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Kinetics of the Base-Catalyzed Decomposition of α-Hydroperoxy Ketones

Yasuhiko Sawaki and Yoshiro Ogata*

Contribution No. 215 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan. *Received March 31, 1975*

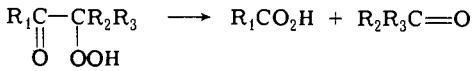
Abstract: The alkoxide-catalyzed decomposition of 15 α-hydroperoxy ketones **1a–o** afforded generally high yields of ketones (80–100%) and esters (70–100%). The high yields of esters show that the α-cleavage reaction proceeds predominantly via an acyclic, carbonyl addition intermediate. The formation of a small amount of carboxylic acid was caused by the reaction of hydroxide ion via the acyclic intermediate rather than via a cyclic 1,2-dioxetane. The pseudo-first-order rate constant, k_{obsd}, with respect to **1** is proportional to [RONa] at lower base concentrations and then approaches a constant at higher ones. The behavior suggests a reaction between RO^- and the undissociated hydroperoxide, and the resulting second-order rate constant (k_{10}) for MeONa ranged from 4.2×10^{-1} M^{-1} sec^{-1} for **1c** to 5.6×10^{-5} M^{-1} sec^{-1} for **1b** in benzene–methanol at 0°. The substitutent effect on α-hydroperoxy-α,α-diphenylacetophenones exhibited positive ρ values of 2.5–3.2 and 0.9–1.7 (with σ) on benzoyl and α-phenyl rings, respectively. Rate-determining fragmentation of the carbonyl addition intermediate was suggested from the observations: (i) the facile transesterification of α-hydroperoxy esters (**3**), (ii) the relative reactivities of **1a–n**, and (iii) the effect of hydroxide or hydroperoxide ion on the ester yield.

α-Hydroperoxy ketones are well known as intermediates in the autoxidation of ketones,[1] which were sometimes isolated and identified to be α-ketohydroperoxide (**1**)[2] rather than 1,2-dioxetane (**2**).[3]

1 **2**

a, $R_1 = R_2 = R_3 = Ph$
b, $R_1 = R_2 = R_3 = Me$
c, $R_1, R_2 = -(CH_2)_4-$; $R_3 = Ph$

The autoxidation of ketones in basic media rapidly forms α-hydroperoxy ketones[1d,4] and gives α-hydroxy ketones in the presence of phosphite.[5] Although α-hydroperoxy ketones can yield α-diketones when $R_2 = H$,[4d,6] a main alkaline reaction of **1** is the α cleavage (eq 1).[1d,4,7]



(1)

The mechanism was often written to involve 1,2-dioxetane (**2**) or its anion,[1d,7a-f] but an alternative acyclic mechanism was also suggested.[7g-j] Recent studies by Richardson[7f] and by Bordwell[7i] reached two different conclusions, cyclic and acyclic, respectively. We wish to report here our results[8] on the alkaline decomposition of 16 α-hydroperoxy ketones, which support the acyclic mechanism for the α-carbon cleavage reaction (eq 1) as a main path.

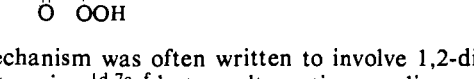
Results

Rate. The reaction of α-hydroperoxy ketones (**1** or R'OOH) with sodium alkoxide in benzene–alcohol (1:1 in volume) at 0° was monitored by iodometry and expressed as:

$$v = k_{obsd}[R'OOH] \quad (2)$$

The values of k_{obsd} were constant up to 70–80% conversion except at low concentration of alkoxide, where the constancy was observed only at initial 10–20% conversion. The k_{obsd} value is proportional to [RONa] at [EtONa] < 0.01 M or at [MeONa] < 0.1 and then approachs a constant (Table I). The validity of eq 2 at constant [RONa] with varying [R'OOH] is also shown in Table IIB. This result, which denies the induced radical decomposition of **1**, together with the high yield of esters (>60%) suggests the unimportance of a base-catalyzed radical decomposition.

Products. The reaction of **1a** with alkoxides produced benzophenone and benzoate (Table II).



