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A Kinetic Study on the Homogeneous Liquid-phase Oxidation of Cumene in the Presence of Triphenylsulfonium Chloride

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A kinetic study of the homogeneous liquid-phase oxidation of cumene was carried out in order to clarify the characteristic behavior of triphenylsulfonium chloride as an autoxidation catalyst. The reaction proceeded with no incubation period. The experimental dependence of the rate upon catalyst and hydrocarbon concentrations and also upon the oxygen pressure was reproduced with a good analytic fit by the following equation:

$$r=k'(\mathrm{RH})^{1.27}(\mathrm{O_2})^{0.68}(\mathrm{Cat.})_0\ (e^{-at}-e^{-bt})\quad (a,\ b,\ \text{and}\ k'\ \text{are constants}).$$

A reaction mechanism was proposed to derive the rate equation. It seems likely from this scheme that sulfonium chloride activates molecular oxygen by means of a reversible molecular association with it.

It is well known that some transition metal compounds and some halogen compounds are effective catalysts for the liquid-phase reactions of hydrocarbons with molecular oxygen. Recently, several onium compounds, in particular sulfonium and phosphonium salts, have been found to accelerate this type of oxidation. In view of the distinguishing character[1] of the behavior of these compounds as autoxidation catalysts, a kinetic study appeared significant. In the present paper, a kinetic study of cumene oxidation catalyzed by triphenylsulfonium chloride will be reported.

The kinetic study was carried out with particular reference to the initial short reaction time. In this initial range, the decomposition of cumene hydroperoxide, which would give free radicals, was disregarded since the concentration of hydroperoxide was very low, and the product was accumulated as hydroperoxide. The dependency of the initial rate upon the catalyst and hydrocarbon concentrations, and also upon the oxygen pressure, was determined. A tentative reaction mechanism will be proposed. The stationary-state method was employed to solve kinetic equations describing the mechanism. The experimental results can be well interpreted by the proposed mechanism, in which the behavior of the sulfonium catalyst is characterized in terms of forming a complex with molecular oxygen.

Experimental

Measurement of Oxygen Absorption. The course of oxidation reaction was followed by measuring the volume changes of the oxygen absorbed; the volume was observed every minute in the initial stage of the reaction and every ten minutes thereafter.

The reaction apparatus used the one described in an earlier report.[2]

The reaction vessel was thermostatically controlled in an oil bath; the temperature range was kept constant within ±0.05°C, and the speed of stirring was regulated at more than 500 rpm/min. The rate of oxygen absorption was found to be independent of the stirring frequency in the above range.

Preparation of Catalyst. Equimolar quantities of phenylmagnesium bromide and diphenylsulfoxide were refluxed in benzene for 48 hr to form a precipitate of triphenylsulfoxymagnesium bromide. The precipitate was triturated with 20% tetrafluoroboric acid, and the resulting crystal of triphenylsulfonium tetrafluoroborate was recrystallized from chloroform and ether to give pure colorless crystals which melted at 192—193°C. An equimolar mixture of triphenylsulfonium tetrafluoroborate and potassium chloride was kept standing for a day in ethyl alcohol. The potassium tetrafluoroborate was then filtered off and the filtrate was removed to afford colorless needles of triphenylsulfonium chloride melting at 297—298°C (recrystallized from chloroform and ether).

Found: Cl, 11.6%. Calcd for $C_{18}H_{15}SCl$: Cl, 11.9%.

Oxidation Procedure. Homogeneous solutions of triphenylsulfonium chloride in cumene were prepared in a nitrogen atmosphere. Each ten-milliliter portion of the solution contained 3.35×10^{-4}, 1.68×10^{-4}, and 0.84×10^{-4} mol/*l* of the catalyst; these solutions were taken as the samples of the oxidation reaction. Oxidation was carried out at the temperatures of 50, 65, 70, and 80°C, and the rates of oxygen absorption were studied by graphical differentiation of the absorption curves of oxygen. The reaction rate was regarded as

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[1] K. Fukui, K. Ohkubo and T. Yamabe, This Bulletin, **42**, 312 (1969).

[2] K. Fukui, K. Kanai, T. Takezono and H. Kitano, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **67**, 1131 (1964).

corresponding to that of the formation of cumene hydroperoxide, since the moles of oxygen absorbed were equal to those of the hydroperoxide formed in the initial step of the oxidation.

