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The Decomposition of Cyclohexyl Hydroperoxide in the Presence of Cyclohexanone and a Novel Rearrangement Product

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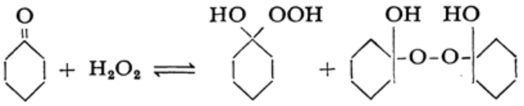
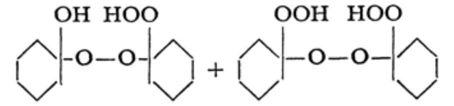
One of the major reaction products besides cyclohexanol from the reaction of cyclohexyl hydroperoxide with cyclohexanone was isolated and confirmed as ε-cyclohexyloxycaproic acid. The rate of formation of ε-cyclohexyloxycaproic acid was measured in excess cyclohexanone and found to follow a first order law for cyclohexyl hydroperoxide. The activation energy of 10.1 kcal/mol was found for the formation of the acid. The rate of decomposition of cyclohexyl hydroperoxide in cyclohexane was measured in the presence of various concentrations of cyclohexanone and the rates of formation of cyclohexanol and the free carboxylic acids were also measured. An adduct formation between cyclohexyl hydroperoxide and cyclohexanone followed by homolytic decomposition of the adduct was suggested to explain the experimental results.

The reaction of hydrogen peroxide with cyclohexanone has been studied by Criegee *et al.*[1] and they showed the formation of four rather stable peroxides at 40°C.





(1)

Denisov *et al.*[2] have studied the free-radical formation in the similar reaction by means of α-naphthylamine technique at 120—140°C. It is also known that alkyl hydroperoxides were strong oxidizing

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[1] R. Criegee, W. Schnorrenberg and J. Becke, *Ann.*, **565**, 7 (1949).

[2] E. T. Denisov, V. V. Kharitonov and E. N Raspopova, *Kinetika i Kataliz*, **5**, 981 (1964).

agents in the presence of alkali hydroxides and cleaved alkyl aryl ketones into corresponding aryl carboxylic acids and alkyl alcohols.[3,4] Cyclohexanone was found to be inert on treatment with *t*-butyl hydroperoxide in the presence of an alkali hydroxide.[3] On the other hand, cyclohexanone reacts readily with peracids to produce ε-caprolactone.[5,6]

This report deals with the decomposition of cyclohexyl hydroperoxide in the presence of cyclohexanone and a novel rearrangement product, namely ε-cyclohexyloxycaproic acid, $C_6H_{11}\cdot O\cdot (CH_2)_5\cdot COOH$ (I). Some kinetic investigations were carried out to estimate the reaction mechanism to this reaction and the characteristic nature of the decomposition of cyclohexyl hydroperoxide in the presence of cyclohexanone was elucidated.

Experimental

Reagents. Commercial cyclohexane and cyclohexanone were fractionated using 2 feet Vigreaux column, bp 80.7°C for cyclohexane and bp 156—156.5°C for cyclohexanone.

Cyclohexyl hydroperoxide was prepared by the following procedure. The air-oxidation of cyclohexane was carried out using an aluminum walled autoclave at 140°C for three hours by passing approximately one *l*/min of air, and the oxidate solution was concentrated by evaporating cyclohexane at a room temperature under a reduced pressure employing a water aspirator until approximately 0.3 mol/*l* of the hydroperoxide concentration was attained. The conecntrated oxidate solution was washed with an equal volume of aqueous 10% Na_2CO_3 solution to remove free acids. The amount of the hydroperoxide in the solution was determined by an iodometric titration of an aliquot of the solution. Two equivalents of NaOH as 40% aqueous solution were added dropwise to the oxidate solution with vigorous stirring at around 5°C. The precipitated salt of hydroperoxide was separated by means of a centrifuge and washed with cyclohexane several times and dried in a desiccator under the reduced pressure of 10mmHg. Dried precipitate was dissolved in the least volume of ice-water and neutralized with 50% acetic acid to pH 6. The solution was extracted with an equal volume of diethyl ether three times. The ether layer was dried and ether was evaporated at a room temperature under the reduced pressure of 3 mmHg.