(3)

The yield of the ester decreased at lower [RONa] (Tables IIA and IIC) and a small amount of benzoic acid was detected.[9] The addition of water decreased considerably the yield of esters but only slightly the rate of decomposition (Table IIE), which suggests that HO^- as well as alkoxide ion can react to form benzoic acid according to eq 3. Ester

Table I. Rate Constants of Alkaline Decomposition of α-Hydroperoxy Ketones in Benzene–ROH (1:1) at 0.0°[a]

[RONa], *M*	10^3k_{obsd}, sec^{-1}			
	1a + EtONa	**1a** + MeONa	**1b** + MeONa[b]	1c[c] + MeONa
0.001	~0.064			
0.002	0.131	~0.038		~0.71
0.005	0.49	0.088		2.09
0.010	0.92	0.184		4.34
0.020	1.36	0.378	0.015	9.2
0.050	1.87	0.852	0.0402	
0.10	2.26	1.44	0.0778	
0.20	2.15	1.94	0.129	
0.30		2.10	0.156	
0.50			0.184	

[a] Observed first-order rate constants with [**1**] = 0.010 *M* and ROH = EtOH or MeOH. [b] Reaction at 25°. [c] α-Hydroperoxy-α-phenylcyclohexanone.

formation is also the predominant pathway for other α-hydroperoxy ketones as stated below.

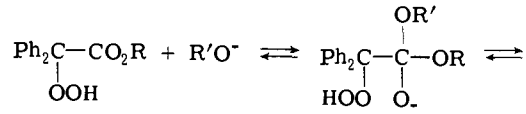
Substituent Effect. The substitutent effect for the alkoxide decomposition of α-hydroperoxy-α,α-diphenylacetophenone (**1a**) is summarized in Table III. Products with 0.05 *M* RONa are the corresponding benzophenones (80–100%) and esters (70–100%). The effect in the benzoyl ring resulted in positive ρ's of 2.5–3.2 (vs. σ) with 0.002–0.05 *M* RONa (Table IIIA). The effect on α-phenyl ring afforded lower ρ's of 0.9–1.7 (vs. σ) (Table IIIB). The identity of ρ values with various [RONa] suggests that the dissociation constants of R'OOH are of similar magnitude, if the overall rates involve the constants.

The reaction of various α-hydroperoxy ketones with methoxide is shown in Table IV, where esters are formed in a yield of over 80% for most cases. The exceptional case is **1o** (R_1 = *i*-Pr) (30–50% yield of ester), where the reaction is very slow and hence produced ester is partially hydrolyzed (10–20% conversion). Even if this hydrolysis is corrected, the selectivity for ester is 35–55%. However, the reaction with HO^- to produce isobutyric acid is probably operative (eq 3). The relative rate of HO^- vs. MeO^- is probably higher for **1o** (R_1 = *i*-Pr) than for **1b** (R_1 = Me) because of steric hindrance of *i*-Pr. In fact, addition of water results in a 7–8% increase in rate for the reaction of **1o** in benzene–methanol.[10]

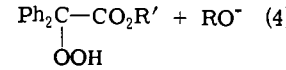
α-Hydroperoxy cyclic ketone (**1c**) has the fastest rate. As for the acyclic ketones, replacing methyl with phenyl resulted in an approximately tenfold increase in the rate, i.e., **1b** ≪ **1n** < **1p** ≪ **1k** < **1a** (Table IV). The orders of **1k** (R_3 = Me) ≫ **1l** (R_3 = Et) > **1m** (R_3 = $PhCH_2$) and of **1b** (R_1 = Me) > **1o** (R_1 = *i*-Pr) reflect a steric effect (E_s) in addition to inductive effect (σ*). But a quantitative treatment is impossible because of unavailable σ* and E_s values for $C(OOH)R_2R_3$.

Temperature Effect. As shown in Table V, the changes in E_a (15–17 kcal/mol) and $\Delta S^{\ddagger}$ (−5 to −11 eu) are small in spite of the ca. 200-fold difference in rate and there appears no clear-cut tendency between them.

Transesterification of α-Hydroperoxy Esters. Table VI illustrates the preliminary transesterification of α-hydroperoxy ester (**3**) without its decomposition at 0°. This shows that eq 4 is reversible without the fragmentation of adduct



3 **4**



(4)

4. The decomposition of **3** at 25° is due to the reaction with contaminated hydroxide ion, since the addition of water, i.e., HO^-, dramatically increases the decomposition of **3**. It was not known whether the basic decomposition of α-peroxy esters proceeds via **4** or hydrolyzed α-peroxy acid.[11] The above results clearly suggest that the fragmentation mechanism of **4** is not substantiated.