Result

Oxygen Absorption and Reaction Rate. The oxygen absorption of cumene was remarkably accelerated with a sulfonium catalyst. The reaction rate reached a maximum soon after the start of the reaction, without any appreciable incubation period, and then it gradually decreased. The lowering of the temperature decreased the maximum rate and delayed the time of reaching it. A typical curve of oxygen absorption is indicated in Fig. 1, while that of the initial range in particular is shown in Fig. 2. Figure 3 shows the rate curves indicating the characteristic feature[1] of sulfonium catalysts in accelerating the oxygen absorption at the initial step. The variation of the rate (r: $\text{mol}^{-1} l^{-1}\ \text{sec}^{-1}$) with the reaction time was analyzed from these curves; it can apparently be represented by the equation:

$$r = k(e^{-at} - e^{-bt}),\ (b>a) \tag{1}$$

where $k\,(\text{mol}\,l^{-1}\,\text{sec}^{-1})$, $a\,(\text{sec}^{-1})$, and $b\,(\text{sec}^{-1})$ are constants and where t (sec) is the reaction time. In Fig. 4 the curves calculated from Eq. (1) by the use of the most fitting values of a, b, and k are presented by broken lines. The values of a, b and k are summarized in Table 1. From Table 1 it can be found that the a and b constants are not much influenced by the catalyst concentration, while k is linearly dependent upon the catalyst

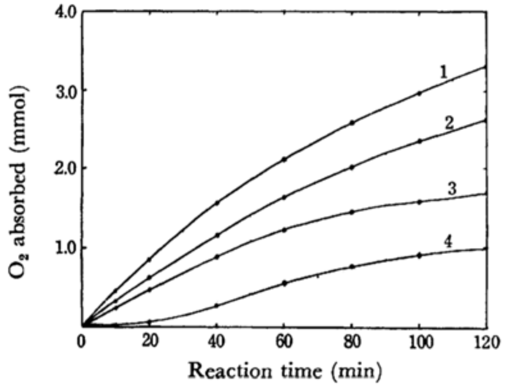

Fig. 1. Absorption curves of oxygen at 70°C.
1: 3.35×10^{-4} mol/l of $(C_6H_5)_3SCl$
2: 1.68×10^{-4} mol/l of $(C_6H_5)_3SCl$
3: 0.84×10^{-4} mol/l of $(C_6H_5)_3SCl$
4: none

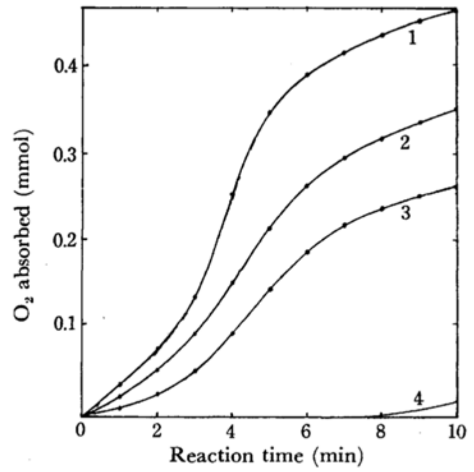

Fig. 2. Absorption curves of oxygen in the initial range at 70°C.
1: 3.35×10^{-4} mol/l of $(C_6H_5)_3SCl$
2: 1.68×10^{-4} mol/l of $(C_6H_5)_3SCl$
3: 0.84×10^{-4} mol/l of $(C_6H_5)_3SCl$
4: none

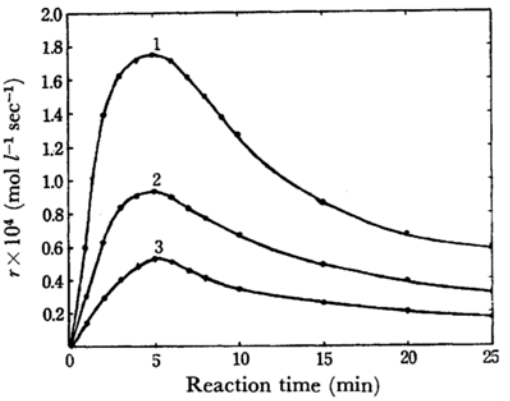

Fig. 3. Rate curves of oxygen absorption at 70°C.
1: 3.35×10^{-4} mol/l of $(C_6H_5)_3SCl$
2: 1.68×10^{-4} mol/l of $(C_6H_5)_3SCl$
3: 0.84×10^{-4} mol/l of $(C_6H_5)_3SCl$

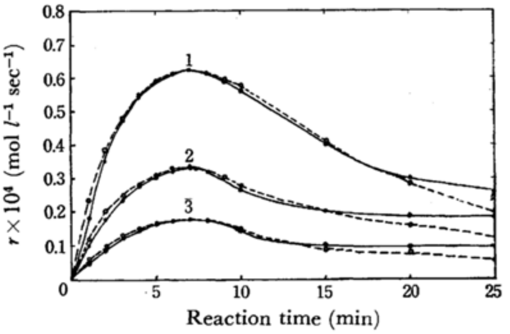

Fig. 4. Rate curves of oxygen absorption at 50°C.
1: 3.35×10^{-4} mol/l of $(C_6H_5)_3SCl$
2: 1.68×10^{-4} mol/l of $(C_6H_5)_3SCl$
3: 0.84×10^{-4} mol/l of $(C_6H_5)_3SCl$
Broken lines represent the rates derived from Eq. (1) with specific values of a, b and k (in Table 1).