Isolated cyclohexyl hydroperoxide was 85—90% pure and stored in a refrigerator. The identity of the hydroperoxide was established by an infrared and an NMR spectra. IR spectrum (Hitachi model EPI-S2) (γ_{max}, 1450, 1365, 1160, 1150, 1020, 950 and 840 cm^{-1}). NMR spectrum (Nihon Denshi model JNM 3H-60) measured at 60 Mc (2.16τ(−OOH)(singlet)(1H), 6.08τ (=CH–O–)(multiplet)(1H) and mutiplets centerd around 8.5 τ (–CH_2–)(10H)).

Methyl-ε-cyclohexyloxycaproate. A mixture of cyclohexanone and cyclohexyl hydroperoxide (1:1 molar ratio) was heated at 140°C for 2 hr in a round bottom flask. The reaction mixture was treated with an ethereal solution of diazomethane and the methyl esters of the produced acids were analyzed on the gas liquid partition chromatography, glpc, (Hitachi model KGL-2B), using a 2 m column packed with silanized kieselguhr (30—60 mesh) impregnated with 25% diethyleneglycol succinate operating at 160°C with helium as a carrier gas. A few mg of the comparatively pure unknown compound was obtained by repeated condensation of the eluted vapor corresponding to one of the two major products besides cyclohexanol and identified as methyl-ε-cyclohexyloxycaproate, $C_6H_{11}\cdot O\cdot (CH_2)_5COOCH_3$ (II).

Found: C, 68.2; H, 8.8% (F & M glpc type analyzer). Calcd for $C_{13}H_{24}O_3$; C, 58.4; H, 10.5%.

Infrared spectrum (ν_{max}, 2980, 2920, 1750, 1460, 1440, 1370, 1200, 1180, 1110, 1025 and 955 cm^{-1}). NMR spectrum (6.32τ(−$COOCH_3$)(sing.) (3H), 6.53τ (–CH_2O–)(tripl.)(2H), 7.70τ(–CH_2COO–) (tripl.)(2H), multiplets centerd around 8.5τ(–CH_2–) (16H) and multiplet around 6.35τ(=CHO–)(1H) seemed to be overlapped with the methyl singlet). The structure of the unknown compound was confirmed by the comparison with the spectra of authentic methyl-ε-cyclohexyloxycaproate. The other major product was identified as dimethyl adipate. The total carboxylate content was determined by the use of potentiometric automatic titrater (Hiranuma Sangyo model RA-1) after saponification of the reaction mixture.

Synthesis of Methyl-ε-cyclohexyloxycaproate. In a 500 m*l* round bottom flask 200 g of cyclohexanol was heated with 5.8 g (0.25 mol) of metallic sodium for several hours until homogeneous solution was obtained. ε-Chlorocaproic acid, 15.1 g (0.1 mol), was then added dropwise with vigorous stirring to the solution and heating was continued further for one hour after the addition. The excess cyclohexanol was removed under a reduced pressure and the residue was digested with 150 g of water. Unreacted alkoxide was neutralized by bubbling sufficient volume of carbon dioxide gas through the solution, which was then evaporated to dryness. The solid residue was dissolved in 100 m*l* of water, washed with ether and then acidified. The aqueous solution was extracted with ether. The ether layer was dried and treated with the ethereal diazomethane, and ether was removed to give crude methyl ester of ε-cyclohexyloxycaproic acid, which was then fractionated, bp 115°C at 2 mmHg. Yield 16.4 g (72% of the theoretical yield).

Found: C, 68.4; H, 10.5%. Calcd for $C_{13}H_{24}O_3$: C, 68.4; H, 10.5%.

The IR and NMR spectra of this compound agreed with those of the unknown compound.

Decomposition of Cyclohexyl Hydroperoxide. Thermal decomposition of cyclohexyl hydroperoxide in cyclohexane in the presence of cyclohexanone was studied in an aluminum walled autoclave at 130°C under a stream of nitrogen (1.5 *l*/min). Cyclohexane solutions (300 m*l*) containing *ca.* 0.15 mol of cyclohexyl hydroperoxide and three different concentrations of cyclohexanone were placed in the autoclave, heated to 130°C with vigorous stirring (800 rpm) and maintained at that temperature. Aliquots were withdrawn at specified

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[3] K. Maruyama, R. Goto and H. Suzuki, *Nippon Kagaku Zasshi, (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **80**, 521 (1959).

[4] K. Maruyama, This Bulletin, **34**, 102, 105 (1961).

[5] S. L. Fries and P. E. Frankenberg, *J. Am. Chem. Soc.*, **74**, 2679 (1952).

