β Scission of Acyl Radicals in the Radical Decomposition of Various α-Hydroperoxy Ketones[1]

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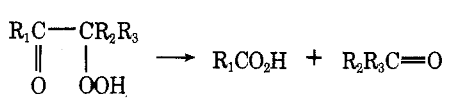
Thermolysis of α-hydroperoxy ketones ($R_1COCR_2R_3OOH$, 1) at 130 or 250 °C was shown to give mainly carboxylic acids (R_1CO_2H) and ketones ($R_2R_3C{=}O$). Diketones (R_1COCOR_2) accompanied as a minor product (2–20% yield) when $R_3 = ArCH_2$. The redox reaction of $PhCOCPhR_3OOH$ with Fe^{2+} in aqueous MeOH at 25 °C afforded benzil (PhCOCOPh, ~20%) together with ketones ($PhR_3C{=}O$, 80–100%). The addition of $FeCl_3$ to this system afforded R_1CO_2Me (40–65%) and R_3Cl (0–18%) additionally. These results suggest a competitive scission of acyl and benzyl radicals from α-acylalkoxy radical $R_1COCR_2R_3O\cdot$ (2). The ligand transfer from $FeCl_3$ leading to R_3Cl and R_1CO_2Me is an evidence for the intermediacy of $R_3\cdot$ and $R_1\dot{C}{=}O$ (e.g., $R_1\dot{C}{=}O \rightarrow R_1COCl \rightarrow R_1CO_2Me$). The product ratios give the order of β scission of radicals from 2 at 25 and 250 °C: $i\text{-}Pr\dot{C}{=}O > Me\dot{C}{=}O > Ph\dot{C}{=}O \gg PhCH_2\cdot$. The scission of benzyl radicals showed a substituent effect of ρ (with σ^+) = −1.11 (70% MeOH, 25 °C) and −0.54 (vapor phase, 250 °C).

α-Hydroperoxy ketones (1) are intermediates in the autoxidative cleavage of ketones to carboxylic acids and carbonyl



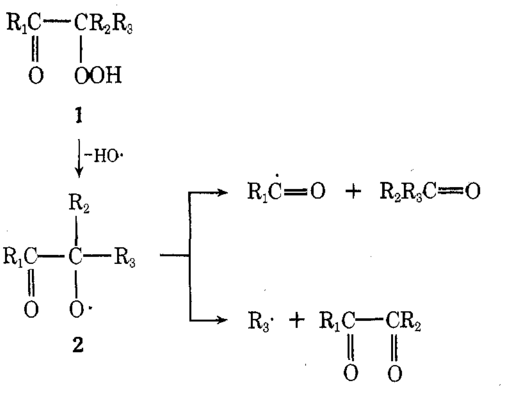
$$R_1C(=O)\text{—}CR_2R_3(OOH) \longrightarrow R_1CO_2H + R_2R_3C{=}O \qquad (1)$$

1

compounds.[2] The decomposition of 1 in alkaline media has been shown to proceed mainly via an acyclic C=O addition mechanism[3a] rather than a cyclic dioxetane mechanism.[3b] On the other hand, the thermal decomposition of 1 proceeds homolytically,[4] but is complicated because of competitive acid-catalyzed heterolysis.[4a,5] Our previous report[6] described the thermal and redox decomposition of two typical peroxides, **1a** and **1c**, to proceed via the O–O homolysis followed by a facile scission of benzoyl radical. Here, we extend the study to various types of 1 to see the structural effects on the β scission of acyl radicals.

