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Kinetic Studies on the Cobalt(II) Naphthenate Catalyzed Decomposition of "Cumene Hydroperoxide" in Benzene

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The cobalt(II) naphthenate[Co(Nap)$_2$] catalyzed decomposition of cumene hydroperoxide(CHP) gave a mixture of α-cumyl alcohol, acetophenone and di-α-cumyl peroxide in benzene at 25 °C. All experimentally observed time courses of disappearing CHP and an increasing of three products compared well with theoretical values.

Much attention has been paid to the metal-ion-catalyzed decomposition of organic hydroperoxides, which are important intermediates in both the oxidation of lipids *in vivo*[1)] and the autoxidation of hydrocarbons.[2)] Numerous attempts have been made to obtain a mechanism for the metal-ion-catalyzed decomposition of organic hydroperoxides.[3)] Previously, Hiatt et al. proposed a radical chain mechanism for a metal-catalyzed decomposition of *t*-alkyl hydroperoxides, based on kinetic data regarding only the disappearance of the peroxides, due to a lack of detailed kinetic data concerning each product.[4)] Thus, in order to examine the Hiatt mechanism, which seemed to be the most plausible one among hitherto proposed mechanisms, we initiated a detailed products analysis of a cobalt naphthenate catalyzed decomposition of 1-methyl-1-phenylethyl hydroperoxide ("cumene hydroperoxide," abbreviated as CHP) and kinetic studies of not only the disappearance of CHP, but also each product formation.

Results and Discussion

When the Co(Nap)$_2$ catalyzed decomposition of CHP was carried out in benzene at 25 °C, 1-methyl-1-phenylethyl alcohol (α-cumyl alcohol, abbreviated as CA) was obtained as the major product, with acetophenone (AP) and di-α-cumyl peroxide (DCP) as minor products.

$$\underset{\textbf{CHP}}{\mathrm{PhCMe_2OOH}} \xrightarrow[\text{In benzene}]{\mathrm{Co(Nap)_2}}$$

$$\underset{\textbf{CA}}{\mathrm{PhCMe_2OH}} + \underset{\textbf{AP}}{\mathrm{PhCOMe}} + \underset{\textbf{DCP}}{\mathrm{PhCMe_2OOCMe_2Ph}}$$

The effect of the initial concentration of CHP on the product distribution is shown in Fig. 1. The products which resulted from the solvent could not be detected. CA, AP, and DCP explained about 100% of the CHP consumed in all reactions, with different initial [CHP] ranging from 0.59 M to 5.35 M (M=mol dm^{-3}) (Table 1).

According to Hiatt's mechanism (Scheme 1), the processes of a cobalt(II) naphthenate catalyzed decomposition of CHP consist of the following three classes of reactions: (**1**) Cobalt(II)-ion-catalyzed decomposi-

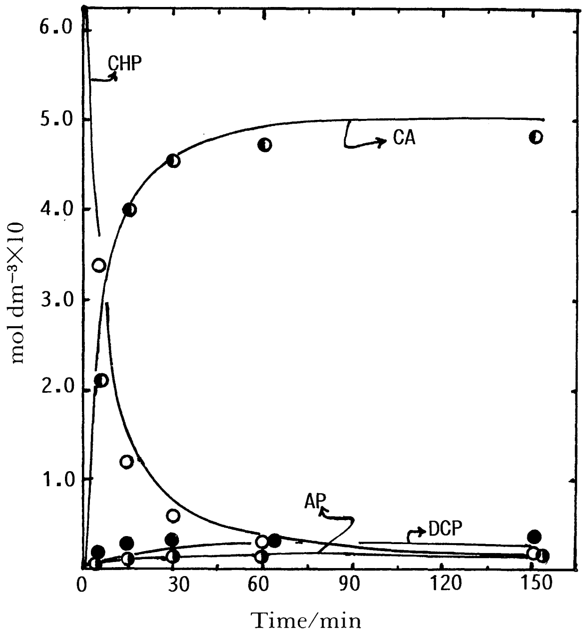


Fig. 1. Co(Nap)$_2$ catalyzed decomposition of CHP in benzene at 25 °C with [CHP]$_0$=0.59 mol dm^{-3} and [Co(Nap)$_2$]$_0$=4.48×10^{-3} mol dm^{-3}. Experimental observed value: CHP, ○; CA, ◐; AP, ◑; DCP, ●. Each solid line is theoretical (k_1=3.4 l mol^{-1} min^{-1}, k_4'=16, k_3'=145 l mol^{-1}).

