(10) The total product was analyzed after isomerization of IV to VI was complete.

(11) The rates of exchange of I and IV in 0.05 M DPO_4^{2-}–D_2O solutions at ca. 35 °C were 5.3×10^{-4} and 1.6×10^{-4} s^{-1}, respectively.

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Photolysis of α-Hydroperoxy Ketones

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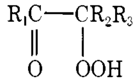
Abstract: Photolysis of α-hydroperoxy ketones (**1**) has been studied, and a radical chain mechanism involving an acyl radical is proposed. Thus, the photolysis of α-hydroperoxy-α,α-diphenylacetophenone (**1a**) in benzene affords benzophenone and benzoic acid together with a small amount of biphenyl and phenol. The addition of O_2 or CCl_4 affords peracid or benzoyl chloride, respectively; and the photolysis in the presence of toluene gives products from benzyl radical. Similar products were obtained from other α-ketohydroperoxides. Quantum yields are mostly in the range of 2–3, which together with the product study suggests a radical chain decomposition involving the acyl radical as a chain carrier. Sensitization experiments indicate that the primary photoreaction of **1** is the O–O homolysis rather than the type-I or the type-II reaction as a ketone.

α-Hydroperoxy ketones (**1**) are intermediates in the autoxidative cleavage of ketones[1] and in the reaction of olefins with ozone.[2] Recently, we have shown that the alkaline decomposition of **1** proceeds mainly via a C=O addition mechanism[3] and that the thermal or redox decomposition produces acyl radicals.[4] Our interests extended to the photolysis of **1** from a viewpoint of photochemistry of ketones and photochemical air pollution. The Norrish type-I and -II reactions have been well established for the photolysis of ketones,[5] and a recent communication[6] describes the type-II reaction for the photolysis of **1**. As will be described, however, our data favor an O–O homolysis mechanism involving acyl radicals.



$R_1C(=O)-CR_2R_3(OOH)$

1

a, $R_1 = R_2 = R_3 = Ph$
b, $R_1 = p\text{-MeOPh}, R_2 = R_3 = Ph$
c, $R_1 = R_2 = Ph, R_3 = Me$
d, $R_1 = R_2 = Ph, R_3 = PhCH_2$
e, $R_1 = Mes, R_2 = R_3 = Me$
f, $R_1 = i\text{-Pr}, R_2 = R_3 = Me$
g, $R_1 = R_2 = R_3 = Me$
($Ph = C_6H_5$ or C_6H_4; Mes = mesityl)

Results and Discussion

Photolysis Products. The photolysis of α-hydroperoxy ketones (**1**) in benzene occurred easily by Pyrex-filtered irradiation. As shown in Table I, the products in benzene are ketones (55–100%) and carboxylic acids (50–80%) together with a small amount of biphenyl (1–3%) and phenol (3–5%). On addition of toluene to the reaction mixture there were obtained additional products which seem to be derived from benzyl radical, e.g., bibenzyl, benzyl alcohol, and 1,1,2-triphenylethanol.

The photolysis under O_2 affords peracids in 22–84% selectivities. These yields are lower limits, since the peracid is probably consumed by its induced decomposition.[7] The peracid formation under O_2 suggests the intervention of acyl radical; this could be ascertained by the formation of benzoyl chloride (34–94%) in the presence of CCl_4 for the case of peroxides with $R_1 = Ph$. Peracid was also formed from a photolysis of a parent ketone $PhCOCHPh_2$ under O_2 (Table I).

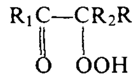
Product ratios at low conversions (<50%) were not significantly altered from those of high conversions (>95%). For example, the photolysis of **1a** in benzene resulted always in similar product ratios, i.e., PhCHO (2–4%), Ph_2 + PhOH (total 2–4%), $PhCO_2H$ (70–80%), and $Ph_2C{=}O$ (>95%). The selectivities of peracid in the presence of O_2 and acyl chloride in 50% CCl_4 were higher at lower conversions; e.g., 84% perbenzoic acid and 94% benzoyl chloride were obtained at 48 and 17% conversions, respectively.