Table II. Rates and Products for Alkaline Decomposition of **1a** in Benzene–EtOH (1:1) at 0.0°[a]

[EtONa], *M*	Reaction condition[b]	10^3k_{obsd}, sec^{-1}	Products, %[c]		
			$PhCO_2Me$	$PhCO_2Et$	$Ph_2C{=}O$
		(A) Effect of [EtONa]			
0.005		0.49		62	100
0.02		1.36		79	98
0.05		1.87		87	96
0.10		2.26		94	103
		(B) Effect of [**1a**]			
0.05	[**1a**] = 0.00125			80	98
0.05	[**1a**] = 0.005	1.91		80	96
0.05	[**1a**] = 0.010	1.87		86	96
0.05	[**1a**] = 0.020	1.93			
		(C) Effect of [MeONa]			
0.005	B–M (1:1)	0.088	64		93
0.020	B–M (1:1)	0.374	100		97
0.05	B–M (1:1)	0.852	93		98
		(D) Effect of [ROH][d]			
0.05	E–M = 9:1	1.84	24.2	68.9	104
0.05	E–M = 4:1	1.61	48.6	55.5	101
0.05	E–M = **1**:1	1.24	84.0	19.1	105
		(E) Effect of [H_2O][e]			
0.05	[H_2O] = 0.02 *M*	1.93		94	105
0.05	[H_2O] = 0.5 *M*	1.94		73	100
0.05	[H_2O] = 1.0 *M*	1.67		53[f]	97

[a] With [**1a**] = 0.010 *M* and reaction time of 2–5 hr. [b] B = benzene, M = MeOH, and E = EtOH. [c] Products were determined by GLC analysis after 2–5 hr of reaction (±5%). [d] Benzene–ROH (1:1) and ROH = MeOH + EtOH in volume. [e] Reaction time of 20 min. [f] Benzoic acid (40%) was determined after esterification with diazomethane.

Table III. Substituent Effect for the Basic Decomposition of **1a** (Ph = C_6H_5 or C_6H_4)[a]

	$R_1C(=O)-CR_2R_3(OOH)$			10^3k_{obsd}, sec^{-1}				
	R_1	R_2	R_3	0.002 *M* EtONa	0.01 *M* EtONa	0.05 *M* EtONa	0.01 *M* MeONa	0.05 *M* MeONa
				(A) Effect on R_1				
1d	*p*-MeOPh	Ph	Ph	~0.019	0.128	0.287	0.0217	0.113
1e	*p*-MePh	Ph	Ph	~0.040	0.326	0.686	0.0628	0.292
1a	Ph	Ph	Ph	0.13	0.915	1.99	0.191	0.857
1f	*p*-ClPh	Ph	Ph		4.61	7.06	0.925	4.45
1g	*m*-ClPh	Ph	Ph	0.834	8.87	15.9	2.96	11.3
		$\rho(\sigma)$		2.53	2.73	2.66	3.22	3.08
		r[b]		0.995	0.996	0.997	0.998	0.998
				(B) Effect on R_2				
1h	Ph	*p*-MeOPh	Ph		0.536	1.70	0.0782	0.541
1i	Ph	*p*-MePh	Ph		0.516	1.58	0.0862	0.490
1j	Ph	*p*-ClPh	Ph		1.75	4.62	0.486	3.28
		$\rho(\sigma)$			1.12	~0.91	1.68	1.66
		r[b]			0.977	0.896	0.990	0.948

[a] Reaction with [R'OOH] = 0.01 *M* in benzene–ROH (1:1) at 0.0°, where ROH is EtOH or MeOH. Products with 0.05 *M* RONa were R_1CO_2R (70–100%) and $R_2R_3C{=}O$ (80–100%). [b] Correlation coefficient.

Table IV. Substituent Effect for the Basic Decomposition of Various Types of 1 (Ph = C_6H_5 or C_6H_4) at 0.0°[a]

	$R_1C(=O)-CR_2R_3(OOH)$						Products, %	
	R_1	R_2	R_3	10^3k_{obsd}, sec^{-1}	10^3k_2,[b] M^{-1} sec^{-1}	Relative rate	R_1CO_2Me	$R_2R_3C{=}O$
1a	Ph	Ph	Ph	0.852	17.0	308	93	98
1k	Ph	Ph	Me	0.721	14.4	258	91	100
1l	Ph	Ph	Et	0.0292	0.58	10.5	89	81
1m	Ph	Ph	CH_2Ph	0.0135	0.27	4.9	78[c]	77[c]
1n	Ph	Me	Me	0.0261	0.52	9.4	97[c]	
1b	Me	Me	Me	0.00278	0.056	(1.00)		
1b[d]	Me	Me	Me	0.0402	0.804		90[e]	96[e]
1o[d]	*i*-Pr	Me	Me	0.00314	0.0628	0.078[d]	30–50[f]	
1p	Me	Ph	Ph	0.12	1.2	22		
1c	$-(CH_2)_4-$		Ph	21[g]	420	7550	77[h]	