Results and Discussion

α-Hydroperoxy ketones (1) were decomposed under three conditions: (1) vapor phase thermolysis (thermolysis GLC) at 250 °C; (2) thermolysis in chlorobenzene at 130 °C; (3) redox reaction with $FeSO_4$ or $FeSO_4$–$FeCl_3$ in 70% MeOH at 25 °C. In every case, the decomposition of 1 affords products which suggest a formation of α-acylalkoxy radical (2) followed by the β scission of acyl (eq 2a) or alkyl radical (eq 2b) as reported previously.[6]



$$R_1\dot{C}{=}O + R_2R_3C{=}O \qquad (2a)$$

$$R_3\cdot + R_1C(=O)\text{—}C(=O)R_2 \qquad (2b)$$

Thermolysis GLC. A small amount (~4 μl) of a 0.01 M benzene solution of 1 was injected into GLC (injection temperature 250 °C, carrier gas N_2) and products were analyzed. Since the solvent vaporizes immediately after the injection, the decomposition of 1 occurs practically in vapor phase.[7] Similar results were obtained with the injection temperature of 180 or 290 °C.

Major products are ketone and carboxylic acid as shown in Table I. Peroxides with R_1 = Ph afford 4–16% yields of biphenyl and peroxides with $R_3 = ArCH_2$ give diketones in 2–22% yields. Interestingly, the yields of α-hydroxy ketones were quite poor (<2%).

The yield of biphenyl was not changed by a tenfold increase of the amount of **1a** in benzene, but reduced to zero when toluene or alcohols were used in place of benzene. In the case of toluene, there appeared typical products from the hydrogen abstraction of methyl, i.e., bibenzyl and benzyl alcohol. Hence, biphenyl is formed by a radical pathway:

$$Ph\dot{C}{=}O \xrightarrow{-CO} Ph\cdot \xrightarrow{PhH} Ph_2 \qquad (3)$$

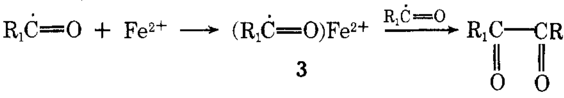
The same reaction of $Ph\dot{C}{=}O$ is known in liquid phase.[8]

The formation of diketone via eq 2b was observed only when $R_3 = ArCH_2$. An alternative pathway via the dimerization of acyl radicals is excluded by the fact that benzil was not detected even by a tenfold increase of the amount of **1a**.

Thermal Decomposition in Chlorobenzene. Thermal decomposition in chlorobenzene at 130 °C afforded a similar result to that of the thermolysis GLC. Benzil was formed only with $R_3 = ArCH_2$ and α-hydroxy ketones were obtained in a yield less than 5% (Table II). The decomposition in chlorobenzene is much faster than that in xylene, which seems to be a typical solvent effect for radical decomposition.[9] However, the homolysis cannot always be a main reaction, since an alternative acid-catalyzed decomposition of 1 is also probable.[5,10]

Redox Reaction. When 1 with R_1 = Ph was reduced by ferrous ion in 70% aqueous MeOH at 25 °C, benzil (~20%) was accompanied by ketones $R_2R_3C{=}O$ (80–100%) (Table III). α-Hydroxy ketones were also a minor product (<1%). In contrast, the reduction of cumene hydroperoxide afforded cumyl alcohol as a main product (Table III), and similar results were reported for other hydroperoxides.[11]

The formation of benzil proceeds probably via the Fe^{2+}-catalyzed dimerization of benzoyl radicals (eq 4). Dimerization



$$R_1\dot{C}{=}O + Fe^{2+} \longrightarrow \underset{\mathbf{3}}{(R_1\dot{C}{=}O)Fe^{2+}} \xrightarrow{R_1\dot{C}=O} R_1C(=O)\text{—}C(=O)R_1 \qquad (4)$$

of $R_1\dot{C}{=}O$ is apparent, since **1a** and **1b** gave benzil and *p,p'*-dimethoxybenzil, respectively, and since their yields were almost reduced to zero by the addition of $FeCl_3$ (Table IV). The assumption of a metastable complex **3** is based on the fact that the yield of benzil was constant even when 1 was dropped

Table I. Pyrolysis GLC (250 °C) of α-Hydroperoxy Ketones (1)[a]