Photolysis of peroxide **1e** (R_1 = Mes) and **1f** (R_1 = *i*-Pr) for 30 min under O_2 (78 and 33% conversions) yielded peracids in 30 and 38% selectivities, respectively. But photolysis of the parent ketones, $MesCOCHMe_2$ and *i*-$PrCOCHMe_2$, under the same conditions was very slow (<5% conversion), affording no peracid.

Noticeably, the yields of α-hydroxy ketones were always low (<1%) in contrast to the case of other hydroperoxides, where the alcohol formation is a main reaction.[8]

Quantum Yields and Sensitizations. The photolysis of **1a** (0.005–0.02 M) in benzene afforded comparable quantum yields of ca. 2.5; but the yields varied with the photolysis conditions, i.e., solvents or the presence of O_2 (Table II). Lower yields were obtained for the photolysis of **1a** in CCl_4 ($\Phi = 0.9$) and in *n*-hexane ($\Phi = 1.3$), and the lowest value seems to be in agreement with the reported values of $\Phi = 0.5$–1.4 for 0.025–0.5 M of **1c** in CCl_4.[6] However the photolysis of **1a** and **1d** under various conditions mostly resulted in the quantum

Table I. Products of Photolysis of α-Hydroperoxy Ketones (**1**)[a]

 $R_1C(=O)-CR_2R_3(OOH)$				Conditions[b]	Conversion (%)	Products (%)[c]					
	R_1	R_2	R_3			R_1CHO	R_1CO_2H	Ph_2	PhOH	$R_2R_3C{=}O$	Others[d]
1a	Ph	Ph	Ph		>98	4	65	1	3	90	
				Under O_2	90	8	71	2	9	103	R_1CO_3H (45%)[e]
				50% *i*-PrOH	96	5	58	0	1	68	Ph_2CHOH (2%)
				50% CCl_4	>98	2	25	1.5	4	88	PhCOCl (65%)[f]
				50% toluene	>98	18	64	0	5	52	$PhCH_2OH$ (2%), $(PhCH_2)_2$ (19%), $Ph_2C(OH)CH_2Ph$ (21%), $PhCOCH_2Ph$ (9%)
				0.01 M PhSH	>98	45	48	1	6	93	PhCOSPh (6%)
1b	*p*-MeOPh	Ph	Ph		>98	4	51			93	
				Under O_2	91	9	45			102	R_1CO_3H (12%), *p*-MeOPhCOPh (2%)
1c	Ph	Ph	Me		>98	7	65	1.5	5	103	$Ph_2C{=}O$ (1%)
				Under O_2	94	4	82	4	21	97	R_1CO_3H (22%), $Ph_2C{=}O$ (3%)
				50% CCl_4	>98	0	42	2	0	100	PhCOCl (34%)
				50% toluene	>98	20	72	0	5	107	$Ph_2C{=}O$ (2%), $(PhCH_2)_2$ (2%), $PhCOCH_2Ph$ (2%)
1d	Ph	Ph	$PhCH_2$		>98	0	49	3	4	55	PhCOCOPh (1%)
1e	Mes	Me	Me		>98	0	67			84[g]	R_1OH (17%)
	$PhCOCHPh_2$[h]				56	6	2	0	0	3	$(Ph_2CH)_2$ (21%), PhCOCOPh (8%)
				Under O_2	86	24	47	5	8	47	R_1CO_3H (39%), Ph_2CHOOH (26%), Ph_2CHOH (17%), $(PH_2CH)_2$ (3%), PhCOCOPh (1%)

[a] Irradiation (1 h) of a 0.01 M solution of **1** through a Pyrex filter; Ph = C_6H_5 or C_6H_4 and Mes = mesityl. [b] Benzene solution under nitrogen unless otherwise noted. Volume % in benzene. [c] Determined by GLC except for the case of peroxides, which were done by iodometry. [d] A small amount (<1%) of α-hydroxy ketones was detected for some cases. [e] Fifteen minutes of irradiation (48% conversion) afforded perbenzoic acid in 84% selectivity. [f] After 17% conversion PhCOCl was produced in 94% yield. [g] Determined as 2,4-dinitrophenylhydrazone. [h] Parent ketone of **1a**.