[a] The reaction with [**1**] = 0.010 *M* and [MeONa] = 0.05 *M* in benzene–MeOH (1:1). [b] Second-order rate constants estimated from $v = k_{obsd}[1]_S = k_2[MeONa][1]_S$ at [MeONa] = 0.05 *M*, where k_{obsd} is proportional to [MeONa]. [c] With 0.1 *M* MeONa at 25° for 1–3 hr. [d] At 25°. [e] With [1b] = 0.15 *M* and [MeONa] = 0.3 *M* at 25° for 4 hr. Methyl acetate was determined by GLC (±10%); acetone as 2,4-dinitrophenylhydrazone. [f] Reaction with [MeONa] = 0.2–0.5 *M* in methanol at 25° for 5–20 hr resulted in 20–50% conversion and the selectivity for methyl isobutyrate is shown (six runs). [g] Extrapolated from k_{obsd} with 0.002–0.020 *M* MeONa (Table I). [h] Yield of methyl δ-benzoylvalerate with 0.1 *M* MeONa. Its yield was constant (74 ± 4%) with 0.002–0.2 *M* MeONa.

Table V. Temperature Effect on the Basic Decomposition of α-Hydroperoxy Ketones in Benzene–MeOH[a]

		10^3k_{obsd}, sec^{-1}						
R'OOH	[MeONa], *M*	0.0°	15.0°	25.0°	k_2[b](25°), M^{-1} sec^{-1}	E_a[c]	$\Delta H^{\ddagger}$[c]	$-\Delta S^{\ddagger}$[d]
1a	0.010	0.141	0.582	1.44	0.144	15.1	13.9	10.9
1d	0.050	0.117	0.539	1.35	0.0270	15.8	14.6	8.4
1k	0.010	0.155	0.660	1.61	0.161	15.1	13.9	7.9
1l	0.050	0.0292	0.160	0.424	0.0085	17.1	15.9	7.4
1n	0.050	0.0261	0.130	0.367	0.0073	17.1	15.9	5.2
1b	0.050	0.00278		0.0402	0.00080	17.2	16.0	9.6

[a] With [R'OOH] = 0.010 *M* in benzene–MeOH (1:1). [b] See footnote *b* in Table IV. [c] ±1 kcal/mol. [d] ±3 eu.

Table VI. Transesterification of α-Hydroperoxy Esters (0.01 *M*) in the Presence of 0.1 *M* RONa in Benzene–ROH

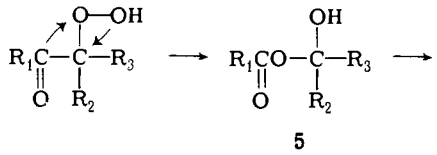
$Ph_2C(X)CO_2R$				$Ph_2C(X)CO_2R$, %[c]		
X	R	Reaction conditions[a] (temp, °C; time, hr)	Remaining peroxide, %[b]	R = Me	R = Et	$Ph_2C{=}O$, %
OOH	Et	B–M–MeONa (0; 16)	>98	46	30	0.4
OOH	Et	B–M–MeONa (25; 1.6)	>98	43	21	1.4
OOH	Et	B–M–MeONa (25; 16)	73	70	5.5	7.2
OOH	Me	B–E–EtONa (0; 16)	>98	42	37	1.8
OOH	Me	B–E–EtONa (25; 16)	74	11	52	10
H	Me	B–E–EtONa (0; 16)		0	100	
H	Et	B–M–MeONa (0; 16)		41	59	
H	Et	B–M–MeONa (25; 16)		91	8	

[a] B = benzene, M = MeOH, and E = EtOH. [b] By iodometry. [c] α-Hydroperoxy esters were determined by GLC analysis after neutralization with AcOH and the reduction of the peroxides with Ph_3P to the corresponding α-hydroxy esters.