Table 1. The variation in a, b and k values with the reaction temperature and the catalyst concentration

Reaction temperature (°C)	Initial catalyst concentration (mol/l)	$a\times10^3$ (sec^{-1})	$b\times10^3$ (sec^{-1})	$k\times10^4$ (mol $l^{-1}\cdot$ sec^{-1})
50	3.35×10^{-4}	1.38	3.90	1.37
	1.68×10^{-4}	1.10	4.40	0.685
	0.84×10^{-4}	0.96	4.80	0.360
70	3.35×10^{-4}	0.840	8.40	2.62
	1.68×10^{-4}	0.643	9.65	1.34
	0.84×10^{-4}	1.34	6.70	0.700
80	3.35×10^{-4}	2.38	6.67	4.78
	1.68×10^{-4}	2.29	6.86	2.50
	0.84×10^{-4}	2.20	7.04	1.55

concentration, as will be discussed in the next paragraph.

The Variation in the Rate with the Catalyst Concentration. The effect of the catalyst on the rate of oxygen absorption was studied by the varying catalyst concentrations to 3.35×10^{-4}, 1.68×10^{-4}, and 0.84×10^{-4} mol/l. Figure 5 shows the log k *versus* log (Cat.)$_0$ plot, where (Cat.)$_0$ denotes the initial concentration of the catalyst; the plot is a straight line with a slope equal to about 1.0. The linear relation is expressed as follows: $k\propto(\text{Cat.})_0^{0.940}$ at 50°C, $k\propto(\text{Cat.})_0^{0.952}$ at 70°C, and $k\propto(\text{Cat.})_0^{0.803}$ at 80°C. From these results, the dependency of k upon (Cat.)$_0$ can be represented, at least at lower temperatures, as follows:

$$k\propto(\text{Cat.})_0 \qquad (2)$$

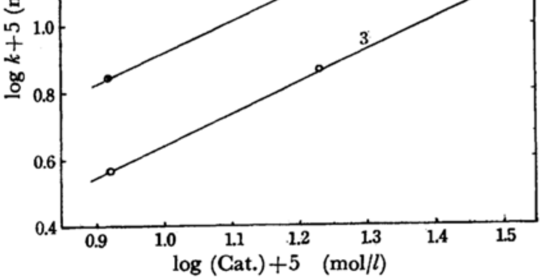

Fig. 5. The dependency of the constant, k, upon (Cat.).
-●- : at 80°C, -◑- : at 70°C, -○- : at 50°C

The Variation in the Rate with the Hydrocarbon Concentration. In order to investigate the rate dependency upon the hydrocarbon concentration, (RH), the oxidation of cumene (6.75, 6.31, 6.12, 5.03, and 3.80 mol/l) using chlorobenzene as the diluent was carried out under atmospheric pressure at 65°C in the presence of 3.35×10^{-4} mol/l of the catalyst. Figure 6 indicates the oxygen absorption rate at various hydrocarbon concentrations and shows a plot of the oxygen absorption rate against the reaction time. The most suitable values of a, b and k are listed in Table 2. Table 2 suggests that the a and b constants, are slightly affected by the initial value of (RH). Figure 7 shows the plot of log$k$ against log (RH). The slope of the straight line obtained is 1.27, giving the relationship:

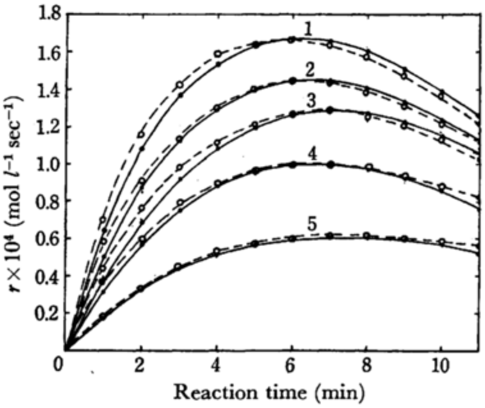

Fig. 6. Rate curves of oxygen absorption with varing concentration of cumene.
1: 6.75 mol/l 2: 6.31 mol/l 3: 6.12 mol/l
4: 5.03 mol/l 5: 3.80 mol/l
Broken lines are derived from Eq. (1) with specific values of a, b and k (in Table 2).

