given to the time-conversions of unstable

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1) H. Kropf, *Ann.*, **637**, 73 (1960); H. Kropf and Hd. Hoffmann *Tetrahedron Lett.*, **1967**, 659.

2) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U. S.*, **22**, 210 (1936); L. Pauling, *Nature*, **203**, 182 (1964); J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956); J. J. Weiss, *Nature*, **202**, 83 (1964); *ibid.*, **203**, 183 (1964); R. D. Harcourt, *Int. J. Quantum Chem.*, **5**, 479 (1971).

3) K. Fukui, K. Ohkubo, and T. Yamabe, This Bulletin, **42**, 312 (1969); K. Okhubo, T. Yamabe, and K. Fukui, *ibid.*, **42**, 2220 (1969); K. Okhubo and T. Yamabe, *Bull. Jap. Petrol. Inst.*, **12**, 130 (1970).

4) K. Ohkubo, T. Yamabe, and K. Fukui, This Bulletin, **42**. 1800 (1969).

5) K. Ohkubo and T. Yamabe, *J. Org. Chem.*, **36**, 3149 (1971).

6) K. Ohkubo, *Tetrahedron Lett.*, **1971**, 2571, 2897; K. Ohkubo and T. Yamabe, This Bulletin, **44**, 1183 (1971); K. Ohkubo and H. Kanaeda, *Trans. Faraday Soc.*, **68**, 1164 (1972).

7) The effect of the O_2 pressure on the reaction rate does not generally appear above an O_2 pressure of 200 mmHg.

intermediates, oxidants, and reactants; this initial short stage holds the key to the reaction, though chemical and physical studies of the alkyl radical formation are in an early stage of development.

Procedure of Simulation

Normal reaction sequences can be expressed by the following general form:

$$R_1 + R_2 + \cdots + R_n \xrightarrow{k} P_1 + P_2 + \cdots + P_m \qquad (5)$$

where R_i are reactants, P_i are products, and k is the rate constant. The reaction increments (or decrements) D are shown, with dt representing a very short time interval, as follows:

$$D = k\prod_{i=1}^{n}(R_i)\mathrm{d}t \qquad (6)$$

During such a very short time interval, dt, such increments (or decrements) at the reaction time t, D_t, can be expressed by:

$$D_t = \frac{D_{t+\mathrm{d}t} + D_{t-\mathrm{d}t}}{2} \qquad (7)$$

where $D_{t+\mathrm{d}t}$ and $D_{t-\mathrm{d}t}$ are the reaction increments (or decrements) at the reaction times of $t+\mathrm{d}t$ and $t-\mathrm{d}t$ respectively ($D_{-\mathrm{d}t}=D_0$). The average increments (or decrements), D_{av}, are, then, defined by:

$$D_{av} = \frac{D_t + D_{t+\mathrm{d}t}}{2} \qquad (8)$$

From Eqs. (7) and (8),

$$D_{av} = 1.5D_t - 0.5D_{t-\mathrm{d}t} \qquad (9)$$

The concentrations of reactants (R_i) and products (P_i) are, then, changed with D_{av}:

$$\begin{aligned}(R_i)_t &= (R_i)_{t-\mathrm{d}t} - D_{av}\\ &= (R_i)_{t-\mathrm{d}t} - (1.5D_t - 0.5D_{t-\mathrm{d}t}) \qquad (10a)\end{aligned}$$

$$\begin{aligned}(P_i)_t &= (P_i)_{t-\mathrm{d}t} + D_{av}\\ &= (P_i)_{t-\mathrm{d}t} + (1.5D_t - 0.5D_{t-\mathrm{d}t}) \qquad (10b)\end{aligned}$$

This calculation method gives a trapezoidal averaging which is superior to simple decrementing, and this form of calculation is superior to the Runge-Kutta integration.[8] The present simulations on the oxidation mechanism without the ROOH decomposition were carried out in the following way. A series of increments ($D(i)$, i=1—7) are defined by the following terms on the basis of the reaction schemes presented previously (see Introduction):

$$D(1) = k_i(O_2)(\mathrm{Cat.})\mathrm{d}t \qquad (11a)$$

$$D(2) = k_i'(\mathrm{Cat.\text{-}O_2})\mathrm{d}t \qquad (11b)$$

$$D(3) = k_1(\mathrm{RH})(\mathrm{Cat.\text{-}O_2})\mathrm{d}t \qquad (11c)$$

$$D(4) = k_p(O_2)(\mathrm{R}\cdot)\mathrm{d}t \qquad (11d)$$

$$D(5) = k_2(\mathrm{RH})(\mathrm{RO_2}\cdot)\mathrm{d}t \qquad (11e)$$

$$D(6) = k_t(\mathrm{RO_2}\cdot)^2\mathrm{d}t \qquad (11f)$$

$$D(7) = k_d(\mathrm{Cat.})\mathrm{d}t \qquad (11g)$$

For each chemical equation, there is a corresponding differential term:

$$\begin{aligned}\mathrm{d(Cat.)}/\mathrm{d}t &= k_1(\mathrm{RH})(\mathrm{Cat.\text{-}O_2})\\ &\quad + k_1'(\mathrm{Cat.\text{-}O_2}) - k_i(O_2)(\mathrm{Cat.}) - k_d(\mathrm{Cat.}) \qquad (12a)\end{aligned}$$

$$\begin{aligned}\mathrm{d(Cat.\text{-}O_2)}/\mathrm{d}t &= k_i(O_2)(\mathrm{Cat.})\\ &\quad - k_1(\mathrm{RH})(\mathrm{Cat.\text{-}O_2}) - k_i'(\mathrm{Cat.\text{-}O_2}) \qquad (12b)\end{aligned}$$

$$\begin{aligned}\mathrm{d(R\cdot)}/\mathrm{d}t &= k_1(\mathrm{RH})(\mathrm{Cat.\text{-}O_2})\\ &\quad + k_2(\mathrm{RH})(\mathrm{RO_2}\cdot) - k_p(O_2)(\mathrm{R}\cdot) \qquad (12c)\end{aligned}$$

$$\begin{aligned}\mathrm{d(RO_2\cdot)}/\mathrm{d}t &= k_p(O_2)(\mathrm{R}\cdot) - k_2(\mathrm{RH})(\mathrm{RO_2}\cdot)\\ &\quad - k_t(\mathrm{RO_2}\cdot)^2 \qquad (12d)\end{aligned}$$

$$\mathrm{d(ROOH)}/\mathrm{d}t = k_2(\mathrm{RH})(\mathrm{RO_2}\cdot) \qquad (12e)$$

$$\mathrm{d(\cdot O_2H)}/\mathrm{d}t = k_1(\mathrm{RH})(\mathrm{Cat.\text{-}O_2}) \qquad (12f)$$

$$\mathrm{d(inactive\ product)}/\mathrm{d}t = k_t(\mathrm{RO_2}\cdot)^2 \qquad (12g)$$

$$\mathrm{d(inactive\ form)}/\mathrm{d}t = k_d(\mathrm{Cat.}) \qquad (12h)$$

From Eqs. (11a—g) and (12a—h), the following relationships can be derived:

$$D(\mathrm{Cat.})_{av} = D(2)_{av} + D(3)_{av} - D(1)_{av} - D(7)_{av} \qquad (13a)$$

$$D(\mathrm{Cat.\text{-}O_2})_{av} = D(1)_{av} - D(2)_{av} - D(3)_{av} \qquad (13b)$$

$$D(\mathrm{R}\cdot)_{av} = D(3)_{av} + D(5)_{av} - D(4)_{av} \qquad (13c)$$

$$D(\mathrm{RO_2}\cdot)_{av} = D(4)_{av} - D(5)_{av} - D(6)_{av} \qquad (13d)$$

$$D(\mathrm{ROOH})_{av} = D(5)_{av} \qquad (13e)$$

$$D(\cdot\mathrm{O_2H})_{av} = D(3)_{av} \qquad (13f)$$

$$D(\mathrm{inactive\ product})_{av} = D(6)_{av} \qquad (13g)$$

$$D(\mathrm{inactive\ form})_{av} = D(7)_{av} \qquad (13h)$$

The desired concentrations of a component C (reactant, intermediate, or product), $(\mathrm{C})_t$, at the reaction time, t, can be determined by:

$$(\mathrm{C})_t = (\mathrm{C})_i + \int_0^t D(\mathrm{C})_{av}\mathrm{d}t \qquad (14)$$

where $(\mathrm{C})_i$ and $D(\mathrm{C})_{av}$ are, respectively, the initial concentrations of the components, C, and the over-all increments (or decrements) changing with t. In this paper, the $(\mathrm{C})_t$ values were evaluated every 0.1 sec.

Simulation Results and Discussion

Determination of Rate Constants. Mention should first be made of some characteristic features of the liquid-phase oxidation of cumene (RH) catalyzed by triphenylsulfonium chloride. The oxidation proceeds without any appreciable incubation period; its reaction rate soon reaches its maximum after the start of the reaction (usually up to 600 sec) and then gradually decreases to its stationary state. Moreover, the decomposition of the cumene hydroperoxide (ROOH) accumulated can be neglected for *ca.* 1 hr after the start under the usual reaction conditions.[4] In the previous kinetic study[4] of this cumene oxidation, some values of the rate constants in Eqs. (4a—f) have been determined at 65°C as below:

$$k_i = 2.23\times10^{-2}\,\mathrm{mol^{-1}\cdot}l\mathrm{\cdot sec^{-1}};\quad k_i' = 0.82\times10^{-3}\,\mathrm{sec^{-1}};$$

$$k_1 = 0.794\times10^{-3}\,\mathrm{mol^{-1}\cdot}l\mathrm{\cdot sec^{-1}};\ k_d = 1.39\times10^{-3}\,\mathrm{sec^{-1}}.$$