Discussion

Mechanism. Postulated mechanisms for the α fission of α-hydroperoxy ketones are as follows:

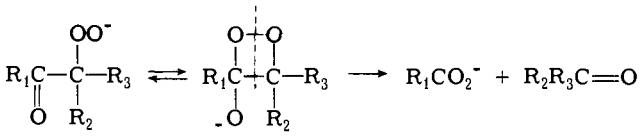
Mechanism A (1,2-rearrangement mechanism)[12]



5

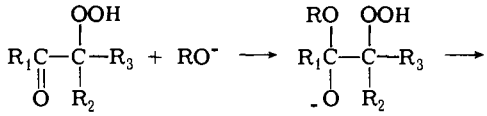
$$R_1CO_2H + R_2R_3C{=}O \quad (5)$$

Mechanism B (dioxetane mechanism)[7c,f]



1A 2A (6)

Mechanism C (intermolecular C=O addition mechanism)[7i]



1 6

$$R_1CO_2R + R_2R_3C{=}O + HO^- \quad (7)$$

Mechanism A was proposed for the spontaneous decomposition of α-hydroperoxy α-alkoxy ketone,[12] whose high reactivity arises probably from the acceleration by the α-alkoxy group.[13] However, our peroxidic ketones are much more stable in organic solvents and decompose only by strong acid or base and eq 5 cannot explain the high yield of esters from **5**.

Second, the evidences for the dioxetane mechanism are the observed carboxylic acid and chemiluminescence.[7f] But, carboxylic acid is also formed by mechanism C (RO = HO) and the high yield of ester cannot be explained by mechanism B, which must be an unimportant pathway if any. Probably, the high strain energy (~26 kcal/mol) of a 1,2-dioxetane[14] reduces [**2A**] and hence mechanism B. The observation of the chemiluminescence[7f] seems to be indicative of the operation of the cyclic mechanism even in a small extent on the basis of efficient chemiluminescence of other 1,2-dioxetanes.[15] But chemiluminescence is observable from the peroxide decomposition even by an acyclic mechanism[16a] and from the reaction of fluorescein with either alkaline hydrogen peroxide[16b] or *tert*-butyl hydroperoxide,[17] and hence in the presence of fluorescein it is not always the decisive evidence for the dioxetane mechanism. We observed no luminescence from the basic decomposition of α-hydroperoxy ketones (**1a,d,e**) in the presence of fluorescein.[17]

Third, the high yield of esters supports mechanism C as a major pathway. The accompanying acid may be due mostly to a reaction of hydroxide ion (RO = HO in eq 7), since there is no reason for the dramatic change of the mechanism by the addition of only 1–2% of water (Table IIE and footnote 10). That is, since the majority of the base in the presence of 1–2% water exists as alkoxide ion rather than HO^-, it is abnormal to assume that the reaction of the alkoxide (eq 7) is reduced and the reaction via mechanism B (eq 6) is dramatically accelerated by addition of a little water. Mechanism C explains the results as follows.

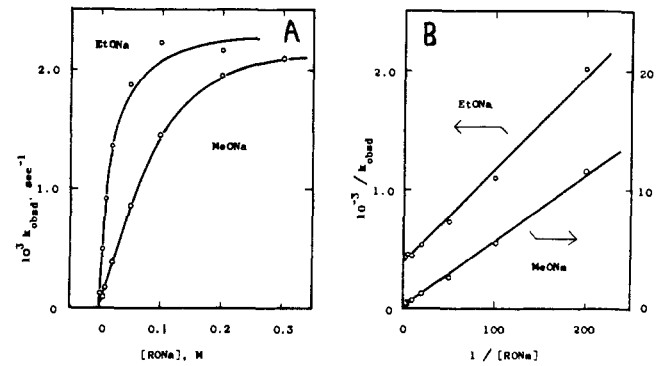


Figure 1. Effect of [RONa] on k_{obsd} for the alkaline decomposition of **1a** (0.010 M) in benzene–ROH (1:1) at 0.0°.

The observed ρ (2.5–3.2) for ring substituents in the benzoyl group is similar to other cases of nucleophilic addition to carbonyl (ρ = 2–3).[18] The effect for α-phenyl is lower (ρ = 0.9–1.7), since the α-phenyl is one atom further removed from the carbonyl. The fast reaction of **1c** reflects the facile carbonyl additions to cyclohexanones.[19] The slower reaction of aliphatic α-hydroperoxy ketones than of aromatic ketones is curious, since nucleophilic additions to acetyl are usually much faster than those to benzoyl.[19,20] This seems to mean that the addition is not rate determining as discussed later.