Table 2. The variation in a, b and k values with the hydrocarbon concentration

Initial hydrocarbon concentration (mol/l)	$a\times10^3$ (sec^{-1})	$b\times10^3$ (sec^{-1})	$k\times10^4$ (mol l^{-1} sec^{-1})
6.75	1.24	5.06	3.31
6.31	1.23	4.81	3.05
6.12	1.21	4.65	2.80
5.03	1.17	4.05	2.30
3.80	1.12	3.40	1.59

$$k\propto(\text{RH})^{1.27} \qquad (3)$$

The Variation in the Rate with the Oxygen Pressure. Since the liquid phase concentration of dissolved oxygen is proportional to the oxygen concentration in the gas phase, designated as (O$_2$),

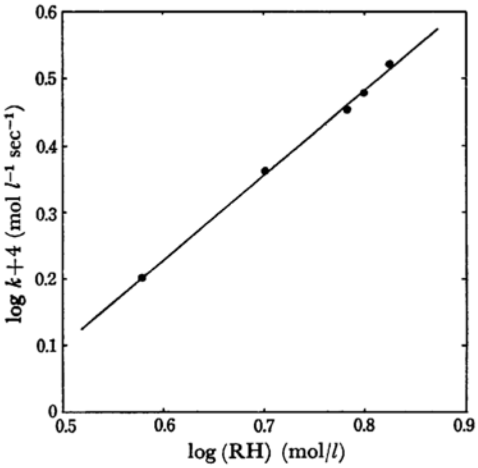

Fig. 7. The dependency of the constant, k, upon (RH) at 65°C.

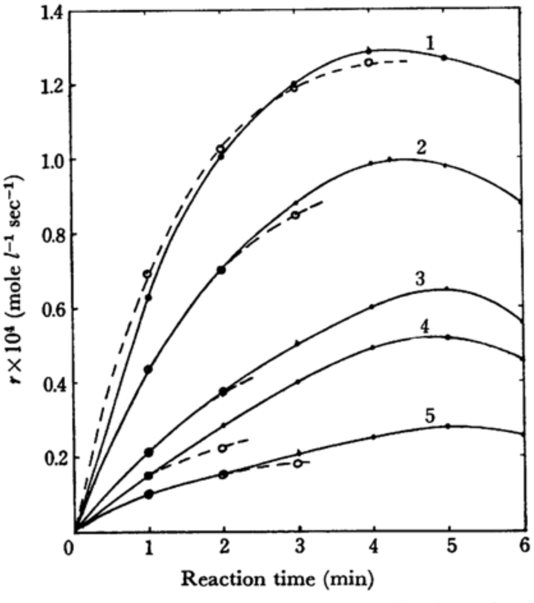

Fig. 8. Rate curves of oxygen absorption in variation with oxygen concentration
1: 4.22×10^{-2} mol/l 2: 2.11×10^{-2} mol/l
3: 0.603×10^{-2} mol/l 4: 0.422×10^{-2} mol/l
5: 0.211×10^{-2} mol/l
Broken lines at initial step are derived from Eq. (1) with specific values of a, b and k (in Table 3).

Table 3. The variation in a, b and k values with the oxygen concentration

Initial oxygen concentration (mol/l)	$a\times10^3$ (sec^{-1})	$b\times10^3$ (sec^{-1})	$k\times10^4$ (mol l^{-1} sec^{-1})
4.22×10^{-2}	1.25	10.0	1.89
2.11×10^{-2}	1.34	7.75	1.53
0.603×10^{-2}	1.36	6.60	0.793
0.422×10^{-2}	1.38	6.62	0.565
0.211×10^{-2}	1.47	6.33	0.388

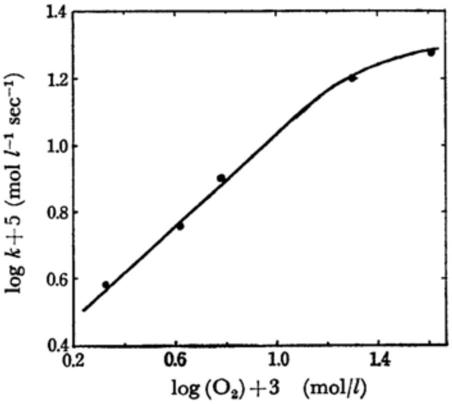

Fig. 9. The dependency of the constant, k, upon (O_2) at 65°C.

the latter variable was adopted in place of the former. At a fixed cumene concentration (6.75 mol/l) and a constant temperature (65°C) in the presence of 3.35×10^{-4} mol/l of the catalyst, mixtures of oxygen and nitrogen were used for examining the effect of the oxygen concentration. Figure 8 indicates the influence of the oxygen concentration upon the rate of oxygen absorption in the initial stage of the reaction. The values of the constants (a, b and k) fitting the initial rates are listed in Table 3; a and b are influenced by the initial value of (O_2). Figure 9 shows the shape of the $\log k$ *versus* $\log(O_2)$ curve. The initial part of the curve is a straight line with a slope of 0.68, so that we have:

$$k \propto (O_2)^{0.68} \tag{4}$$

From Eq., (2), (3) and (4), the dependency of k upon $(\mathrm{Cat.})_0$, (RH) and (O_2) can be represented by:

$$k \propto (\mathrm{RH})^{1.27}(O_2)^{0.68}(\mathrm{Cat.})_0 \tag{5}$$

The rate shown in Eq. (1) may then be rewritten by the following expression:

$$r = k'(\mathrm{RH})^{1.27}(O_2)^{0.68}(\mathrm{Cat.})_0(e^{-at}-e^{-bt}) \tag{6}$$

where k' is a constant which is dependent upon neither the hydrocarbon nor oxygen concentrations, nor upon the catalyst concentration.