	$R_1C(=O)-CR_2R_3(OOH)$				Products, %[a]				
	R_1	R_2	R_3	Solvent	$R_2R_3C{=}O$	R_1CO_2H	Ph_2	R_1COCOR_2	Others
1a	Ph	Ph	Ph	PhH	98	78	5	0	
				PhMe[b]	99	79	0	0	$(PhCH_2)_2$, 7%; $PhCH_2OH$, 7%; PhCHO, 17%
1b	p-MeOPh	Ph	Ph	PhH	100	c	c	0	
1c	Ph	Ph	$PhCH_2$[d]	PhH	95	80	6	5.4	
1d	Ph	Ph	p-$ClPhCH_2$	PhH	90	74	4	4.2	
1e	Ph	Ph	p-$MePhCH_2$	MeOH	62	c	0	5.0	
1f	Ph	Ph	p-$MeOPhCH_2$	PhH	55	68	5	7.9	
1g	Ph	Ph	PhCH(Et)	MeOH	87	c	0	21.8	PhCH(Et)OH, 5.7%; α-HO ketone,[e] 2%
1h	Ph	Ph	i-Pr	PhH	69	c	16	0	
1i	Me	Ph	$PhCH_2$	MeOH	71	c	0	1.7	α-HO ketone,[e] 2%
1j	i-Pr	Ph	$PhCH_2$	MeOH	74	c	0	6.3	α-HO ketone,[e] 1%

[a] Ca. 4 μl of a 0.01 M solution was injected into GLC (injection temperature 250 °C, column temperature 80–250 °C, carrier gas nitrogen). Ph = C_6H_5 or C_6H_4. Yields are averages of two to six runs. [b] Data from ref 6. [c] Not determined. [d] Yields were the same when tenfold of the solution was injected. [e] The corresponding α-hydroxy ketone.

very slowly or added in one portion in an open flask. Since the reaction of hydroperoxides with ferrous ion is very fast[12] and completed within 1 min, the yield of benzil, without assuming the intermediacy of **3**, should be decreased by the slow dropping in air, which was not the case. A similar complex has been isolated or suggested for other radicals.[13]

The formation of acyl radical (eq 2a) was confirmed by the redox reaction of **1** with $FeSO_4$–$FeCl_3$ (Table IV). The presence of $FeCl_3$ reduced the benzil formation and instead produced methyl benzoate probably via a sequence

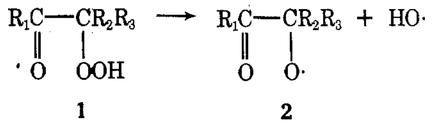
$$R_1\dot{C}{=}O \xrightarrow{FeCl_3} R_1COCl \xrightarrow{MeOH} R_1CO_2Me \qquad (5)$$

The β scission of benzyl radicals (eq 2b) when $R_3 = ArCH_2$ was likewise ascertained by a ligand transfer reaction:

$$R_3\cdot \xrightarrow{FeCl_3} R_3Cl \qquad (6)$$

The ligand transfer of halogen to a carbon radical is well known.[14]

Mechanism. A main reaction for the thermolysis of **1** can be written as a radical sequence as follows:



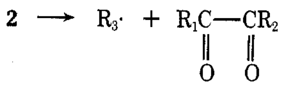
$$\underset{\mathbf{1}}{R_1C(=O)-CR_2R_3(OOH)} \longrightarrow \underset{\mathbf{2}}{R_1C(=O)-CR_2R_3(O\cdot)} + HO\cdot \qquad (7)$$

$$\mathbf{2} \longrightarrow R_1\dot{C}{=}O + R_2R_3C{=}O \qquad (8)$$

$$R_1\dot{C}{=}O + \mathbf{1} \longrightarrow R_1CO_2H + \mathbf{2} \qquad (9)$$

This radical chain decomposition mechanism is based on the following facts: (1) much faster decomposition in chlorobenzene than that in xylene or toluene.[9] (2) The high quantum yield of 2–4 observed for the photolysis of **1a** or **1c**.[10] (3) Trapping of $R_1\dot{C}{=}O$ by $FeCl_3$ (eq 5). (4) Formation of high yields of R_1CO_2H. A very low yield of α-ketol shows that the β scission of **2** (eq 8) is much faster than the hydrogen abstraction from solvent, etc. The major products, ketone and carboxylic acid, can be explained by the chain sequence (eq 8 and 9). Reaction 9 is an induced decomposition (SH2 reaction on O–O) of **1** with acyl radical. The induced decomposition of hydroperoxides[15] and the SH2 reaction of $Ph\dot{C}{=}O$ with peroxide[16] are known.