The k_{obsd} value for the basic decomposition of **1** (R'OOH) increases with [RONa] but approaches a constant at high basicity (Figure 1A). This effect is explicable by mechanism C (eq 7), which involves an attack of alkoxide on **1** as follows:

$$R'OOH + RO^- \overset{K_8}{\rightleftharpoons} R'OO^- + ROH \quad (8)$$

$$R'OOH + RO^- \xrightarrow{k_9} \text{products} \quad (9)$$

Assuming the products are formed by eq 10

$$v = k_{obsd}[R'OOH]_s = k_9[R'OOH][RO^-] \quad (10)$$

Here, [ ]$_s$ denotes stoichiometric concentration. Then,

$$\frac{1}{k_{obsd}} = \frac{1}{k_9[RO^-]} + \frac{K_8}{k_9} \quad (11)$$

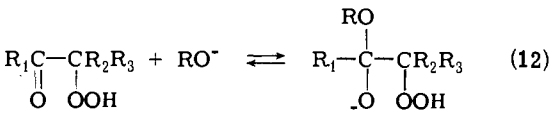
The plot of $1/k_{obsd}$ vs. $1/[RO^-]$ is linear (Figure 1B) and the intercept and the slope give K_8 = 3.8 and 71 M^{-1} and k_9 = 0.0192 and 0.175 M^{-1} sec^{-1} for the reaction of **1a** with MeO^- and EtO^-, respectively. Peroxide **1a** is too unstable to determine the K_8 value directly under these basic conditions, but this order is acceptable in comparison to the K_8 value of 18 M^{-1} for α-hydroperoxy ester **3** (R = Me) in methanol,[21] and to the acidity difference between MeOH and EtOH.[22]

The similar treatment for **1b** with methoxide resulted in $K_8 \sim 4$ M^{-1} and k_9 = 0.0011 M^{-1} sec^{-1} in benzene–methanol at 25°. On the other hand, the K_8 from uv absorbance[23] was 12 M^{-1}. The difference (ca. threefold) is considerable but not so large in view of the accuracy of K_8 from eq 12; e.g., the calculated K_8 increases up to 5.6 M^{-1} by a 20% increase of k_{obsd} at lower [MeO^-].

The k_9 value of **1a** with EtO^- (0.175 M^{-1} sec^{-1}) in benzene–ethanol is considerably larger in comparison to k_9 with MeO^- (0.019 M^{-1} sec^{-1}) in benzene–methanol. This difference is largely due to a solvent effect. That is, the k_{obsd} value, selectivities (Tables IID and IIE), and acidities of water and alcohols[22] afford approximate k_9 values of

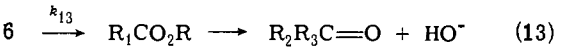
0.12, 0.035, and 0.023 M^{-1} sec^{-1} for HO^-, EtO^-, and MeO^-, respectively, in benzene-EtOH-MeOH. There appears no large difference in reactivities between MeO^- and EtO^- in the same solvent. In contrast to the ordinary carbonyl reactions, the reactivity of HO^- is usually high, resulting in a certain amount of acid formation even in the presence of a trace of water.

Rate-Determining Step. The above treatments do not decide whether the rate-determining step is addition (eq 12) or fragmentation (eq 13). The following considerations lead to a conclusion that eq 13 determines the rate.



(12)

1 6



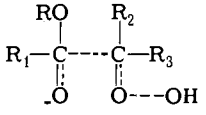
(13)

(i) The facile transesterification of α-hydroperoxy esters (R_1 = MeO or EtO) shows the mobile addition, and the same is probably true for the case of ketones (R_1 = alkyl or phenyl). Moreover, carbonyl additions to ketones are generally much faster than those to esters, e.g., saponification.[24]

(ii) The addition of HO^- or HOO^- reduces the yields of ester from **1a**, which is different from the reaction of phenyl benzoates and benzoic anhydride, where C=O addition is rate determining (Table VII). That is, although EtO^- and MeO^- exhibit the similar relative reactivities on both substrates, HO^- is effective only for **1a**, and HOO^- is highly effective only for the benzoates. This suggests the rate-determining C=O addition to **1a**, since HO^- is usually 10–100-fold less effective than alkoxide as a nucleophile[22] and HOO^- is a potent reagent with α effect, its steric requirement being less than water.[13,25] The high reactivity of HO^- is explicable by the favored attack of less hindered HO^- compared to the attack of EtO^- on the hindered tertiary ketone **1a**, although the equilibirum constants for PhCHO + $RO^- \rightleftarrows$ $PhCHO^-(OR)$ are of the same magnitude (0.16 M^{-1} for HO^- in water[26] and 0.22 M^{-1} for MeO^- in methanol[27]).