The Variation in the Rate with the Reaction Temperature. The reaction was studied in the temperature range from 50 to 80°C by the use of catalysts in the amounts of 3.35×10^{-4}, 1.68×10^{-4}, and 0.84×10^{-4} mol/l. Figure 10 shows the Arrhenius plots. The overall energy of activation of this process comes out to be $E_{\mathrm{overall}}=5.25$—6.15 kcal/mol from the temperature dependence of the overall velocity constant (k).

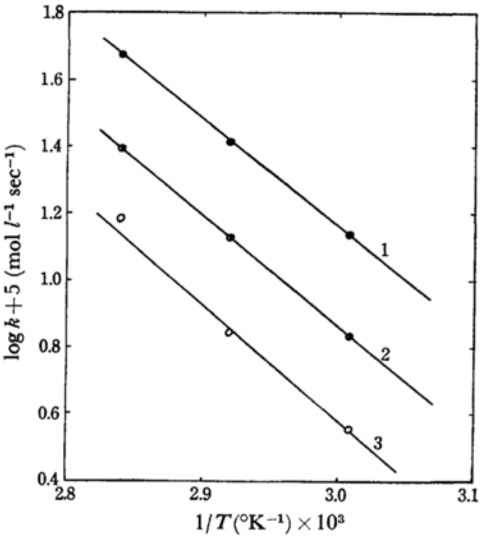

Fig. 10. Arrhenius plots of $\log k$ against $1/T$.
(1): 3.35×10^{-4} mol/l of $(C_6H_5)_3SCl$
(2): 1.68×10^{-4} mol/l of $(C_6H_5)_3SCl$
(3): 0.84×10^{-4} mol/l of $(C_6H_5)_3SCl$

It should be stressed here that, in this kinetic study, triphenylsulfonium chloride could not act as a radical source, as was discussed in a previous report.[1)] Neither chloride compounds, such as alkyl chloride and hydrogen chloride, nor decomposed fragments of such catalysts as benzene, chlorobenzene, sulfide, and sulfoxide were detected.

In addition, the catalytic action of sulfonium chloride was not based mainly upon the chloride anion. This will be discussed in detail in a subsequent paper.

Discussion

The main purpose of this kinetic study was to clarify the features of the catalytic action of the sulfonium compounds. The analysis of the experimental results so far obtained would make it possible to build a tentative reaction mechanism. The nature of the reaction is most probably radical and not ionic, for the reaction is stopped by a radical inhibitor such as phenol. A "complex" formation between the catalyst and the oxygen molecule has been suggested in a previous paper;[1)] such a formation would be capable of hydrogen abstraction from hydrocarbon molecules. It is worth summing up here the important experimental results:

a) The activity of the catalyst is characterized in the initial stage, in which the oxygen absorption occurs essentially with no incubation period. b) The shape of the rate curves expressed in Figs. 3, 4 and 5 suggests the involvement of a catalyst deactivation. c) The value of the overall energy of activation is relatively small. This may indicate radical reaction caused by catalytic hydrogen abstraction by the "complex."

The experimental results, then, lead to the following reaction scheme. The first step consists of the formation of a complex between the catalyst $(\mathrm{Cat.})_0$ and the oxygen molecule (discussed in detail in a previous report[1)]):

$$\mathrm{Cat.} + \mathrm{O_2} \underset{k'_c}{\overset{k_c}{\rightleftarrows}} \mathrm{Cat.}\cdots\mathrm{O_2} \tag{7a}$$

Such a complex then abstracts an active hydrogen from hydrocarbon (RH) to produce an alkyl radical (R·):

$$\mathrm{Cat.}\cdots\mathrm{O_2} + \mathrm{RH} \xrightarrow{k_1} \mathrm{R}\cdot + \mathrm{Cat.} + \cdot\mathrm{O_2H} \tag{7b}$$

followed by the usual propagation steps:

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_p} \mathrm{RO_2}\cdot \tag{7c}$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH}+\mathrm{R}\cdot \tag{7d}$$

