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Mechanism of Decomposition of α,α-Dimethylbenzyl Hydroperoxide Producing Acetophenone and α,α-Dimethylbenzyl Alcohol in a Constant Proportion of 2 to 1

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In the decomposition of α,α-dimethylbenzyl hydroperoxide (**1**) by use of copper(II) chlorocomplexes, the novel fact was found that the product ratio of acetophenone (**2**) to α,α-dimethylbenzyl alcohol (**3**) is 2 to 1. The kinetics of this result was investigated and a mechanism consistent with the experimental result is proposed.

(Keywords: Hydroperoxide; Kinetics)

Mechanismus der Zersetzung von α,α-Dimethylbenzylhydroperoxid unter Bildung von Acetophenon und α,α-Dimethylbenzylakohol in einem konstanten Verhältnis von 2 : 1

Bei der Zersetzung von α,α-Dimethylbenzylhydroperoxid (**1**) unter Verwendung eines Kupfer(II)chlorkomplexes wurde die neue Feststellung gemacht, daß das Produktverhältnis Acetophenon (**2**) : α,α-Dimethylbenzylalkohol (**3**) stets 2 : 1 ist. Die Kinetik der Reaktion wurde untersucht und ein Mechanismus vorgeschlagen, der mit dem experimentellen Resultat konsistent ist.

Introduction

Products in acid decomposition[1] of α,α-dimethylbenzyl hydroperoxide (**1**) are generally phenol and acetone, and the amount of acetophenone (**2**) as a by-product increases if the temperature of the decomposition is higher than 80 °C. On the other hand, it is known that the main product[2] is **2** in the thermal decomposition of **1** at neutrality or α,α-dimethylbenzyl alcohol (**3**) in the decomposition of **1** under alkaline conditions. But no example is known that **2** and **3** are produced

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in a constant proportion. In this paper, we report a novel fact that **2** and **3** are produced in a constant proportion of 2 to 1 in the decomposition of **1** by copper(II) chlorocomplexes[3–7] and propose a possible mechanism.

Experimental

Glacial acetic acid (reagent grade) was purified. Copper(II) acetate (reagent grade) was dried at 115 °C in vacuum. Lithium chloride (reagent grade) was dried at 120 °C in vacuum. Commercial nitrogen gas was passed through 30% aqueous potassium hydroxide solution, a solution of one part 15% aqueous pyrogallol solution and three parts 30% aqueous potassium hydroxide solution, and conc. sulfuric acid before being used. **1** was synthesized from isopropylbenzene and was purified[8]. A 200 ml four-necked flask equipped with a condenser, a thermometer, and a tube for bubbling nitrogen gas was used as a reaction flask. Decomposition was carried out in acetic acid at 60 °C in a nitrogen atmosphere and the reaction temperature was controlled by a thermoregulator. Decompositions were carried out with the ratio of initially added lithium chloride concentration to initially added dimeric copper(II) acetate being 20 to 1.

Quantification of **1** was performed according to iodometry of *Wagner* et al.[9]. 25 ml of isopropyl alcohol, 3 ml of acetic acid, and 5 ml of isopropyl alcohol, which was saturated with sodium iodide, were put into a 100 ml *Erlenmeyer* flask and 5 ml of sample solution was added. The solution was refluxed in a nitrogen atmosphere for 10 min at 70 °C. After cooling 7 ml of water was added, and titration with 1/10 *N* aqueous sodium thiosulfate solution was performed in a nitrogen atmosphere until the yellow color disappeared.

Analysis of **2** and **3** was carried out with a Hitachi model 063 gas chromatography equipped with FID as detector. A 1.5 m column packed with 20% PEG 6000 coated on Celite 545 was used at 170 °C. 1,2,4,5,-Tetramethylbenzene was used as an internal standard. The analysis was performed after non-reacted **1** was treated with triphenylphosphine and thereby changed into **3**.

Measurements of visible spectra were carried out with a Hitachi model 124 spectrometer.