A minor reaction for the thermolysis of **1** is eq 10 and 11 in place of eq 8 and 9.



$$\mathbf{2} \longrightarrow R_3\cdot + R_1C(=O)-CR_2(=O) \qquad (10)$$

$$R_3\cdot + \mathbf{1} \longrightarrow R_3OH + \mathbf{2} \qquad (11)$$

This propagation is operative only when R_3 = benzyls, R_3OH being detectable (6%) for the case of **1g**. Radical $R_3\cdot$ is also trapped by $FeCl_3$ (eq 6).

The redox reaction of **1** with Fe^{2+} seems to be the same as the well-known process for other hydroperoxides.[17]

$$\mathbf{1} + Fe^{2+} \longrightarrow \mathbf{2} + (HO\cdot)Fe^{3+} \qquad (12)$$

This is followed by the competitive reactions, 8 and 10, and then by a ligand transfer reactions 4, 5, and 6.

β-Scission Reaction. The β scission of *tert*-alkoxy radicals has been established[11,18] and previous reports include the information on the scission of halomethyl,[18a,h] alkoxymethyl,[18h,i] alkoxycarbonyl,[18h,i] and acyl radicals.[19] The present results of low-yield formation of α-ketols (mostly <1%) shows that β scission reactions 8 and/or 10 are over 100-fold faster than the hydrogen abstraction of **2** from the solvent. The relative β-scission reactivities can be obtained

Table II. Thermal Decomposition of 1 in Chlorobenzene at 130 °C for 2 h[a]

		Products, %[b]				
Peroxide	Atmosphere	R_1CO_2H	$R_2R_3C{=}O$	$R_1\underset{O}{\underset{\|}{C}}-\underset{OH}{\underset{\vert}{C}}R_2R_3$	$Ph\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}Ph$	Others[c]
1a	Air	92	99	<1	0	
1a	N_2	76	99	<1	0	
1c	Air	80	71	4.6	1.1	$(PhCH_2)_2$, 1.4%
1c	N_2	82	74	1.8	1.7	$(PhCH_2)_2$, 1.2%
1f	N_2	85	54	4.2	1.3	
1d	N_2	88	67	1.5	0	
1h	N_2	94	99	<1	0	

[a] Reaction with [1] = 0.01 M. [b] Determined by GLC. [c] The other minor products (<1%) were not determined.

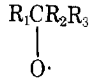
Table III. Reaction of 1 with Fe^{2+} in 70% MeOH at 25 °C[a]

	Products, %[b]		
Peroxide	$R_2R_3C{=}O$	$R_1\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}R_1$	$R_1\underset{O}{\underset{\|}{C}}-\underset{OH}{\underset{\vert}{C}}R_2R_3$
1a	95	17[c]	<1
1b	92	17[c]	<1
1c	81	20[c]	<1
1h	100	21[c]	1.3
1i	102	*d*	<1
1j	104	*e*	<1
$PhCMe_2OOH$[f]	12[g]		69[h]

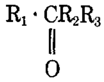
[a] Reaction with [1] = 0.01 M and [$FeSO_4$] = 0.1 M under air. [b] Determined by GLC after extraction with $CHCl_3$. R_1CO_2H was not determined. [c] According to eq 4, this value should be duplicated. [d] Biacetyl was not determined. Another diketone MeCOCOPh was produced in 0.79% yield. [e] Diketone *i*-PrCOCOPh of 0.36% yield was detected. [f] Cumene hydroperoxide. [g] Acetophenone. [h] Cumyl alcohol.

from the product ratios (Table V). The scission of acyl radicals is much faster than that of benzyl or *tert*-butyl radical, the latter being the fastest one thus far known.[18d] There is not a large difference between the relative scissions in 70% MeOH at 25 °C or in vapor phase at 250 °C.