With respect to the rate constant of the termination

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[8] E. Whitaker and A. Robinson, "The Calculation of Observations," Blackie and Son, London (1944), p. 132; H. Margenau and G. H. Murphy, "The Mathematics of Physics and Chemistry," D. van Nostrand, New York (1943), p. 450; R. W. Southwork and S. L. Deleeuw, "Digital Computation and Numerical Methods," McGraw Hill, New York (1965), p. 420.

reaction (Eq. (4e)) Melville and Richards[9] have reported $k_t=3.3\times10^4\,\text{mol}^{-2}\cdot l^2\cdot\text{sec}^{-1}$ at 65°C in the cumene oxidation. We will here determine the k_p and k_2 values, with a good analytic fit for the simulation analyses. Figure 1 indicates the dependence of the ROOH concentration, (ROOH), upon various k_p and k_2 values (from $k_p(O_2)_i$[10]$=\sim10^6$ to $k_p(O_2)_i=\sim10^2$ with a factor of ten); the time-conversion curves are not directly influenced by the settled k_p values, but are directly changed by k_2 values. Bearing in mind that k_p values usually fall in the range from $\sim10^6$ to $\sim10^7$,[11] the k_p value for the cumene oxidation at 65°C can be set at 1.185×10^7 ($k_p(O_2)_i=5.0\times10^5$).

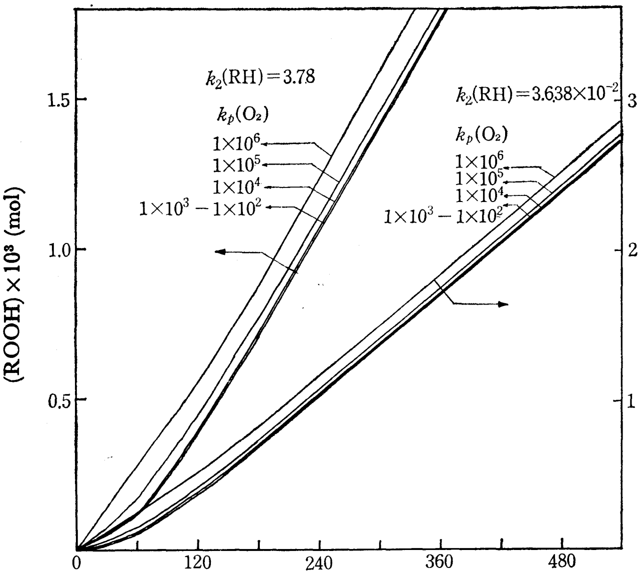

Fig. 1. Variation in time-conversion of (ROOH) with $k_p(O_2)$ and k_2(RH) values.
Initial condition: $(\text{Cat.})_i=3.35\times10^{-4}\text{mol}/l$; $(\text{RH})_i=6.75\ \text{mol}/l$; $(O_2)_i=4.22\times10^{-2}\ \text{mol}/l$.

Next, let us determine the k_2 value, which usually falls in the range of 10^{-1}—10^{-2} as a factor of ten in the autoxidation of cumene, tetralin, or ethyl linoleate at 25—65°C.[14] Figure 2 shows the time-conversion curves of (ROOH) at various k_2 values, together with the experimental curve obtained from cumene (6.75 mol/l) oxidation catalyzed by triphenylsulfonium chloride (3.35×10^{-4} mol/l) at 65°C under atmospheric pressure. As can be seen from Fig. 2, (ROOH) varies in parallel with the k_2(RH) value at a fixed $k_p(O_2)$ value, and the k_2 value of $9.63\times10^{-2}\,\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$ ($k_2(\text{RH})_i=0.65$) can be taken as the most preferable value with a good analytic fit. Tests of the fitness of k_2 value ($9.63\times10^{-2}\,\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$) for the simulation analyses well made. The results of these tests are shown in Fig. 3, where the variations in the time-conversion of the rate of ROOH formation (r(ROOH)) with $(\text{Cat.})_i$ are illustrated, together with the experimental data.[15] From Fig. 3, $k_2=9.63\times10^{-2}\,\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$ is considered to be fit for the present simulations

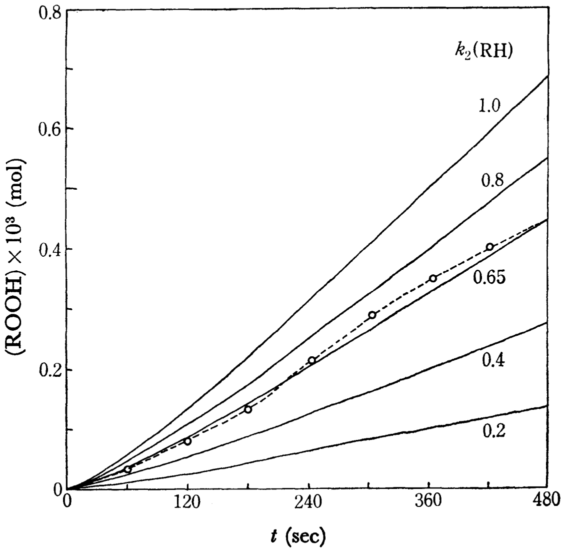

Fig. 2. Variation in time-conversion of (ROOH) with k_2(RH) values. (Dotted curve indicates the experimental result.) Initial condition: $(\text{Cat.})_i=3.35\times10^{-4}\ \text{mol}/l$; $(\text{RH})_i=6.75\ \text{mol}/l$; $(O_2)_i=4.22\times10^{-2}\ \text{mol}/l$.