Results and Discussion

Reaction

2 and **3** were identified as the main products in the decomposition of **1** under the experimental conditions. α,α-Dimethylbenzyl chloride and α-methylstyrene were not formed in the decomposition of **1**. Typical patterns of the productions of **2** and **3**, and the decomposition of **1**, are shown in Fig. 1 and 2.

In Fig. 1 and at least at the early stage of decomposition of **1** (Fig. 2) the amount of **3** was about half the amount of **2**. In Fig. 2, after the early stage of the decomposition of **1**, the amount of **3** was less than half

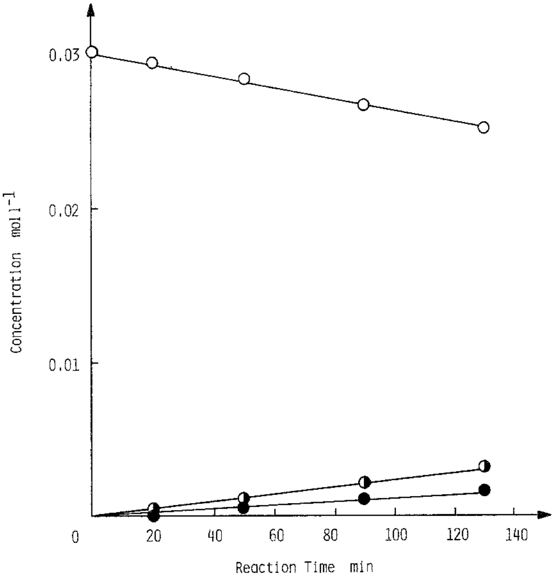


Fig. 1. Decomposition of **1**; [**1**] = 0.03 mol l^{-1}; concentration of initially added dimeric copper(II) acetate $[Cu_2(OAc)_4]$ = 0.0002 mol l^{-1}; concentration of initially added lithium chloride [LiCl] = 0.004 mol l^{-1}; ○ = **1**; ◑ = **2**; ● = **3**

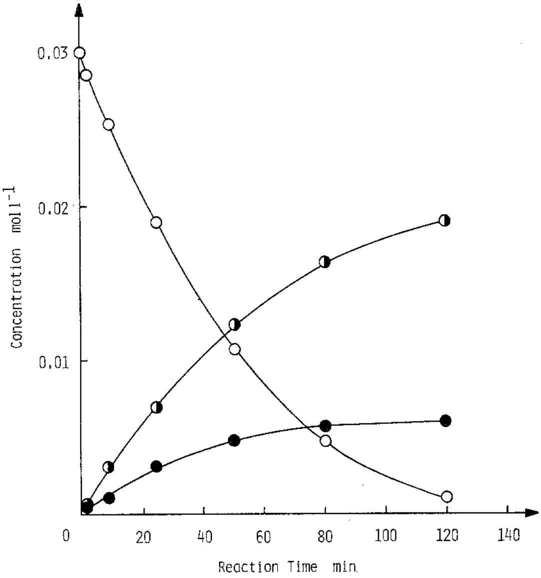
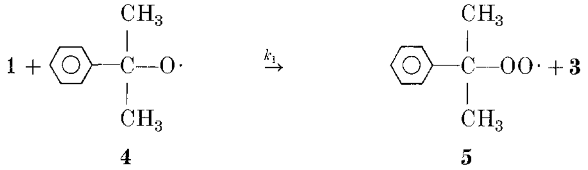


Fig. 2. Decomposition of **1**; [**1**] = 0.03 mol l^{-1}; $[Cu_2(OAc)_4]$ = 0.004 mol l^{-1}; [LiCl] = 0.08 mol l^{-1}; ○ = **1**; ◑ = **2**; ● = **3**

the amount of **2**. The following reaction seems to be largely responsible for this fact:



(1)

The reaction (eq. 1) does not proceed readily because of the decrease of **1**. The change of the visible spectrum of the reaction solution at the beginning of the decomposition of **1** was small.