Table 1. Effect of the Concentration of CHP on Co(Nap)$_2$$^{a)}$ Catalyzed Decomposition of CHP in Benzene at 25 °C for 60 min

Initial concn of CHP/M	Products/M			
	CA	AP	DCP	CHP$^{b)}$
0.59$^{c)}$	0.40	0.01	0.03	0.12
3.80	2.98	0.11	0.54	0.10
5.35	3.80	0.17	1.20	0.16

a) Concentration of Co(Nap)$_2$: 4.47 mM. b) Concentration of residual CHP. c) Reaction time: 15 min.

$$\mathrm{PhCMe_2OOH} + \mathrm{Co^{2+}} \xrightarrow{k_1} \mathrm{PhCMe_2O\cdot} + \mathrm{OH^-} + \mathrm{Co^{3+}} \qquad (1)$$

$$\mathrm{PhCMe_2OOH} + \mathrm{Co^{3+}} \xrightarrow{k_2} \mathrm{PhCMe_2OO\cdot} + \mathrm{H^+} + \mathrm{Co^{2+}} \qquad (2)$$

$$\mathrm{PhCMe_2O\cdot} + \mathrm{PhCMe_2OOH} \xrightarrow{k_3} \mathrm{PhCMe_2OH} + \mathrm{PhCMe_2OO\cdot} \qquad (3)$$

$$2\mathrm{PhCMe_2OO\cdot} \xrightarrow{k_4} 2\mathrm{PhCMe_2O\cdot} + \mathrm{O_2} \qquad (4)$$

$$2\mathrm{PhCMe_2OO\cdot} \xrightarrow{k_5} \mathrm{PhCMe_2OOCMe_2Ph} + \mathrm{O_2} \qquad (5)$$

$$\mathrm{PhCMe_2O\cdot} \xrightarrow{k_6} \mathrm{PhCOMe} + \mathrm{Me\cdot} \xrightarrow{\mathrm{O_2}} \mathrm{MeOO\cdot} \qquad (6)$$

$$\mathrm{MeOO\cdot} + \mathrm{PhCMe_2OO\cdot} \xrightarrow{k_7} \mathrm{HCHO} + \mathrm{O_2} + \mathrm{PhCMe_2OH} \qquad (7)$$

Scheme 1.

tions of CHP to provide α -cumyloxyl radical (Eq. 1) and α-cumylperoxyl radical (Eq. 2). (**2**) Chain reaction carried by α-cumyloxyl radical (Eqs. 3 and 4). (**3**) Termination reactions: reactions 6 and 7, to which Hiatt did not pay any attention, were newly added as some of termination reactions, in addition to reaction 5, since formation of a certain amount of AP was observed in this investigation.

Assuming steady states for [PhCMe$_2$O·], [PhCMe$_2$OO·], [MeOO·], [Co^{2+}], and [Co^{3+}], Eqs. 8—11 are derived from the decomposition mechanism of CHP shown in Scheme 1.

$$k_1[\mathrm{CHP}][\mathrm{Co^{2+}}] = k_2[\mathrm{CHP}][\mathrm{Co^{3+}}] \qquad (8)$$

$$\mathrm{d}[\mathrm{MeOO\cdot}]/\mathrm{d}t = k_6[\mathrm{PhCMe_2O\cdot}] - k_7[\mathrm{MeOO\cdot}][\mathrm{PhCMe_2OO\cdot}] = 0 \qquad (9)$$

$$\mathrm{d}[\mathrm{PhCMe_2O\cdot}]/\mathrm{d}t = k_1[\mathrm{CHP}][\mathrm{Co^{2+}}] - k_3[\mathrm{PhCMe_2O\cdot}][\mathrm{CHP}] + 2k_4[\mathrm{PhCMe_2OO\cdot}]^2 - k_6[\mathrm{PhCMe_2O\cdot}] = 0 \qquad (10)$$

$$\mathrm{d}[\mathrm{PhCMe_2OO\cdot}]/\mathrm{d}t = k_1[\mathrm{PhCMe_2OOH}][\mathrm{Co^{2+}}] + k_3[\mathrm{PhCMe_2O\cdot}][\mathrm{CHP}] - 2k_4[\mathrm{PhCMe_2OO\cdot}]^2 - 2k_5[\mathrm{PhCMe_2OO\cdot}]^2 - k_7[\mathrm{MeOO\cdot}][\mathrm{PhCMe_2OO\cdot}]^2 = 0 \qquad (11)$$

$$[\mathrm{PhCMe_2O\cdot}] = \{(2k_1k_4 + k_1k_5)/(2k_4k_6 + k_5k_6 + k_3k_5[\mathrm{CHP}])\}[\mathrm{CHP}][\mathrm{Co^{2+}}] \qquad (12)$$