(iii) The relative reactivities, **1b**:**1n** = 1:9 and **1p**:**1a** = 1:14 (Table IV), are abnormal (acetyl ≪ benzoyl), since nucleophilic additions to acetyl are generally much easier than those to benzoyl.[19,20] The observed reverse order is comprehensible only if the C=O addition is not rate determining.

The above examinations support the rate-determining fragmentation from **6** (eq 13). A ca. tenfold increase in rate by substituting Ph in R_1 or R_2 for Me suggests that a driving force of fragmentation of **6** is the formation of the two carbonyls in products, ketone and ester. That is, the growing carbonyl in the transition state **7** is stabilized by the resonance with phenyl.



7

The order of rates, **1k** (R_3 = Me) ≫ **1l** (R_3 = Et) > **1m** (R_3 = $PhCH_2$), seems to reflect the steric inhibition of the coplanarity of Ph (=R_2) with C=O. Another driving force is surely the effect of α oxyanion as is the case for other concerted peroxide fragmentations[28] and for the well-known benzilic acid rearrangements.[29]

Cyclic or Acyclic. Ester formation and kinetics from the alkoxide decomposition of **1a–p** are consistent with mechanism C as a predominant pathway. Usually esters were obtained in 80–100% yield and these values are the lower limit for the acyclic mechanism, since hydroxide ion was also shown to be a potent reagent to afford carboxylic acid. Our explanation for the exceptional low yield (30–50%) of ester from **1o** (R_1 = *i*-Pr) is that the reaction with HO^- via mechanism C occurs to some extent in contrast to the lower estimation by Richardson et al.[7f] It is noteworthy that the selectivity for the ester from **1o** remains constant (~30%)[7f] even if 90% of R'OOH is dissociated into $R'OO^-$.[30,31] Probably, the high strain (~26 kcal/mol) of 1,2-dioxetane reduces **2A** or mechanism B to a minor reaction.

Experimental Section

All melting points and boiling points were uncorrected. NMR were recorded with a JNM-C60HL (Japan Electron Optics), and ir with a Perkin-Elmer 337 spectrophotometer. The GLC analysis was performed with a Yanagimoto 550F gas chromatograph.

Materials. Starting ketones were obtained by various methods (see Table VIII). The ketones, **a**, **i**, and **j**, were synthesized from desyl chloride and benzenes,[32] the reaction temperature (time, min) being 80° (15), 80° (15), and 110° (30), respectively (method A).

Method B is exemplified for the preparation of 2-phenylpropiophenone (**k**) as follows. Dropwise addition of sulfuryl chloride (27 g, 0.2 mol) to propiophenone (27 g, 0.2 mol) with stirring below 40° afforded α-chloropropiophenone (80%), bp 126–128° (18 mm). Phenylmagnesium bromide (0.12 mol) in ether was dropped with stirring into ice water cooled α-chloro ketone (20.4 g, 0.12 mol) in benzene (50 ml) and the reaction mixture was refluxed for 2 hr. The usual work-up afforded 80% yield of 2-phenylpropiophenone (96% pure by GLC), bp 130–145° (2.5 mm), which was purified by crystallization from methanol, mp 50–51° (lit.[33] 49°). Ketones **c** and **l** were obtained similarly from the corresponding α-chloro ketones.

Ketone **e** was prepared from diphenylacetyl chloride and toluene[32] and ketone **d** by the reaction in anisole–hexane (1:1) (method C). Methods D,[34] E,[35] F,[36] and G[37] are the literature methods. All the starting ketones were checked by GLC to be >98% pure.

Preparation of α-Hydroperoxy Ketones. α-Hydroperoxy-α,α-diphenylacetophenones were generally obtained by method H, the ethoxide catalyzed autoxidation of ketones (see Table VIII). α,α-Diphenylacetophenone (2.16 g, 8 mmol) in DMF (40 ml) was cooled to −20° and 1 *M* sodium ethoxide in ethanol (11 ml, 11 mmol) was added dropwise with gentle bubbling of oxygen (ca. 4 min). After the gentle bubbling for 20 min, the cold reaction mixture was poured into cold 2–3% aqueous acetic acid (400 ml) and extracted with benzene (100 ml). The extract was washed with water, 3% KH_2PO_4 aqueous, and water. Iodometry indicates 30–70% yield of α-hydroperoxy ketone. After drying with Na_2SO_4, benzene was evaporated under reduced pressure, the residue being dissolved in ether (20 ml), cooled at 0° for 2 hr to filter off the unreacted ketones. Most of the ether was evaporated off under a slightly reduced pressure and a crystallization from petroleum ether afforded **1a** (10–30%), mp 115–116°. Repeated recrystallizations were unsuccessful to remove a little contamination of the starting ketone. Other hydroperoxides, **1d–j**, were synthesized similarly by method H, but the reaction time for **1d** being 30 min and for **1f** and **1g** being 10 min.