The termination step may be described by the following scheme:

$$\mathrm{RO_2}\cdot \xrightarrow{k_t} \text{inactive products} \tag{7e}$$

$$\mathrm{Cat.} \xrightarrow{k_d} \text{inactive form} \tag{7f}$$

Terminations of other types ($\mathrm{R}\cdot+\mathrm{R}\cdot$ or $\mathrm{R}\cdot+\mathrm{RO_2}\cdot$) are negligible compared to the process of (7e) at oxygen pressures above 200 mm of mercury. The disappearance of $\mathrm{RO_2}\cdot$ may be a first or second-order process. Here the first-order termination is assumed for mathematical convenience. The deactivation of the sulfonium catalyst (7f) is considered to be another important process in retarding the reaction. It may be caused partly by interaction with oxidation products such as hydroperoxide. In view of the fact that more than 70% of the catalyst is recovered from the reaction mixture by the use of larger amounts of catalyst, as was reported in the previous paper,[1)] it is very likely that the "deactivation" is due to the masking action*[1] of some reaction products.

According to the reaction scheme discussed above, the following differential equations are obtained:

$$\mathrm{d(Cat.)}/\mathrm{d}t = (k_1(\mathrm{RH}) + k_c')(\mathrm{Cat.}\cdots\mathrm{O_2}) - (k_c(\mathrm{O_2}) + k_d)(\mathrm{Cat.}) \tag{8a}$$

$$\mathrm{d(Cat.}\cdots\mathrm{O_2)}/\mathrm{d}t = k_c(\mathrm{O_2})(\mathrm{Cat.}) - (k_1(\mathrm{RH}) + k_c')(\mathrm{Cat.}\cdots\mathrm{O_2}) \tag{8b}$$

$$\mathrm{d(R\cdot)}/\mathrm{d}t = k_1(\mathrm{RH})(\mathrm{Cat.}\cdots\mathrm{O_2}) + k_2(\mathrm{RH})(\mathrm{RO_2}\cdot) - k_p(\mathrm{O_2})(\mathrm{R}\cdot) \tag{8c}$$

$$\mathrm{d(RO_2\cdot)}/\mathrm{d}t = k_p(\mathrm{O_2})(\mathrm{R}\cdot) - (k_2(\mathrm{RH}) + k_t)(\mathrm{RO_2}\cdot) \tag{8d}$$

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*[1] This subject will be discussed in a subsequent paper.

$$d(\mathrm{ROOH})/dt = k_2(\mathrm{RH})(\mathrm{RO_2}\bullet) \tag{8e}$$

Assuming the stationary-state for the concentrations of $R\cdot$ and $RO_2\cdot$, the overall rate of oxygen absorption (r) can be represented by the equation:

$$r = \frac{k_1k_2(\mathrm{RH})^2}{k_t}(\mathrm{Cat.}\cdots\mathrm{O_2}) \tag{8f}$$

The time change of $(\mathrm{Cat.}\cdots\mathrm{O_2})$ is controlled by Eqs. (8a) and (8b), which are solved simultaneously. The solution of $(\mathrm{Cat.}\cdots\mathrm{O_2})$ is introduced into Eq. (8f), giving;

$$r = \frac{k_1k_2k_c(\mathrm{RH})^2(\mathrm{O_2})(\mathrm{Cat.})_0}{k_t(\lambda_2-\lambda_1)}(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{9}$$

where:

$$\lambda_1 = \frac{1}{2}\left\{k_c(\mathrm{O_2}) + k_c' + k_1(\mathrm{RH}) + k_d\right\} \times \left[1 - \sqrt{1 - \frac{4k_d(k_c' + k_1(\mathrm{RH}))}{k_c(\mathrm{O_2}) + k_c' + k_1(\mathrm{RH}) + k_d)^2}}\right] \tag{9a}$$

$$\lambda_2 = \frac{1}{2}\left\{k_c(\mathrm{O_2}) + k_c' + k_1(\mathrm{RH}) + k_d\right\} \times \left[1 + \sqrt{1 - \frac{4k_d(k_c' + k_1(\mathrm{RH}))}{(k_c(\mathrm{O_2}) + k_c' + k_1(\mathrm{RH}) + k_d)^2}}\right] \tag{9b}$$

Here the oxygen and the hydrocarbon concentrations can be assumed to be unchanged, namely, to be equal to the initial value. Equation (9) is in accordance with Eq. (1), which is obtained experimentally, and is in qualitative agreement with the rate dependency upon (RH), (O_2) and $(\mathrm{Cat.})_0$ shown by Eq. (6). Therefore, the a, b and k constants are correspondingly represented by;

$$a = \lambda_1 \tag{10a}$$

$$b = \lambda_2 \tag{10b}$$

$$k = \frac{k_1k_2k_c(\mathrm{RH})^2(\mathrm{O_2})(\mathrm{Cat.})_0}{k_t(\lambda_2 - \lambda_1)} \tag{10c}$$