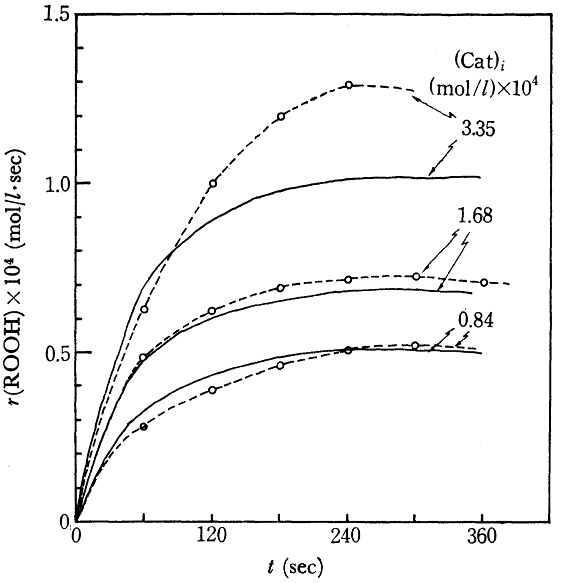

Fig. 3. Variations in time-conversion of ROOH concentration with initial concentration of Cat. (Solid and dotted curves indicate simulation and experimental results respectively.)
Initial condition: $(\text{Cat.})_i$=variable; $(\text{RH})_i=6.75\ \text{mol}/l$; $(O_2)_i=4.22\times10^{-2}\ \text{mol}/l$.

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[9] H. W. Melville and S. Richards, *J. Chem. Soc.*, **1954**, 944,

[10] $(O_2)_i$ means the initial concentration of O_2. Hereafter, the initial concentrations of the components, (C), will be expressed by $(C)_i$; for instance, $(\text{RH})_i$, $(\text{Cat.})_i$, $(\text{R}\cdot)_i$, *etc.*

[11] For example, $k_i(\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1})$ at 25°C$=6.76\times10^7$,[12] 1.0×10^7,[13] and 1.0×10^6 [13] for tetralin, ethyl linoleate, and digeranyl respectively.

[12] C. H. Banford and M. J. S. Dewar, *Proc. Roy. Soc., Ser. A*, **198**, 252 (1949).

[13] L. Bateman, *Quart. Rev.*, **8**, 147 (1954).

[14] C. Walling, "Free Radicals in Solution," John Wiley, New York (1957), p. 422.

[15] The experimental rate curves can be reproduced with a good analytic fit by $r=k(\text{RH})_i^{1.27}(O_2)_i^{0.68}(\text{Cat.})_i(e^{-at}-e^{-bt})$, where k, a, and b are constants the values of which have been reported in Ref. 4.

of the initial short stage of the oxidation, within the range of observational and calculational errors.[16] Here, the time-conversions of the concentrations of reactants, intermediates, and a product, (Cat.), (Cat.–O_2), ($\cdot O_2H$), ($R\cdot$), ($RO_2\cdot$), and (ROOH), are shown in Fig. 4 for the sake of understanding the reaction system; (Cat.–O_2), ($RO_2\cdot$), and ($R\cdot$) soon arrived at their maxima (t=300 sec) and then gradually lowered to their apparent stationary concentrations. Their distributions were, for instance, at 300 sec, roughly expressed by:

$$(\text{Cat.-}O_2):(R\cdot):(RO_2\cdot):(\text{ROOH}) \simeq 1:7\times10^{-8}:5\times10^{-2}:10$$

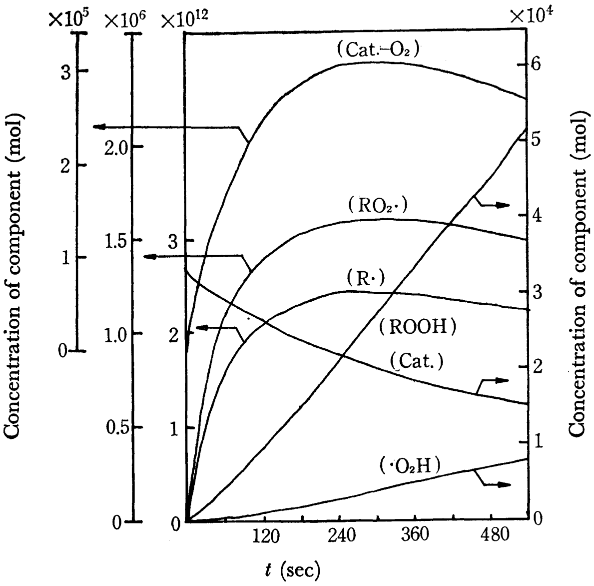

Fig. 4. Time-conversion curves of concentrations of components produced or consumed.
Initial condition: $(\text{Cat.})_i=3.35\times10^{-4}$ mol/l; $(\text{RH})_i=6.75$ mol/l; $(O_2)_i=4.22\times10^{-2}$ mol/l.