[6] M. F. Hawthorne and W. D. Emmons, *ibid.*, **80**, 6398 (1959).

intervals through a sample outlet device. The hydroperoxide concentrations in the aliquots were determined by the iodometric titration and the total free carboxylate contents were determined by the use of potentiometric automatic titrater. The total carbonyl contents were estimated by the method described in an earlier publication.[7] Cyclohexanone and cyclohexanol contents in the aliquots were determined by glpc (Hitachi model KGL-2A), using a 3 m column packed with kieselguhr (30—60 mesh) impregnated with 25% of polyethyleneglycol 3000 operating at 140°C with helium as a carrier gas. Chlorobenzene was used as an inner standard. Since the remaining cyclohexyl hydroperoxide in the sample decomposed on glpc and also gave cyclohexanone and cyclohexanol, their amounts should be deduced from the measured values to obtain true concentrations of cyclohexanone and cyclohexanol in the samples. Glpc of 91 mmol/*l* and 183 mmol/*l* of cyclohexyl hydroperoxide solution in cyclohexane gave 52 mmol/*l* and 97 mmol/*l* of cyclohexanone and 42 mmol/*l* and 92 mmol/*l* of cyclohexanol respectively.

Results and Discussion

The decomposition of cyclohexyl hydroperoxide (100 mmol) in 1 mol of cyclohexanone at 140°C for three hours gave 3 mmol of adipic acid and 3.9 mmol of ε-cyclohexyloxycaproic acid. The total carboxylate content after saponification of the reaction mixture was 34.2 meq. There was some indication of the presence of a higher boiling substance which was revealed by glpc using a capillary column, but no dodecanedioic acid was found in the reaction mixture.

The rates of formation of ε-cyclohexyloxycaproic acid were followed at the three different temperatures, (see Table 1) and an over-all activation energy for the first order rate constants was calculated as 10.1 kcal/mol.

TABLE 1. RATE CONSTANTS OF ε-CYCOLHEXYLOXYCAPROIC ACID FORMATION*

Temp. (°C)	$k\times 10^{-6}$ (sec^{-1})
105	4.60
120	7.80
130	10.44

* Initial cyclohexyl hydroperoxide concentration is 775 mmol/kg in cyclohexanone.

The rates of decomposition of cyclohexyl hydroperoxide in the presence of three different concentrations of cyclohexanone in cyclohexane solution at 130°C were followed by iodometry, and the rates of formation of cyclohexanone, cyclohexanol and the total free acids in the reaction mixture were also measured. (see Tables 2, 3)

The rate of formation of the total free acids (expressed in meq) was found to obey the equation,

$$\frac{\mathrm{d(FA)}}{\mathrm{d}t} = k_1\cdot(\mathrm{CHPO})\cdot(\mathrm{ANON}), \qquad (2)$$

TABLE 2. DECOMPOSITION OF CYCLOHEXYL HYDROPEROXIDE IN CYCLOHEXANE IN THE PRESENCE OF CYCLOHEXANONE AT 130°C

Run No.	Time (min)	CHPO (mmol)	ANON* titd. (mmol)	ANON* glpc** (mmol)	ANOL (mmol)	Free Carboxylic Acids (meq)
A-19	0	150.6	207	194.7	42.7	4.4
	40	99.9	210	205.1	88.1	13.6
	80	62.3	220	214.9	122.9	25.5
	120	41.9	229	227.1	147.1	31.5
	160	27.2	226	226.4	161.4	36.6
A-18	0	156.1	381	384.0	50.0	4.5
	40	79.5	383	382.3	108.3	20.2
	84	41.9	380	402.1	147.1	35.2
	120	23.0	385	402.5	164.5	43.1
	160	12.9	382	395.5	174.5	47.6
A-20	0	148.8	677	653.6	45.6	4.6
	40	62.3	670	659.9	112.9	28.5
	80	27.7	662	650.2	144.2	48.4
	120	12.6	662	657.7	160.7	48.4
	160	6.6	672	660.7	166.7	59.3

* Initial cyclohexanone concentrations; 0.22 mol/*l* for A-19; 0.38 mol/*l* for A-18; 0.67 mol/*l* for A-20.
** ANON (glpc) and ANOL (glpc) were corrected by considering the decomposition of CHPO on glpc.