From Eqs. (9a) and (9b) we obtain:

$$(\lambda_1)_{(\mathrm{RH})=0} = \frac{1}{2}\left\{k_c(\mathrm{O_2}) + k_c' + k_d\right\} \times \left[1 - \sqrt{1 - \frac{4k_dk_c'}{(k_c(\mathrm{O_2}) + k_c' + k_d)^2}}\right] \tag{11a}$$

$$(\lambda_2)_{(\mathrm{RH})=0} = \frac{1}{2}\left\{k_c(\mathrm{O_2}) + k_c' + k_d\right\} \times \left[1 + \sqrt{1 - \frac{4k_dk_c'}{(k_c(\mathrm{O})_2 + k_c' + k_d)^2}}\right] \tag{11b}$$

where $(\lambda_1)_{(\mathrm{RH})=0}$ and $(\lambda_2)_{(\mathrm{RH})=0}$ are extreme values of λ_1 and λ_2 respectively when (RH) is extrapolated to zero.

From Eqs. (11a) and (11b), it follows that;

$$(\lambda_1)_{(\mathrm{RH})=0} + (\lambda_2)_{(\mathrm{RH})=0} = k_c(\mathrm{O_2}) + k_c' + k_d \tag{12a}$$

$$(\lambda_2)_{(\mathrm{RH})=0} - (\lambda_1)_{(\mathrm{RH})=0} = \sqrt{(k_c(\mathrm{O_2}) + k_c' + k_d)^2 - 4k_dk_c'} \tag{12b}$$

Similarly, we get;

$$(\lambda_1)_{(\mathrm{O_2})=0} = k_d \tag{12c}$$

$$(\lambda_2)_{(\mathrm{O_2})=0} = k_c' + k_1(\mathrm{RH}) \tag{12d}$$

Figures 11 and 12 show the plots of the values of a and b against (RH) and (O_2) respectively, giving the following extrapolated values:

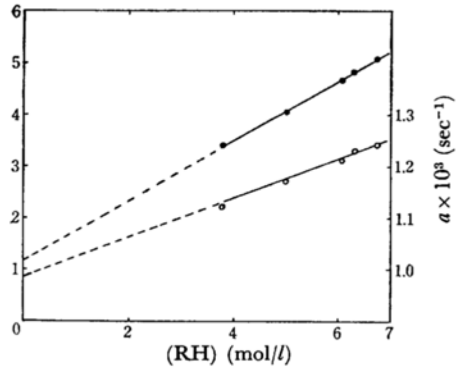

Fig. 11. The dependency of the constants, a and b upon (RH) at 65°C.
-●- : The plots of b against (RH)
-○- : The plots of a against (RH)

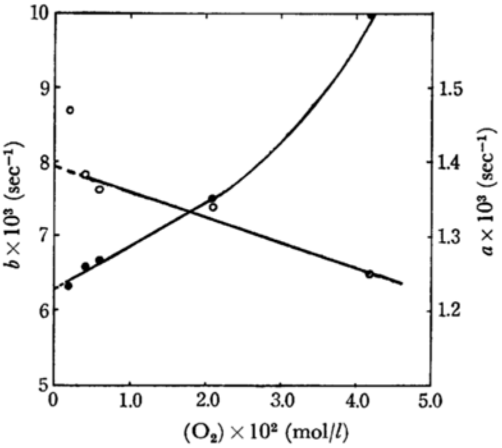

Fig. 12. The dependency of the constants, a and b, upon (O_2) at 65°C.
-●- : The plots of b against (O_2)
-○- : The plots of a against (O_2)

$$(\lambda_1)_{(\mathrm{RH})=0} = 0.95 \times 10^{-3}\ \mathrm{sec^{-1}} \tag{13a}$$

$$(\lambda_2)_{(\mathrm{RH})=0} = 1.195 \times 10^{-3}\ \mathrm{sec^{-1}} \tag{13b}$$

$$(\lambda_1)_{(\mathrm{O_2})=0} = 1.392 \times 10^{-3}\ \mathrm{sec^{-1}} \tag{13c}$$

$$(\lambda_2)_{(\mathrm{O_2})=0} = 6.18 \times 10^{-3}\ \mathrm{sec^{-1}} \tag{13d}$$

from Eqs. (12a—12d) and (13a—13d), the rate constants at 65°C can be determined to be as follows:

$$k_c = 2.23\times10^{-2}\ \mathrm{mol}^{-1}l\ \mathrm{sec}^{-1}$$
$$k_c(\mathrm{O_2}) = 0.94\times10^{-3}\ \mathrm{sec}^{-1}$$
$$k_c' = 0.82\times10^{-3}\ \mathrm{sec}^{-1}$$
$$k_1 = 0.794\times10^{-3}\ \mathrm{mol}^{-1}l\ \mathrm{sec}^{-1}$$
$$k_1(\mathrm{RH}) = 5.36\times10^{-3}\ \mathrm{sec}^{-1}$$
$$k_d = 1.39\times10^{-3}\ \mathrm{sec}^{-1}$$