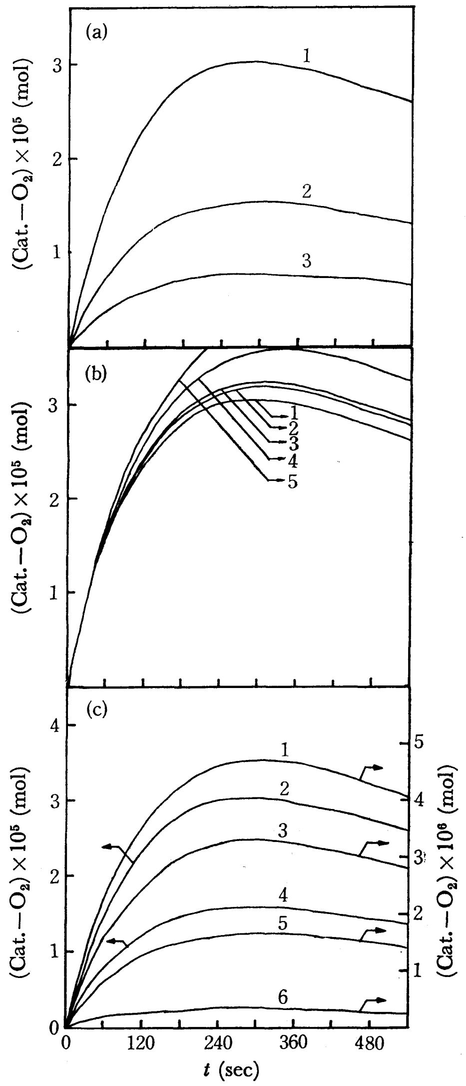

Fig. 5. Variation in time-conversion of (Cat.—O_2) with initial concentrations of Cat., RH, and O_2.
(a) Initial condition
$(\text{RH})_i=6.75$ mol/l; $(O_2)_i=4.22\times10^{-2}$ mol/l.
$(\text{Cat.})_i$ 1: 3.35×10^{-4} mol/l, 2: 1.68×10^{-4} mol/l, 3: 0.84×10^{-4} mol/l.
(b) Initial condition
$(\text{Cat.})_i=3.35\times10^{-4}$ mol/l, $(O_2)_i=4.22\times10^{-2}$ mol/l.
$(\text{RH})_i$ 1:6.75 mol/l, 2: 6.31 mol/l, 3: 6.12 mol/l, 4: 5.03 mol/l, 5: 3.80 mol/l.
(c) Initial condition
$(\text{Cat.})_i=3.35\times10^{-4}$ mol/l; $(\text{RH})_i=6.75$ mol/l;
$(O_2)_i$ 1: 6.03×10^{-3} mol/l, 2: 4.22×10^{-2} mol/l, 3: 4.22×10^{-3} mol/l, 4: 2.11×10^{-2} mol/l, 5: 2.11×10^{-3} mol/l 6: 4.22×10^{-4} mol/l.

Time Conversion of the Complex, Cat.–O_2. Some remarks should be made before discussing the simulation results. Cat. (*viz.* triphenylsulfonium chloride) interacts with O_2 to form a complex,[5,6] Cat.–O_2, in which the distance between the central S and the center of the O–O bond axis is 2.5—3.0 Å,[6] and in whcih the O–O bond is stretched to a value above 1.30 Å (from 1.2072 Å of the $^3\Sigma_g^- O_2$). In regard to (Cat.–O_2), the simulation results gave at first the time conversions of (Cat.–O_2). The variations in the time conversions of (Cat.–O_2) with $(\text{Cat.})_i$, $(O_2)_i$, and $(\text{RH})_i$ are shown in Fig. 5. Figure 5 indicates that (Cat.–O_2) possessing the maximum ascends with an increase in $(\text{Cat.})_i$ or $(O_2)_i$, whilst, interestingly, $(\text{RH})_i$ has little influence on (Cat.–O_2) during the very short stage up to 60 sec. The latter phenomenon may be ascribed to a constant enhancement of the intermolecular interaction between Cat.–O_2 and RH during the above-mentioned period. It is of interest here to pay attention to the dependence of the initial rate of Cat.–O_2 formation, r_i(Cat.–O_2), on $(\text{Cat.})_i$, $(O_2)_i$, or $(\text{RH})_i$. As shown in Fig. 6, log r_i (Cat.–O_2) *vs.* log $(\text{Cat.})_i$, log $(O_2)_i$, and/or log·$(\text{RH})_i$ plots gave straight lines and the following relationships can be obtained:

$$r_i(\text{Cat.-}O_2) \propto (\text{Cat.})_i^{0.970} \tag{15a}$$

$$r_i(\text{Cat.-}O_2) \propto (O_2)_i^{0.964} \tag{15b}$$

$$r_i(\text{Cat.-}O_2) \propto (\text{RH})_i^{0.0} \tag{15c}$$

Eqs. (15a—c) can be rewritten as:

$$r_i(\text{Cat.-}O_2) \simeq 1.243\times10^{-2}(\text{Cat.})_i^{0.970}(O_2)_i^{0.964}(\text{RH})_i^{0.0} \quad \text{mol}/l\cdot\text{min} \tag{16}$$

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[16] The experimental data were obtained by the graphic differentiation of the time-conversion curve of (ROOH), this procedure brought about observational errors.

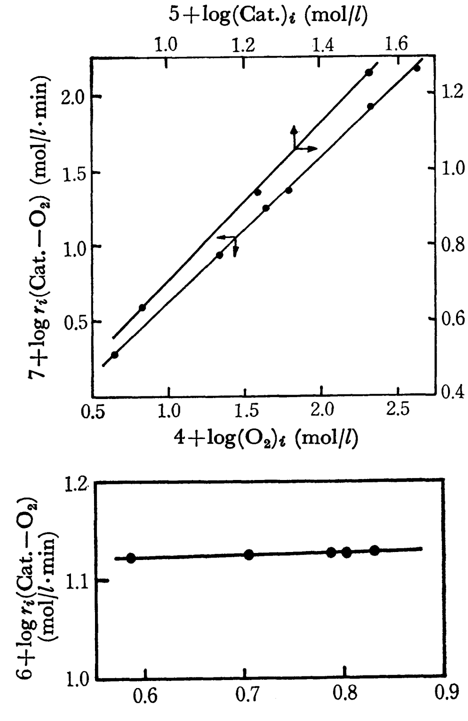

Fig. 6. Plots of log r_i (Cat.—O$_2$)$_i$ *vs.* log(Cat.)$_i$, log(O$_2$)$_i$, and log(RH)$_i$.

Time Conversion of Alkyl Radicals, R·. The process of the R· formation plays an important role in the oxidation reaction, specifically during the initial stage, since the R radical itself acts as a source for the propagating radical chains (Eqs. (4c) and (4d)). Figure 7 indicates the variations in the time conversion of (R·) with (Cat.)$_i$, (O$_2$)$_i$, and (RH)$_i$. As can be seen from Fig. 7, the higher (Cat.)$_i$ and (RH)$_i$ become, the larger becomes the amount of (R·), whilst (O$_2$)$_i$ depresses the R· formation, perhaps because of its predominant consumption of R· through Eq. (4c). The Linear relationships of log r_i (R·) *vs.* log (Cat.)$_i$, log (RH)$_i$, and/or log (O$_2$)$_i$ were rewritten as:

$$r_i(\mathrm{R\cdot}) \propto (\mathrm{Cat.})_i^{0.648} \tag{17a}$$

$$r_i(\mathrm{R\cdot}) \propto (\mathrm{RH})_i^{1.856} \tag{17b}$$

$$r_i(\mathrm{R\cdot}) \propto (\mathrm{O_2})_i^{-0.422} \tag{17c}$$

Eqs. (17a—c) can be rearranged as:

$$r_i(\mathrm{R\cdot}) \simeq 4.705\times10^{-12}(\mathrm{Cat.})_i^{0.648}(\mathrm{RH})_i^{1.886}(\mathrm{O_2})_i^{-0.422}\ \mathrm{mol}/l\cdot\mathrm{min} \tag{18}$$

Time Conversion of Alkylperoxy Radicals, RO$_2$·. Considering that (RO$_2$·) directly controls the rate of ROOH formation through Reaction (4d), the RO$_2$ radical must also play an impotant role in the oxidation reaction. We will, then, adjust the simulation results as to (RO$_2$·) similarly to the cases of (Cat.–O$_2$) and (R·). The variations in the time conversion of (RO$_2$·) with (Cat.)$_i$, (RH)$_i$, and (O$_2$)$_i$, and the plots of log r_i (RO$_2$·) *vs.* log (Cat.)$_i$, log (RH)$_i$, and log (O$_2$)$_i$ gave the following relationships:

$$r_i(\mathrm{RO_2\cdot}) \propto (\mathrm{Cat.})_i^{0.316} \tag{19a}$$

$$r_i(\mathrm{RO_2\cdot}) \propto (\mathrm{RH})_i^{0.509} \tag{19b}$$

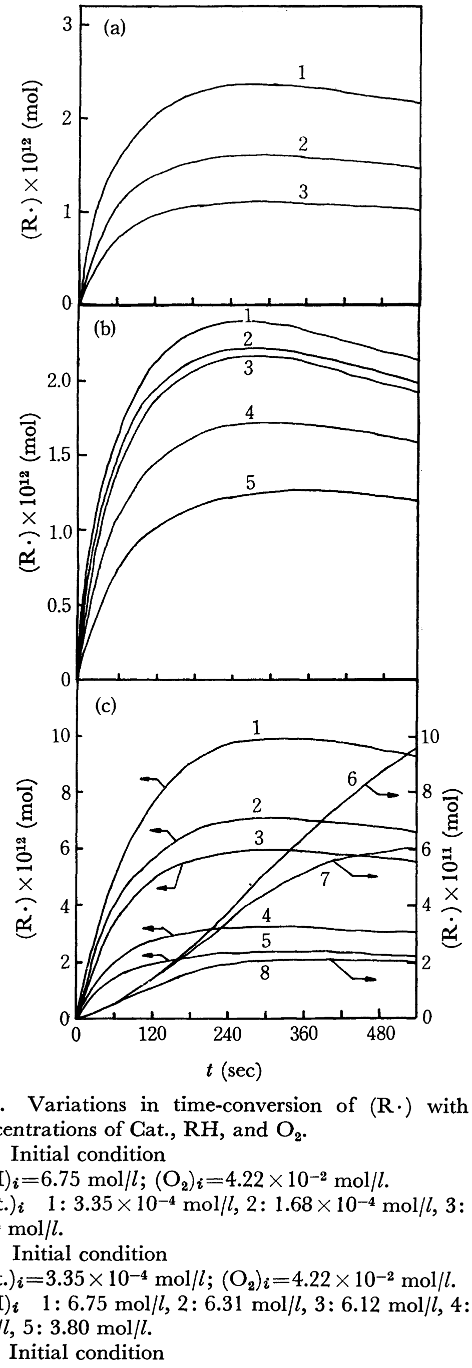

Fig. 7. Variations in time-conversion of (R·) with initial concentrations of Cat., RH, and O$_2$.
(a) Initial condition
(RH)$_i$=6.75 mol/l; (O$_2$)$_i$=4.22×10^{-2} mol/l.
(Cat.)$_i$ 1: 3.35×10^{-4} mol/l, 2: 1.68×10^{-4} mol/l, 3: 0.84×10^{-4} mol/l.
(b) Initial condition
(Cat.)$_i$=3.35×10^{-4} mol/l; (O$_2$)$_i$=4.22×10^{-2} mol/l.
(RH)$_i$ 1: 6.75 mol/l, 2: 6.31 mol/l, 3: 6.12 mol/l, 4: 5.03 mol/l, 5: 3.80 mol/l.
(c) Initial condition
(Cat.)$_i$=3.35×10^{-4} mol/l; (RH)$_i$=6.75 mol/l.
(O$_2$)$_i$ 1: 2.11×10^{-3} mol/l, 2: 4.22×10^{-3} mol/l, 3: 6.03×10^{-3} mol/l, 4: 2.11×10^{-2} mol/l, 5: 4.22×10^{-2} mol/l, 6: 4.22×10^{-6} mol/l, 7: 4.22×10^{-5} mol/l, 8: 4.22×10^{-4} mol/l.

$$r_i(\mathrm{RO_2\cdot}) \propto (\mathrm{O_2})_i^{0.737} \tag{19c}$$

Then,

$$r_i(\mathrm{RO_2\cdot}) \simeq 5.837\times10^{-12}(\mathrm{Cat.})_i^{0.316}(\mathrm{RH})_i^{0.509}(\mathrm{O_2})_i^{0.737}\ \mathrm{mol}/l\cdot\mathrm{min} \tag{20}$$

Time Conversion of Hydroperoxide, ROOH. In the liquid-phase oxidation of hydrocarbons catalyzed by transition-metal catalysts, it is generally believed that the reaction can proceed after the decomposition of ROOH accumulated during the incubation period (the so-called induction period). The phenomena of ROOH

TABLE 1. ACTIVATION ENERGIES AND RATE CONSTANTS OF REACTION STEPS

Reaction number	Reaction	d_{12} (Å)	$\mu\times10^{23}$ (g)	E (kcal/mol)	Rate constant
(1)	$\text{Cat.}+O_2\rightarrow\text{Cat.}-O_2$	4.284	4.80	19.93	$9.389\times10^9\sqrt{T}\ e^{-19.93/RT}$ $\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$
(2)	$\text{Cat.}-O_2\rightarrow\text{Cat.}+O_2$	7.36	54.9	21.37	$2.898\times10^9\sqrt{T}\ e^{-21.37/RT}$ sec^{-1}
(3)	$\text{Cat.}-O_2+RH\rightarrow R\cdot+\text{Cat.}+\cdot O_2H$	7.03	14.6	22.46	$1.447\times10^{10}\sqrt{T}\ e^{-22.46/RT}$ $\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$
(4)	$R\cdot+O_2\rightarrow RO_2\cdot$	3.95	4.19	6.38	$8.538\times10^9\sqrt{T}\ e^{-6.38/RT}$ $\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$
(5)	$RO_2\cdot+RH\rightarrow ROOH+R\cdot$	6.88	11.1	19.30	$1.592\times10^{10}\sqrt{T}\ e^{-19.30/RT}$ $\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$
(6)	$RO_2\cdot+RO_2\cdot\rightarrow$ inactive product	7.07	12.55	10.74	$1.582\times10^{10}\sqrt{T}\ e^{-10.74/RT}$ $\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1}$