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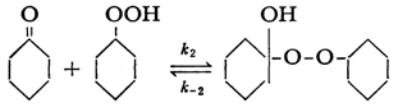
7) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," (Japanese Edition), Maruzen, Tokyo (1957), p. 26.

TABLE 3. FORMATION OF CYCLOHEXANOL AND TOTAL FREE ACIDS IN THE DECOMPOSITION OF CYCLOHEXYL HYDROPEROXIDE IN CYCLOHEXANE IN THE PRESENCE OF CYCLOHEXANONE AT 130°C

Run No.	Time (min)	CHPO (Decd.) (mmol)	ANON (Formed) titd. (mmol)	ANON (Formed) glpc (mmol)	ANOL (mmol)	Free Carboxylic Acids (meq)
A-10	0	0.0	0	0.0	0.0	0.0
	40	50.7	3	10.4	45.4	9.2
	80	88.3	13	20.2	80.2	21.2
	120	108.7	22	32.4	104.4	27.1
	160	123.4	19	31.7	118.7	32.2
A-18	0	0.0	0	0.0	0.0	0.0
	40	76.6	2	−1.7	58.3	15.7
	84	114.2	−1	18.1	97.1	30.7
	120	133.1	4	10.5	114.5	35.6
	160	143.2	1	11.5	124.5	43.1
A-20	0	0.0	0	0.0	0.0	0.0
	40	86.5	−7	6.3	67.3	23.9
	80	121.1	−15	−3.6	98.6	43.8
	120	136.2	−15	4.6	115.1	53.4
	160	142.2	−5	7.1	121.1	54.7

where, FA, total free acids; CHPO, cyclohexyl hydroperoxide; ANON, cyclohexanone. (see Figs. 1, 2)

It might be expected that cyclohexyl hydroperoxide forms an adduct (III) with cyclohexanone-like hydrogen peroxide.



(III) (3)

The formation of ε-cyclohexyloxycaproic acid can be explained by the probable –O–O– bond scission of the adduct followed by β-scission of α-hydroxyalkoxy free radical (IV) to produce a rearranged free radical (VI) and the cage recombination of the radical (VI) with incipient alkoxy radical (V).

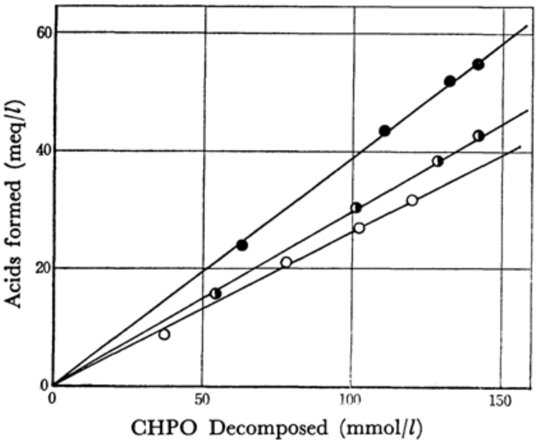


Fig. 1. Relationship between decomposed cyclohexyl hydroperoxide and free acids formed.
●, cyclohexanone 0.67 mol/l; ◑, cyclohexanone 0.38 mol/l; ○, cyclohexanone 0.22 mol/l

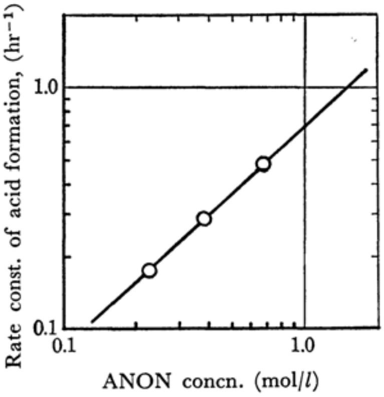
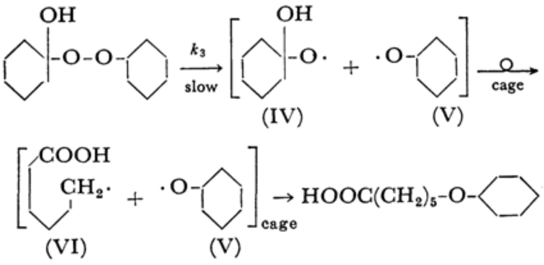


Fig. 2. Relationship between rate constants of acid formation and cyclohexanone concentrations.