From Eqs. 8, 9, 10, 11, and 12, the disappearance rate of CHP and rates of formations of CA, AP, and DCP are written as follows:

$$-\mathrm{d}[\mathrm{CHP}]/\mathrm{d}t = 2k_1[\mathrm{CHP}][\mathrm{Co^{2+}}] + k_3[\mathrm{RO\cdot}][\mathrm{CHP}] = [\{2k_1(k_4' + 1) + k_1k_3'(2k_4' + 3)[\mathrm{CHP}]\} / \{(2k_4' + 1) + k_3'[\mathrm{CHP}]\}][\mathrm{CHP}][\mathrm{Co^{2+}}] \qquad (13)$$

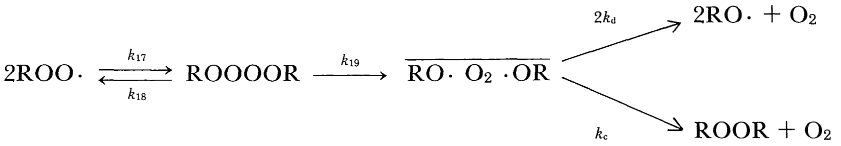
$$\mathrm{d}[\mathrm{CA}]/\mathrm{d}t = k_3[\mathrm{RO\cdot}][\mathrm{CHP}] + k_7[\mathrm{MeOO\cdot}][\mathrm{ROO\cdot}] = [\{k_1(2k_4' + 1)(1 + k_3'[\mathrm{CHP}])\} / \{(2k_4' + 1) + k_3'[\mathrm{CHP}]\}][\mathrm{CHP}][\mathrm{Co^{2+}}] \qquad (14)$$

$$\mathrm{d}[\mathrm{AP}]/\mathrm{d}t = k_6[\mathrm{RO\cdot}] = [\{k_1(2k_4' + 1)/\{(2k_4' + 1) + k_3'[\mathrm{CHP}]\}][\mathrm{CHP}][\mathrm{Co^{2+}}] \qquad (15)$$

$$\mathrm{d}[\mathrm{DCP}]/\mathrm{d}t = 2k_5[\mathrm{ROO\cdot}]^2 = [2k_1k_3'/\{(2k_4' + 1) + k_3'[\mathrm{CHP}]\}][\mathrm{CHP}]^2[\mathrm{Co^{2+}}], \qquad (16)$$

where R=PhCMe$_2$, $k_3'=k_3/k_6$, $k_4'=k_4/k_5$.

Assuming that the initiation rate, k_1[CHP][Co ion], where $k_1=k_2$ and [Co ion] is ([Co^{2+}]+[Co^{3+}]), derived from Eqs. 1, 2, and 8 is equal to the sum of termination rates (Eqs. 5, 6, and 7), the specific rate of reaction (1), k_1, is calculated to be 3.40 l mol^{-1} min^{-1}. This value was chosen to fit the experimental yields of the termination products by applying simplex optimization.[5] The values of k_3' and k_4' were successfully estimated to be 145 and 16 l mol^{-1}, respectively, by applying the Rung–Kutta–Gill method[6] for the experimental data given in Table 1 and k_1=3.4 l mol^{-1} min^{-1}, so as to fit the theoretical time courses of both disappearing CHP and appearing products in the experimental values. As shown in Fig. 1, the theoretical curves (solid line) are in accord with the



Scheme 2.

experimental values depicted by circles, revealing that the mechanisms shown in Scheme 1 is reasonable. Bimolecular reactions of ROO· (Eqs. 4 and 5) are known to proceed by the mechanism shown in Scheme 2.[7]

Eqs. 20 and 21 are obtained under a steady state condition for [ROOOOR] and $[\overline{\text{RO}\cdot\ \text{O}_2\ \cdot\text{OR}}]$.

$$k_4 = (k_d k_{17} k_{19})/\{(2k_d + k_c)(k_{18} + k_{19})\} \tag{20}$$

$$k_5 = (k_c k_{17} k_{19})/\{2(2k_d + k_c)(k_{18} + k_{19})\} \tag{21}$$

The ratio of dissociation to cage recombination, k_d/k_c, can be obtained from Eqs. 20 and 21:

$$k_4' = 2k_d/k_c = 6.7. \tag{22}$$

The fraction of cage collapse, F, i.e. $k_c/(2k_d+k_c)$, is calculated as 0.13 from Eq. 22. This value agrees well with that of the caged *t*-butyloxyl radical pairs formed by the decomposition of di-*t*-butyl hyponitrite (DBH) in "isooctane" (F=0.098) at 45.0 °C (Scheme 3),[8] supporting the mechanism given in Scheme 1. The small difference in the two F values can be rationalized in terms of an easier diffusion out of the *t*-butyloxyl radical pair from the solvent cage than that from sterically bulky α-cumyloxyl radical pair.