Table II. Quantum Yields of the Photolysis of **1** in Benzene[a]

Peroxide	Concn, mM	Conditions[b]	No. of determinations	Φ
1a	5		3	2.46 ± 0.71
	10		5	2.60 ± 0.26
	20		3	2.41 ± 0.88
	10	Air	1	1.69
	10	O_2	1	1.89
	5	50% *i*-PrOH	1	3.13
	10	50% CCl_4	2	0.88 ± 0.11
	10	50% $PhCH_3$	1	2.21
	10	50% *n*-C_6H_{14}	1	1.29
1d	10		3	4.02 ± 0.60
	10	50% CCl_4	1	2.24
$Ph_2C{=}O$	10	100% *i*-PrOH	2	1.60[c]

[a] Quantum yields were determined iodometrically after 5–20% conversion by irradiating mainly at 366 nm using a Corning CS 7-51 and Pyrex filter. Ferrioxalate actinometry was used. [b] Reaction in benzene under N_2 unless otherwise noted. [c] Literature values are 1.48–1.90 for $[Ph_2C{=}O]$ = 1–100 mM; A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59,** 2038 (1963).

yields much higher than 1, which suggests a radical chain decomposition of the hydroperoxides. The yield, and hence the chain length, vary with solvents, which is probably caused by the chain transfer to the solvent.

The photolysis of aliphatic peroxides **1f** and **1g** was sensitized by aromatic ketones (Table III). The peroxy ketones **1f** and **1g** absorb light significantly at 313 nm, ε being 22 and 30, respectively; photolysis in the absence of sensitizers is due to the excitation at 313-nm irradiation. Since 0.001 M sensitizer and 0.01 M **1** were used for the experiments in Table III, the light absorption by the substrate **1f** or **1g** is still significant at 313 nm in view of the absorbances of the sensitizers. But a similar sensitization effect (i.e., % decomposition) was obtained by using 0.01 M sensitizer, where over 99% of the light is absorbed by the sensitizer.

Table III. Sensitized Photolysis of Aliphatic **1**[a]

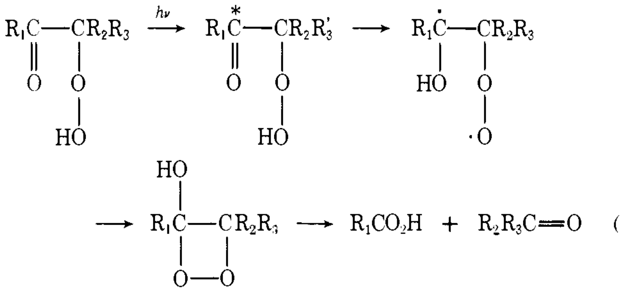
Sensitizer, 0.001 M	E_T (T_1 state),[b,c] kcal/mol	$\Phi_{i\text{-PrOH}}$[c,d]	% decomposition[e]		Sensitization
			1g	**1f**	
None			18.1	19.8	
PhCOPh	69 (n,π)	2.0	44.8	35.0	+
p-MeOPhCO-Ph	69 (n,π*)		59.8	42.4	+
p-HOPhCOPh	68 (n,π*)	0.02	50.7	37.0	+
p-PhPhCOPh	61 (π,π*)	0.2	48.4	36.4	+
α-NaphCOPh	58 (π,π*)	0	41.5	29.0	+
Fluorenone	53 (n,π*)	0	28.6		+
Anthracene	42 (π,π*)	0	7.1		−