Kinetic Studies

The effect of initial concentration of **1** on the initial rate of the decomposition of **1** was investigated where the concentration of initially added dimeric copper(II) acetate and the concentration of initially added lithium chloride were 0.004 mol l^{-1} and 0.08 mol l^{-1}, respectively. The result is shown in Table 1. The initial rate of the decomposition of **1** was about first order with respect to the initial concentration of **1**. The effect of the concentrations of initially added dimeric copper(II) acetate and initially added lithium chloride on the initial rate of the decomposition of **1** were investigated at 0.03 mol l^{-1} initial concentration of **1**. The result is shown in Fig. 3. The slope in Fig. 3 is 1-0.5. The average value of the slope is about 0.8.

Table 1. *Effect of concentration of* **1** *on initial rate of decomposition of* **1**

$[\mathbf{1}]/\mathrm{mol\,l^{-1}}$	$\frac{-d[\mathbf{1}]/dt}{[\mathbf{1}]}\ /\mathrm{s^{-1}}$
0.007	$2.7 \cdot 10^{-4}$
0.010	$2.8 \cdot 10^{-4}$
0.020	$3.0 \cdot 10^{-4}$
0.030	$2.6 \cdot 10^{-4}$
0.040	$2.8 \cdot 10^{-4}$

Mechanism of the Decomposition

In a study of reaction mechanisms, it seems interesting that **2** and **3** are produced in a constant proportion of 2 to 1. A mechanism which could explain the experimental result is suggested.

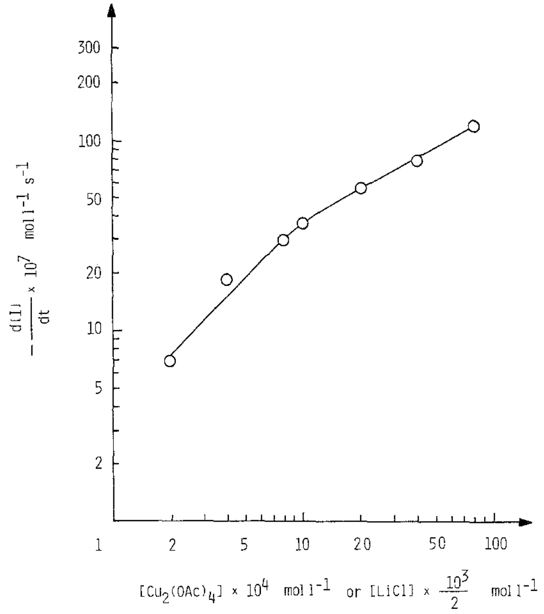


Fig. 3. Effect of initially added concentrations of copper(II) acetate and lithium chloride on initial rates of decomposition of **1**

M^{2+} and M^+ indicate copper(II) ion and copper(I) ion as active species, respectively. Within the range of initially added copper(II) acetate, the following is assumed:

$$[M^{2+}] \propto [\mathrm{Cu_2(O}Ac)_4]^{1-0.5}$$

It is known that metal ions[10–12] decompose hydroperoxides (eq. 2 and 3) and that α,α-dimethylbenzyloxy radical **4**[13,14] produces **2** and methyl radical (eq. 4).

$$\mathbf{1} + M^{2+} \xrightarrow{k_2} \mathbf{5} + \mathrm{H}^+ + M^+ \qquad (2)$$

$$\mathbf{1} + M^+ \xrightarrow{k_3} \mathbf{4} + \mathrm{OH}^- + M^{2+} \qquad (3)$$

$$\mathbf{4} \xrightarrow{k_4} \mathbf{2} + \mathrm{CH_3}\cdot \qquad (4)$$

Methyl radical[15], may react with M^{2+} (eq. 5).

$$\mathrm{CH_3}\cdot + M^{2+} \xrightarrow{k_5} \mathrm{CH_3}^+ + M^+ \qquad (5)$$

4[17–19] may react with **1** (eq. 1).