Eqs. 23 is obtained from Eqs. 14 and 15, suggesting that plots of d[CA]/d[AP] against [CHP] fall on a straight line with a slope of, k_3' (145 l mol^{-1}).

$$\text{d[CA]/d[AP]} = k_3'[\text{CHP}]_t + 1 \tag{23}$$

The terms involved in Eq. 23 may be substituted using experimentally observable values, i.e. $\Delta[\text{CA}]_{ij}/\Delta[\text{AP}]_{ij}$ and $[\text{CHP}]_{ij}$, to obtain the following equation:

$$\Delta[\text{CA}]_{ij}/\Delta[\text{AP}]_{ij} \simeq k_3'[\text{CHP}]_{ij} + 1 \tag{24}$$

Here, $\Delta[\text{CA}]_{ij}$ and $\Delta[\text{AP}]_{ij}$ represent the concentrations of CA and AP, which increased for a time between i and j, while $[\text{CHP}]_{ij}$ denotes the average [CHP] for the same time, approximated as $([\text{CHP}]_i+[\text{CHP}]_j)/2$. These values were calculated from the experimental data given in Fig. 1, and plotted as shown in Fig. 2. The straight line shown in Fig. 2 has a slope of 145 mol l^{-1}. Considering the limited number of a vailable data, one can say that Fig. 2 well satisfies the relationship given by Eq. 23.

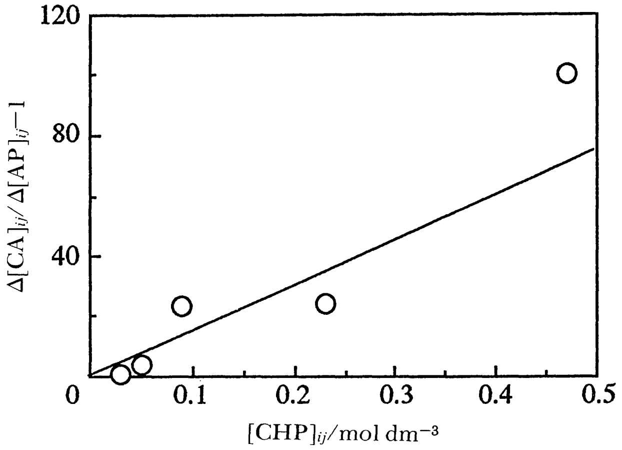
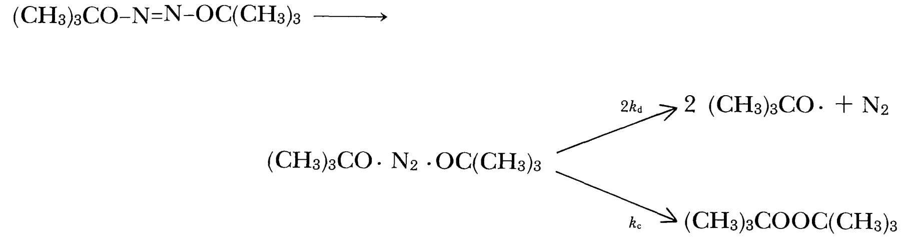


Fig. 2. Relationship between $\Delta[\text{CA}]_{ij}/[\text{AP}]_{ij}$ and $[\text{CHP}]^{\text{av}}$ on Co(Nap)$_2$ catalyzed decomposition of $[\text{CHP}]^{\text{av}}$ in benzene at 25 °C with $[\text{CHP}]_0$=0.59 mol dm^{-3}.

The mechanism of Scheme 1 previously proposed by Hiatt[4] has been verified by our new kinetic investigations which included both the disappearance of CHP and the formation of CA, AP, and DCP in the Co(Nap)$_2$ catalyzed decomposition of CHP in benzene.

Experimental

GC-analysis was performed on a Shimadzu GC-8A gas chromatography with 1.5 m glass column(silicon OV-210, 10%). GC-MS spectra were recorded on a JEOL DX-500 spectrometer.



Scheme 3.

"Cumene hydroperoxide" (commercial grade of Nippon Oil & Fats Co.) was purified via sodium salt by a method described in the literature.[9]

A $Co(Nap)_2$ catalyzed decomposition of CHP was started by the addition of CHP to a catalyst, and an internal standard (benzil)-containing benzene solution immersed in a constant-temperature bath (25.0±0.2 °C) under nitrogen. Each sample was removed by syringe after an appropriate time interval. The residual CHP concentration was determined iodometrically.[10] The concentrations of CA, AP, and DCP were determined by GC after treating with triphenylphosphine to convert CHP to a stable compound, CA.

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