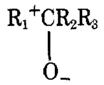
Polar effect in the β scission has been established and its transition state may be written as **4a–c**.[18d,e]


$R_1\underset{O\cdot}{\underset{\vert}{C}}R_2R_3$

4a


$R_1\cdot\underset{O}{\underset{\|}{C}}R_2R_3$

4b


$R_1{}^+\underset{O_-}{\underset{\vert}{C}}R_2R_3$

4c

Acyl radicals are σ radicals and stabilized by the resonance with lone pair electrons of carbonyl oxygen.[20] The observed order of $i\text{-Pr}\dot{C}{=}O > Me\dot{C}{=}O > Ph\dot{C}{=}O$ reflects probably the polar effect, i.e., the order of electron-releasing power (see **4c**). The lowest reactivity of $Ph\dot{C}{=}O$ among the acyl radicals is comprehensible since the radical is not stabilized by the resonance with phenyl.[20] The fast scission of acyl radicals is rational in view of the stability of acyl radicals and their easy formation from aldehydes.[21,22] Moreover, the scission of acyl radical would be facilitated by the polar contribution such as **4c** (R_1 = acyl), since acyl cations are stable carbonium ions[23] and acyl radicals have a nucleophilic character.[20b,24]

Finally, the relative scission of substituted benzyl radicals was obtained from product ratios (Table VB) and correlated with σ^+ to give a negative ρ value. This effect is also explicable by the resonance contribution of **4c** for the β scission. The ρ value of −1.11 in 70% MeOH at 25 °C agrees well with the value of −1.04 from hypochlorite decomposition in CCl_4 at 25 °C.[18d]

Experimental Section

Materials. Starting ketones for **1d,e,f** were obtained from deoxybenzoin and the corresponding benzyl chlorides by the literature method.[25] A starting ketone for **1h** was synthesized by method B in our previous report.[3a] Starting ketones for **1i,j** were obtained by the reaction of *t*-BuOK, $R_1COCH_2R_2$, and $PhCH_2Cl$ (molar ratio of 1:1:1) in DMF-*t*-BuOH (3:1) at 20–30 °C under N_2.

The preparation of α-hydroperoxy ketones, **1a–c,** was described previously.[3a] Peroxides **1d,e,f,h,i,j** were synthesized by method I[3a] and crystallized from benzene–petroleum ether in 12–67% yields, melting points (purity by iodometry) being 153–156 (100%), 148–150 (98%), 147–148 (99%), 75–80 (99%), 104–107 (99%), and 125.5–126.0 °C (98%), respectively. Ir spectra (Nujol mull) of these peroxides show an absorption at ~3300 (OOH) and at ~1700 cm^{-1} (C=O). Also NMR spectra satisfied the formation of α-hydroperoxy ketones. For example, NMR spectra (CCl_4) for **1i** are as follows: δ 2.10 (s, 3 H, CH_3), 3.30 (d, *J* = 15 Hz), and 3.67 (d, *J* = 15 Hz) (each 1 H, asymmetric $PhCH_2$), 6.7–7.2 (broad, 10 H, two Ph), 8.30 (s, 1 H, OOH). Peroxide **1g** was obtained according to the literature method,[26] mp 147–148 °C (100% pure; lit.[26] mp 152–153 °C).

Decomposition and Product Analysis. Products were identified and determined in comparison with an authentic sample by GLC with three different columns (1 m): (1) Apiezon grease L, 15% on Celite 545; (2) PEG 20M, 2% on Chamelite CK; (3) PEG succinate, 13% on Chromosorb. Propiophenone or biphenyl were used as an internal standard.