[a] Ph = C_6H_5 or C_6H_4 and Naph = naphthyl. Irradiation of a 0.01 M benzene solution of **1** under N_2 using a 100-W high-pressure Hg lamp through a Pyrex filter for 60 min. The absorption coefficients (ε) of **1f** and **1g** are less than 0.2 at 366 nm and 36 and 50, respectively, at 310 nm in benzene. Since the irradiation is mainly at 366 nm and ε's of the sensitizers are over 100 at 366 nm, over 95% of the absorbed light is that of the added sensitizer. [b] The energy and the configuration of the lowest triplet state of the sensitizer. [c] Cited from ref 5d,e and 16. [d] Quantum yield of the photoreduction of *i*-PrOH. [e] Means of three to five determinations; probable errors are ca. ±1.0%.

The ketone-sensitized decomposition occurred regardless of sensitizer triplet energy (E_T), configuration (n,π* or π,π*), or hydrogen abstraction ability from *i*-PrOH. The sensitized photolysis of peroxides has been studied,[9] and the benzophenone-sensitization of various types of peroxides occurred at a similar rate.[9b] On the other hand, anthracene retarded the decomposition as an inner filter, which is probably due to its low E_T of 42 kcal/mol.[10]

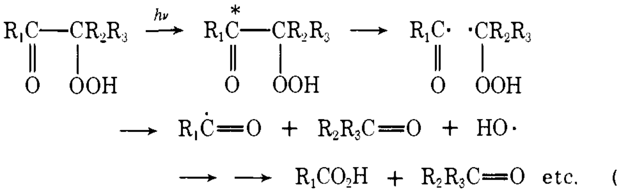
Primary Photolytic Process. On the basis of the photochemistry of ketones[5,12] and peroxides,[6,9] there are four pathways conceivable for the photolysis of α-hydroperoxy ketones:

Mechanism A (the type-II reaction)[6]



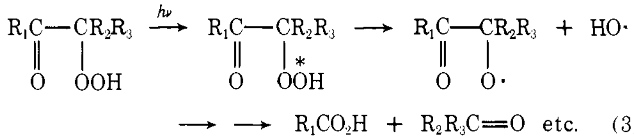
(1)

Mechanism B (the type-I reaction)



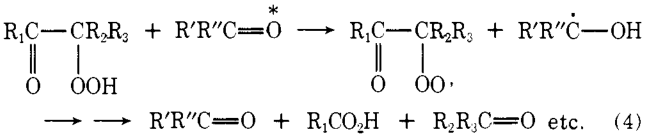
(2)

Mechanism C (O-O homolysis)



(3)

Mechanism D (hydrogen atom abstraction)



(4)

Here, * shows an excited state of the indicated group, and R'R''C=O may be either starting ketone **1**, product ketone $R_2R_3C{=}O$, or added sensitizer.

Mechanism A, which contains a dioxetane produced by a ketone type-II reaction, was suggested to explain the low yield (<1%) of α-ketol.[6] But this mechanism is excluded by trapping acyl radical by CCl_4 or O_2 (Table I) and by the fact that the low yields of α-ketols were also observed in the radical decomposition of **1**.[4] Although mechanism A was proposed to operate solely at concentrations $\leq$0.05 M **1** in CCl_4,[6] the photolysis of **1a** and **1c** in the presence of CCl_4 afforded 34–94% of PhCOCl at a lower concentration (0.01 M) of **1**.

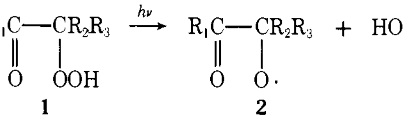
Mechanism D is analogous to the photolysis of *t*-BuOOH,[9b] since triplet ketones may be excellent hydrogen atom abstracters[5] and hydroperoxides are excellent hydrogen atom donors.[13] But, for the present aliphatic peroxides, the ketone-sensitized decomposition occurred regardless of configurations (n,π^* or π,π^*) or of hydrogen-abstraction ability of the ketones (Table III). For the case of aromatic peroxides (**1**, R_1 = Ph), an intermolecular hydrogen abstraction of **1** by **1*** (i.e., R'R''C=O = **1**) is probably impossible, since the type-I reaction of α-oxy ketones is very fast and cannot be quenched by quenchers.[12] These facts disfavor mechanism D, which also cannot explain the predominant formation of R_1CO_2H in place of R_1CHO as discussed below.