(4)

This process may be either stepwise or a concerted one. If the whole course of the reaction scheme involved the fast pre-equilibrium of the adduct formation and the slow decomposition of the adduct, the rate of formation of ε-cyclohexyloxycaproic acid would be expressed as follows.

$$\frac{\mathrm{d(CCA)}}{\mathrm{d}t}=K\cdot k_3\cdot f\cdot(\mathrm{CHPO})\cdot(\mathrm{ANON}), \qquad (5)$$

where, CCA, ε-cyclohexyloxycaproic acid; K, equilibrium constant ($K=k_2/k_{-2}$); k_3, decomposition rate constant; f, fraction of radicals to form CCA.

Hence, the over-all activation energy for this reaction will be expressed by,

$$E_a=E_{k2}-E_{k-2}+E_{k3}, \qquad (6)$$

where, E_{k2}, activation energy for forward reaction; E_{k-2}, activation energy for backward reaction; E_{k3}, activation energy for decomposition reaction.

Denisov *et al.*[2)] reported the value of the heat of formation of the cyclohexanone-H_2O_2 adduct as 6.7 kcal/mol and value of an activation energy for the decomposition rate constant of that adduct as 16.2 kcal/mol. Thus an over-all activation energy of that process would be around 9.5 kcal/mol, which is close to that of ε-cyclohexyloxycaproic acid formation.

The β-scission of the radical (IV) will also be able to give cyclohexanone and hydroxy radical (·OH), but the recombination of hydroxy radical with the alkoxy radical (V) only produces cyclohexyl hydroperoxide and reverses the adduct formation. The main products of the decomposition of cyclohexyl hydroperoxide in the presence of cyclohexanone are clearly cyclohexanol and the carboxylic acids. (see Table 3) This is incompatible with the approximate 1 : 1 formation of cyclohexanone and cyclohexanol in the decomposition of cyclohexyl hydroperoxide on glpc.

The diffusion of the radicals (IV), (V) and hydroxy radical out of the solvent cage may cause the formation of cyclohexanol and the other acidic substances. The initial rate of the formation of cyclohexanol is expressed as

$$\left[\frac{\mathrm{d(ANOL)}}{\mathrm{d}t}\right]_{\mathrm{initial}}=k_4\cdot(\mathrm{ANON})^{0.51}, \qquad (7)$$

where, ANOL, cyclohexanol. (see Fig. 3)

The chain reaction mechanism for the formation of cyclohexanol can be suggested by the approximate one half order dependence of the rate on cyclohexanone concentration and illustrated by the following reaction scheme.

$$\left.\begin{array}{l}\text{Adduct}\rightarrow \mathrm{RO}\cdot+\mathrm{R}'\cdot,\\ \mathrm{R}'\cdot+\mathrm{ROOH}\rightarrow\\ \quad \mathrm{ROO}\cdot+\mathrm{R'H}\text{ or }\mathrm{RO}\cdot+\mathrm{R'OH},\\ \mathrm{RO}\cdot+\mathrm{ROOH}\rightarrow\mathrm{ROO}\cdot+\mathrm{ROH},\\ 2\mathrm{ROO}\cdot\rightarrow 2\mathrm{RO}\cdot+\mathrm{O}_2,\\ 2\mathrm{RO}\cdot\rightarrow\text{molecular products,}\end{array}\right\} \qquad (8)$$

where, RO·, $C_6H_{11}O\cdot$; R’·, other radicals; ROOH, $C_6H_{11}OOH$.

The rate of disappearance of cyclohexyl hydroperoxide was observed to be

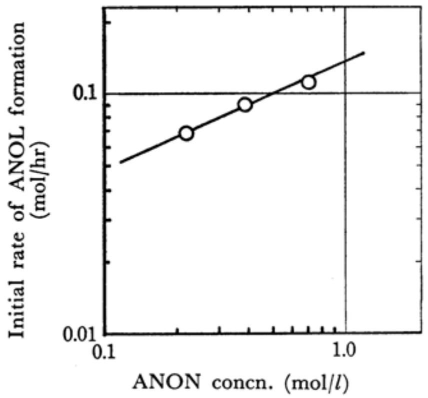


Fig. 3. Relationship between initial rates of cyclohexanol formation and cyclohexanone concentrations.