Pyrolysis GLC was done by injecting ca. 4 μl of a 0.01 M solution of 1 (injection temperature 250 °C, carrier gas N_2, column temperature

Table IV. Reaction of 1 with $FeSO_4$–$FeCl_3$ in 70% Aqueous MeOH at 25 °C[a]

		$R_1\dot{C}{=}O\sim$		$R_3\cdot\sim$		R_3Cl[b]
Peroxide	R_3 in 1	R_1CO_2Me	$R_2R_3C{=}O$	R_3Cl	R_1COCOR_2	$R_2R_3C{=}O$
1a	Ph	60.6	100	0	2[c]	0.00
1d	p-$ClPhCH_2$	52.8	74.1	3.1	2.7	0.042
1c[d]	$PhCH_2$	54.9	81.7	4.9	3.9	0.060
1e	p-$MePhCH_2$	65.5	74.9	8.3	7.9	0.110
1f	p-$MeOPhCH_2$	40.6	51.8	16.8	22.3	0.41
1g	PhCH(Et)	55.0	70.6	18.2	27.9	0.258
1i	$PhCH_2$	*e*	103	2.0	2.05	0.019
1j	$PhCH_2$	*e*	99.5	1.3	1.2	0.013

[a] Reaction with [1] = 0.01 M, [$FeSO_4$] = 0.1 M, and [$FeCl_3$] = 0.05 M under air. Ph = C_6H_5 or C_6H_4. [b] Relative rate of scission of $R_3\cdot$ vs. that of $R_1\dot{C}{=}O$ (see eq 2a, 2b, and 6). [c] Benzil was formed by dimerization of $Ph\dot{C}{=}O$ (eq 4). β-Elimination of Ph· from **2** did not occur, since **1b** (R_1 = p-MeOPh) did not produce *p*-methoxybenzil. [d] Data from ref 6. [e] Not determined.

Table V. Relative Reactivity of β Scission of Acyl and Benzil Radicals from 2

Radicals[a]	Relative rate of β scission 70% MeOH (25 °C)[b]	 Vapor phase (250 °C)[c]
A. Scission of Various Radicals		
i-Pr$\dot{\mathrm{C}}$=O	78.1	263
Me$\dot{\mathrm{C}}$=O	51.5	41.8
Ph$\dot{\mathrm{C}}$=O	16.7	17.5
Ph$\dot{\mathrm{C}}$HEt	4.3	4.4
PhCH$_2$·	(1.00)	(1.00)
B. Substituent Effect in Benzyl Radicals		
p-ClPhCH$_2$·	0.70	0.82
PhCH$_2$·	(1.00)	(1.00)
p-MePhCH$_2$·	1.83	1.44
p-MeOPhCH$_2$·	6.90	2.51
ρ (σ^+)	−1.11 (r = 0.997)	−0.54 (r = 0.999)
ρ (σ)	−1.81 (r = 0.897)	−0.91 (r = 0.926)

[a] Ph = C_6H_5 or C_6H_4. [b] Determined from product ratios of $R_3Cl/R_2R_3C{=}O$ in Table IV. [c] Determined from the ratios of $R_1COCOR_2/R_2R_3C{=}O$ in Table I.

80–250 °C). Since the solvent is vaporized immediately after the injection, the decomposition of 1 occurs practically in vapor phase (N_2 gas). Products were determined in situ by the usual GLC method.

Thermolysis of 1 in chlorobenzene was performed, after air was replaced with N_2, at 130 °C for 2 h and products were determined by GLC.

Redox reaction of 1 with Fe^{2+} was instantaneously completed when a methanolic solution of 1 (0.02 M, 5 ml) was added to a mixture of MeOH (2 ml), aqueous $FeSO_4$, and $FeCl_3$ (total 3 ml) at 25 °C. Products were analyzed by GLC after the extraction with $CHCl_3$.

Registry No.—**1a,** 57196-77-7; **1b,** 57272-35-2; **1c,** 57196-78-8; **1d,** 58966-95-3; **1e,** 58966-96-4; **1f,** 58966-97-5; **1g,** 7492-76-4; **1h,** 58966-98-6; **1i,** 58966-99-7; **1j,** 58967-00-3.

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(1) Contribution No. 225.

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