From these rate constants and from the experimental values of k (shown in Table 2) under the conditions of $(\mathrm{O_2})=4.42\times10^{-2}$ mol/l and $(\mathrm{Cat.})_0=3.35\times10^{-4}$ mol/l, the value of k_2/k_t can be calculated by the use of Eq. (10c) as follows:

$$k_2/k_t = 1.79\times10^{2}\ \mathrm{mol}^{-1}\ l$$

When this value is applied to Eq. (10c), the calculated values of k are consistent with the experimental values, as is shown in Fig. 13. These values of rate constants may supply the following information concerning the elementary processes involved:

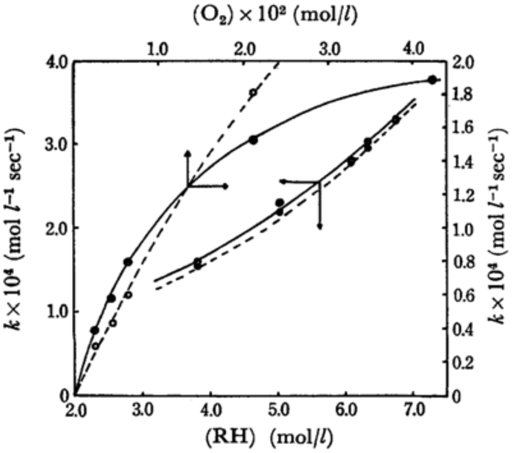

Fig. 13. The dependency of k upon (RH) and $(\mathrm{O_2})$.
-◓- : k against (RH) from experimental result
-⊙- : k against $(\mathrm{O_2})$ from experimental result
-●- : k against (RH) from Eq. (14a)
-○- : k against $(\mathrm{O_2})$ from Eq. (14b)

a) In the case of atmospheric oxygen pressure, $k_c(\mathrm{O_2})$ and k_c' become comparable, so that the conversion is essentially reversible. Accordingly, the complex formations is more favored by a higher oxygen pressure.

b) The small value of k_1 implies that the hydrogen abstraction by the "complex" is a step limitting the overall rate.

c) Traylor reported[3] that the value of k_2 was nearly equal to 5.35×10^{-3} *2 $\mathrm{mol}^{-1}\ l\ \mathrm{sec}^{-1}$ in cumene oxidation in the presence of t-butyl hydroperoxide at 60°C. If this value is applied to the present case, the value of k_t can be calculated to be $2.98\times10^{-5}\ \mathrm{sec}^{-1}$. This value, small compared with k_d, indicates that the termination of peroxy-radical may not play an important role in retarding the rate. The deactivation of the catalyst may be caused by the oxidation products, such as hydroperoxide. This point will be discussed in detail in a subsequent paper.

Next, let us discuss the influence of (RH) and $(\mathrm{O_2})$ upon the rate by the direct use of the values obtained above. The dependency of k upon (RH) is represented by;

$$k = \frac{4.47\times10^{-5}(\mathrm{RH})^2}{\sqrt{0.630(\mathrm{RH})^2 + 0.58(\mathrm{RH}) + 5.39}} \tag{14a}$$

under the conditions of $(\mathrm{Cat.})_0=3.35\times10^{-4}$ mol/l and $(\mathrm{O_2})=4.22\times10^{-2}$ mol/l. From a graphical fit of this expression, we also get the approximate representation;

$$k \simeq 4.47\times10^{-5}\ (\mathrm{RH})^{1.21}\ \mathrm{mol}\ l^{-1}\ \mathrm{sec}^{-1} \tag{14a'}$$

which reflects the experimental result of Eq. (3). Similarly, the dependency of k upon $(\mathrm{O_2})$ at fixed concentrations of $(\mathrm{RH})=6.75$ mol/l and $(\mathrm{Cat.})_0=3.35\times10^{-4}$ mol/l can be shown as follows:

$$k = \frac{4.83\times10^{-3}(\mathrm{O_2})}{\sqrt{4.98(\mathrm{O_2})^2 + 3.37(\mathrm{O_2}) + 0.229}} \tag{14b}$$

It is obvious that such an equation can be a rough approximation of Eq. (4).

The present kinetic study afforded very favorable support to the idea, partly suggested in our previous report,[1] that the distinguishing feature of the catalyst behavior might involve a direct association with molecular oxygen, although the "complex" has not yet been isolated.

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[3] T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, **87**, 3698 (1965).

*2 The value of k_2 was converted in terms of above dimensions from the original value.