Equations (6) and (7) were reported by *Fukuzumi* and *Ono*[20].

$$\mathbf{5} \xrightarrow{k_6} \mathbf{2} + CH_3O\cdot \tag{6}$$

$$CH_3O\cdot + \mathbf{5} \xrightarrow{k_7} \text{stable compounds} \tag{7}$$

Here, it is assumed that **2** is produced according to eq. (7) and steady state treatment is applied in equations (1–7).

When $\frac{d[M^+]}{dt} = -\frac{d[M^{2+}]}{dt} = 0$ and $k_1[\mathbf{1}] \gg k_4$[19],

$-\frac{d[\mathbf{1}]}{dt} = 3k_2[\mathbf{1}][M^{2+}]$, $\frac{d[\mathbf{2}]}{dt} = 2k_2[\mathbf{1}][M^{2+}]$,

$\frac{d[\mathbf{3}]}{dt} = k_2[\mathbf{1}][M^{2+}]$.

Thus, $\dfrac{\frac{d[\mathbf{2}]}{dt}}{\frac{d[\mathbf{3}]}{dt}} = \frac{d[\mathbf{2}]}{d[\mathbf{3}]} = 2.$

Therefore, $[\mathbf{2}] = 2[\mathbf{3}] + C$

Where C is an integration constant.
When [**2**] equals zero, [**3**] equals zero.
Thus, $C = 0$.
Therefore, $\frac{[\mathbf{2}]}{[\mathbf{3}]} = 2.$

These results of the calculation are consistent with the experimental kinetic orders and with the ratio of the amount of **2** to the amount of **3** in the decomposition. It should be noted that this mechanism is compatible with first order decay[20] of **5**.

References

[1] California Research Co., U.S. 2,957,921 (1960).
[2] *Sherwood P. W.*, Petroleum Refiner **33**, 144 (1954).
[3] *Smith G. P.*, *Griffiths, T. R.*, J. Amer. Chem. Soc. **85**, 4051 (1963).
[4] *Hubacek H.*, *Stancic B.*, *Gutmann V.*, Monatsh. Chem. **94**, 1118 (1963).
[5] *Manahan S. E.*, *Iwamoto R. T.*, Inorg. Chem. **4**, 1409 (1965).
[6] *Faye G. H.*, Canad. J. Chem. **44**, 1643 (1966).

[7] *Koshitani J., Hiramatsu, M., Ueno Y., Yoshida T.*, Bull. Chem. Soc. Japan **51**, 3667 (1978).

[8] The Society of Synthetic Organic Chemistry, Japan, Yuki Kagobutsu Goseiho, Vol. 11, p. 34. Tokyo: Gihodo. 1968.

[9] *Wagner C. D., Wmith R. H., Peters E. D.*, Ind. Eng. Chem., Anal. Ed. **19**, 976 (1947).

[10] *Pritzkow W., Müller K. A.*, Chem. Ber. **89**, 2321 (1956).

[11] *Kamiya Y., Beaton S., Lafortune F., Ingold K. U.*, Canad. J. Chem. **41**, 2034 (1963).

[12] *Imamura S., Teramoto M., Sumi T., Aomi H., Teranishi H., Takegami Y.*, Bull. Chem. Soc. Japan **49**, 1659 (1976).

[13] *Bartlett P. D., Traylor T. G.*, J. Amer. Chem. Soc. **85**, 2407 (1963).

[14] *Kamiya Y.*, Bull. Chem. Soc. Japan **43**, 830 (1970).

[15] *Kochi J. K., Subramanian R. V.*, J. Amer. Chem. Soc. **87**, 4855 (1965).

[16] *Jenkins C. L., Kochi J. K.*, J. Amer. Chem. Soc. **94**, 843 (1972).

[17] *Kharasch M. S., Fono A.*, J. Org. Chem. **23**, 324 (1958).

[18] *Blanchard H. S.*, J. Amer. Chem. Soc. **81**, 4548 (1959).

[19] *Howard J. A., Ingold K. U.*, Canad. J. Chem. **47**, 3797 (1969).

[20] *Fukuzumi S., Ono Y.*, J. Chem. Soc., Perkin Trans. II **1977**, 622.