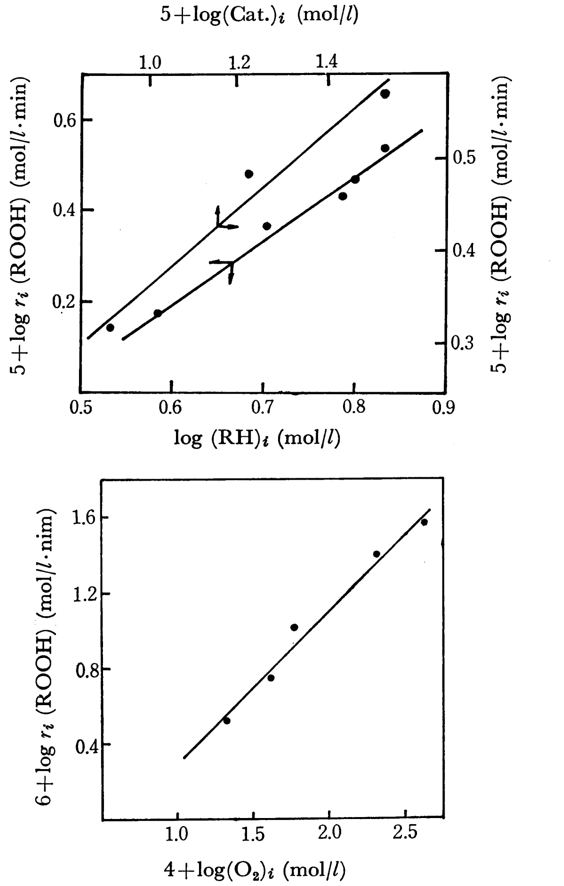

Fig. 8. Plots of log r_i(ROOH) *vs.* log(Cat.)$_i$, log(RH)$_i$, and log(O$_2$)$_i$.

decomposition have been already given in detail,[17–19] but those of ROOH formation during the initial short stage still remain obscure. It is more than of interest —it is necessary— to discuss the dependence of the time conversions of (ROOH) during the above-mentioned period upon the fresh catalyst and the fresh reactants. The plots of log r_i (ROOH) *vs.* log (Cat.)$_i$ and/or log (reactant)$_i$ indicated linear relationships, and we obtained the following equation from the straight lines in Fig. 8:

$$r_i(\text{ROOH})\simeq4.860\times10^{-4}(\text{Cat.})_i^{0.436}(\text{RH})_i^{1.842}(O_2)_i^{0.850}\quad \text{mol}/l\cdot\text{min}\qquad(21)$$

Equation (21) demonstrates that the initial formation of ROOH will be approximately controlled by the square root of (Cat.)$_i$. This implies that we should take into consideration the radical recombination reaction, $RO_2\cdot+RO_2\cdot\longrightarrow$inactive products, even during the initial short stage.

Activation Energies of Reaction Steps. Now, we will estimate the activation energies of the reaction steps (Eqs. (4a—e)) on the basis of the collision theory.[20] The rate constant of the bimolecular reaction, k_{12}, is usually produced by a kinetic theory expression:

$$k_{12}(\text{mol}^{-1}\cdot l\cdot\text{sec}^{-1})=\pi Nd_{12}^2(8kT/\pi\mu)^{1/2}\text{e}^{-E/RT}\times10^{-3}\qquad(22)$$

where N, k, d_{12}, and μ stand for the Avogadro number, the Boltzmann constant, the molecular diameter, and the reduced mass respectively. The activation energies evaluated are tabulated in Table 1, together with the rate constants; the formation of Cat.–O$_2$ is an thermic reaction and, suprisingly, the radical recombinations of Eqs. (4c) and (4e) need appreciable activation energies. The latter phenomena must bedue to the reaction of bulky reactants.

In conclusion, more precise discussions of the oxidation mechanism will be undertaken in a succeeding paper on the basis of such favorable methods as the Monte Carlo simulation.

The calculations were carried out on a FACOM 230-60 computer at the Computation Center of Kyushu University.

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[20] In the present reaction system without solvents (the effect of polar oxidation products can be disregarded during the very initial short stage), we can easily establish the Maxwell-Boltzmann distribution, considering that the ascending of collisions in the liquid-phase accompanies the increase in the rates of activation and the deactivation of activated complexes.