The trapping of acyl radical by O_2 or CCl_4 which resulted in higher yields at lower conversions supports mechanism B or C as a primary photolytic process. The primary process of mechanism B is the type-I reaction as ketones,[5] which is very fast for α-oxy ketones.[12] Mechanism C is also likely because most peroxides can be photolyzed with quantum yield of unity.[9,14] Product studies satisfy both mechanism B and C, but the following examination[15] seems to prefer mechanism C.

(i) It has been shown that triplet energies of ketones are not altered significantly by α-substituent, e.g., α-oxy group.[12] Thus, the triplet energy of C=O in aliphatic **1f** and **1g** is probably over 70 kcal/mol.[16] Hence, the sensitized decomposition of **1f** and **1g** is caused by the energy transfer from aromatic ketones (E_T = 53–69 kcal/mol) to the peroxy group rather than to the aliphatic C=O in **1**.

(ii) The ketone-sensitized decomposition of peroxides is general and effective for the intermolecular[9b] and the intramolecular sensitization.[9d] Hence, for the present case of **1** with R_1 = Ph,[17] the intramolecular energy transfer from C=O* to O-O is probably fast and effective because of the proximity of benzoyl and peroxidic groups.

Scheme I



(5)

$$2 \longrightarrow R_1\dot{C}{=}O + R_2R_3C{=}O \quad (6)$$

$$R_1\dot{C}{=}O + \mathbf{1} \longrightarrow R_1CO_2H + \mathbf{2} \quad (7)$$

Scheme II. ($R_\cdot = R_1CO{-}CR_2R_3{-}$)

$$ROOH + R_1\dot{C}{=}O \longrightarrow ROO\cdot + R_1CHO \quad (8)$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2 \quad (9)$$

$$RO\cdot \longrightarrow R_1\dot{C}{=}O + R_2R_3C{=}O \quad (10)$$

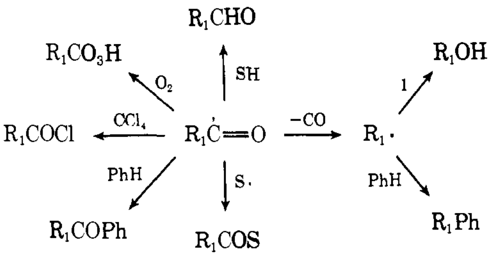
Overall Mechanisms. The overall mechanism of the photolysis of **1** can thus be summarized as the radical chain decomposition given in Scheme I. The observed quantum yield over 1 is explicable by assuming a fast rate in the β-scission of **2** (eq 6)[4] and an acyl radical-induced decomposition of **1** (eq 7).[18] If the quantum yield for the O-O homolysis (eq 5) is 0.5–1, the observed yield of Φ = 2–4 in benzene (Table II) corresponds to the chain length of ca. 2–8. The lower quantum yields in CCl_4 or *n*-hexane reflect a poor ability of $\cdot CCl_3$ or hexyl radical as a chain carrier. The high ability of acyl radical as a chain carrier may be related to the nucleophilicity of the radical[19] and a polar effect (e.g., $\rho > 0$) in the induced decomposition of substituted peroxides.[20] The S_H2 reaction on peroxidic oxygen of hydroperoxides similar to eq 7 has been reported for cumyl, benzyl, and cyclohexyl radicals,[21] and the similar hydroxylation by peracid, a kind of hydroperoxide, is also known.[7a]

An alternative chain scheme is conceivable by analogy to the known chain decomposition of tertiary hydroperoxides[13] (Scheme II). However, this scheme cannot explain the predominant formation of R_1CO_2H, no formation of O_2,[6] and the fact that R_1CHO is a minor product (<10%) in the absence of a suitable hydrogen donor in spite of the efficient trapping of $R_1\dot{C}{=}O$ by O_2 or CCl_4. Since R_1CHO is stable under the photolysis conditions, Scheme II cannot be a major pathway, if it contributes at all.