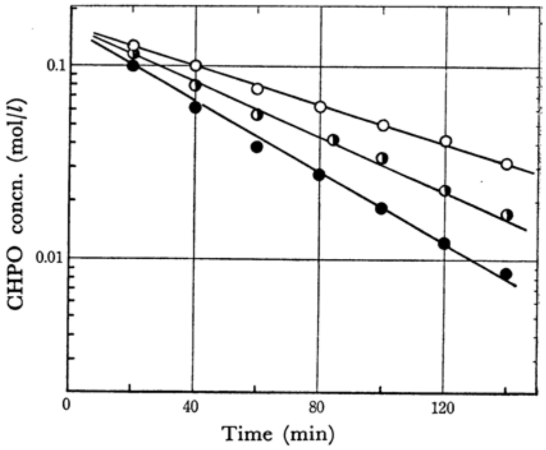


Fig. 4. Disappearance of cyclohexyl hydroperoxide in the presence of cyclohexanone.
●, cyclohexanone 0.67 mol/*l*; ◑, cyclohexanone 0.38 mol/*l*; ○, cyclohexanone 0.22 mol/*l*

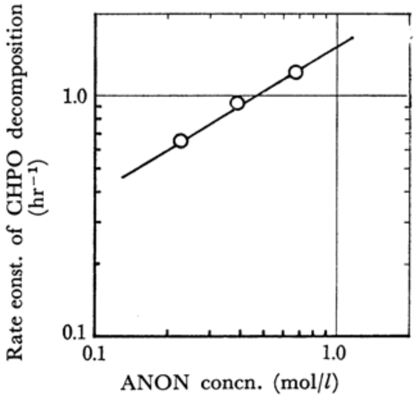


Fig. 5. Relation between decomposition rate constants of cyclohexyl hydroperoxide and cyclohexanone concentrations.

$$-\frac{\mathrm{d(CHPO)}}{\mathrm{d}t} = k_5\cdot\mathrm{(CHPO)}\cdot\mathrm{(ANON)}^{0.67}. \qquad (9)$$

(see Figs 4, 5)

The catalytic effect of the produced acids (up to 35 meq) on the rate of disappearance of cyclohexyl hydroperoxide was examined by the addition of a small amount of carboxylic acids (up to 100 mq) to the reaction mixture and found to be not very significant in our experimental condition. (see Table 4)

TABLE 4. EFFECTS OF ACID CONCENTRATION ON THE RATE CONSTANTS

Run No.	Acid conc. (meq)	k_d* (hr^{-1})	
SA-30	110±13	1.15	Caproic acid was added.
SA-29	38±12	0.93	Adipic acid was added.
SA-31	21±14	0.85	Produced acid only.
SA-21	19±15	0.84	Produced acid only.
SA-34	18±13	0.84	Produced acid only.
---- Extrapolated to zero, 0.78			

Temperature, 130°C; Cyclohexanone concentration, 0.37 mol/*l*.

$$* \ -\frac{\mathrm{d(CHPO)}}{\mathrm{d}t} = k_d\cdot\mathrm{(CHPO)}$$

Consequently, the rate equation of disappearance of cyclohexyl hydroperoxide is considered to involve several independent terms

$$-\frac{\mathrm{d(CHPO)}}{\mathrm{d}t} = k_6\cdot\mathrm{(CHPO)}+K\cdot k_3\cdot\mathrm{(CHPO)}\cdot\mathrm{(ANON)} + k_7\cdot\mathrm{(CHPO)}^m\cdot\mathrm{(ANON)}^n, \qquad (10)$$

where, k_6, first order rate constant for the decomposition of cyclohexyl hydroperoxide; k_7, rate constant for the induced decomposition of cyclohexyl hydroperoxide.

Farkas *et al.*[8] reported the rate constant of the disappearance of cyclohexyl hydroperoxide in cyclohexane (k_6; 0.000143 min^{-1} at 130°C). The presence of cyclohexanone is found to increase the rate of disappearance of cyclohexyl hydroperoxide (k_{obs}; $0.042+\mathrm{(ANON)}^{0.67}$ min^{-1} at 13°C). The observed over-all rate enhancement of disappearance of cyclohexyl hydroperoxide in the presence of cyclohexanone would be the consequence of the combined effect of the terms in the Eq. (10.)

We are indebted to Teijin Limited who granted us permission of publication.

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[8] A. Farkas and E. Passaglia, *J. Am. Chem. Soc.*, **72**, 3333 (1950).