Equation 5–7 thus explain the predominant formation of ketones and carboxylic acids. Most of the other products in Table I, e.g., acyl chloride, biphenyl, and aldehyde, may be derived from acyl radical as shown in Scheme III.

The remaining products in Table I are derived from the known photochemical reactions or couplings of free radicals. For example, benzhydrol from the photolysis of **1a** in *i*-PrOH is formed by the photoreduction of benzophenone, and the

Scheme III. (SH = solvent or additive)



photolysis in toluene afforded bibenzyl and 1,1,2-triphenylethanol.[22] Benzil from **1d** is probably formed by the scission of benzyl radical from **2**, a competitive reaction with eq 6.[4] On the other hand, the photolysis of the parent ketone of **1a** gave benzil by dimerization of benzoyl radical.[12]

Experimental Section

Materials. α-Hydroperoxy ketones, **1a–d,f,g,** have been described previously.[3] Peroxide **1e** was synthesized in 100% yield by method I in the previous report;[3] mp 18–20 °C (petroleum ether); ir (neat) 3380 (OOH) and 1690 cm^{-1} (C=O); NMR (CCl_4) δ 1.45 (s, 6 H, 2 Me), 2.13 (s, 6 H, 2 *o*-Me), 2.21 (s, 3 H, *p*-Me), 6.80 (s, 2 H, 2 *m*-H), and 7.87 (broad s, 1 H, OOH).

Photolysis and Product Analysis. The photolysis of **1** in a Pyrex test tube was carried out mostly with a Halos 300-W high-pressure Hg lamp through a Pyrex filter. Mostly 0.01 M benzene solutions of **1** were irradiated under nitrogen after three to five freeze–pump–thaw cycles.

Quantum yields were determined by iodometry[3] and the ferrioxalate actinometry[23] using a Corning CS 7-51 filter and a Pyrex filter, and the results are listed in Table II. For comparison, the yield for the photoreduction of benzophenone in *i*-PrOH was determined and shown to agree well with the literature value (Table II).

All products were determined by GLC in comparison with an authentic sample using three different columns (1 m; temperature, 80–250 °C): (i) Apiezon grease L, 15% on Celite 545; (ii) PEG 20M, 2% on Chamelite CK; (iii) PEG succinate, 13% on Chromosorb. Propiophenone or benzophenone were used as an internal standard.

The peroxidic mixture of **1** and peracid was determined as follows: An aliquot (2 ml) was added into a mixture of MeOH (5 ml) and Me_2SO (0.5 ml), and peracid was completely consumed by 5 min of standing; the remaining **1** was titrated iodometrically as reported previously.[3] The total peroxide (**1** + peracid) may be determined without the preliminary treatment with Me_2SO. The difference between the two titrations corresponds to the amount of peracid.

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α-Diazobenzylphosphonate Dianions

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Abstract: Aqueous solutions of disodium α-diazobenzylphosphonate can be prepared by the action of alkali on the dicyanoethyl ester of α-diazobenzylphosphonic acid. The salt is somewhat unstable at room temperature even at neutrality; the decomposition is general acid catalyzed. The properties of the dianion are compared with those of the corresponding mono- and dicyanoethyl esters and of other diazo compounds that can serve as reagents for photoaffinity labeling.

Diazo esters have proved useful for the thermal,[1] metal ion catalyzed,[2] and photoaffinity[3,4] labeling of enzymes and other important biological materials. While diazophosphonates might then be expected to prove useful in similar reactions at binding sites for phosphates on enzymes and membranes, no dianion of a diazophosphonate has previously been reported. This paper records the successful preparation of disodium α-diazobenzylphosphonate in aqueous solution. Although the