Method I was applied to the preparation of **1b,c,k–p** and **3a,b**, where *t*-BuOK was used in place of EtONa. That is, *t*-BuOK–*t*-BuOH[38] (3.7 g, 20 mmol) in DMF (40 ml)–*t*-BuOH (10 ml) was cooled to −20° and the starting ketone (10 mmol) was added with gentle bubbling oxygen. The work-up after 15 min reaction is the same as method H except that **1b**, **1n**, and **1o** were extracted with benzene–ether (1:1).

Although method H was carried out for the preparation of α-hydroperoxy ketone **1a,d–j**, a similar yield of the hydroperoxide was obtained by method I except recovering a smaller amount of the starting ketone. For both methods, the yield of the hydroperoxide was sometimes lowered by violent bubbling or shaking and by precipitation of *t*-BuOK or R_1CO_2K. This suggests the radical decomposition of **1**.

Crystallization without recovering unreacted ketone was suc-

Table VII. Comparison of Ester Yield from **1a** with Other C=O Additions in Benzene–EtOH (1:1) at 0°[a]

Reaction conditions		$PhCO_2Et$, %			
[EtONa], *M*	Additives	**1a**	PhCOPh ‖ O	PhCOAr[b] ‖ O	PhCOCPh ‖ O O ‖
0.05		87	105	103	97
0.05	1 *M* H_2O	53	103	103	90
0.05	0.04 *M* H_2O_2	75	0	0	0
0.05	MeOH–EtOH (1:4)	49–56[c]	62–39[c]	56–44[c]	58–44[c]
0.05	MeOH–EtOH (1:1)	84–19[c]	91–11[c]	86–12[c]	87–14[c]

[a] Initial concentration is 0.010 *M* and benzoic acid was not determined. [b] Ar = *p*-$O_2NC_6H_4$. [c] Yields of $PhCO_2Me$–$PhCO_2Et$, respectively.

Table VIII. Preparations, Properties, and Spectra of Starting Ketones and α-Hydroperoxy Ketones (Ph = C_6H_5 or C_6H_4)

	$R_1C(=O)CR_2R_3$ (X)			Ketones (X = H)		α-Hydroperoxy ketones (X = OOH)							
									IR[d]		NMR[e]		
	R_1	R_2	R_3	Method[a]	Mp (solvent)[b]	Method[a]	Mp (solvent)[b]	Purity, %[c]	OOH	C=O	OOH	Aromatic	Other
a	Ph	Ph	Ph	A	135–136° (M)	H or I	115–116° (P)	96	3370	1675, 1680	8.72 (1 H)[f]	(15 H)	
b	Me	Me	Me		Liq (commercial)	I	Liq[g]	95					
c	$-(CH_2)_4-$		Ph	B	57–59° (H)	I	Liq	55	3350	1710			
d	*p*-MeOPh	Ph	Ph	C	129–131° (B–H)	H	118–119° (B–H)	85	3320	1670	9.36		CH_3, 3.74 (s)
e	*p*-MePh	Ph	Ph	C	100–101° (M)	H	112–114° (B–P)	77	3290	1660	Br		CH_3, 2.33 (s)
f	*p*-ClPh	Ph	Ph	D	109–110° (B–H)	H	101–103° (B–H)	88	3380	1680, 1670	8.8		
g	*m*-ClPh	Ph	Ph	D	126–128° (B–H)	H	Liq	67	3340	1690	8.6		
h	Ph	*p*-MeOPh	Ph	E	88–91° (B–H)	H	105–108° (B–P)	99	3330	1670	9.25 (1 H)	(14 H)	CH_3, 3.32 (3 H, s)
i	Ph	*p*-MePh	Ph	A	95–97° (E)	H	Liq	50	3320	1680	Br		CH_3, 3.32 (s)
j	Ph	*p*-ClPh	Ph	A	102–103° (M)	H	Liq	60	3310	1680	8.50		
k	Ph	Ph	Me	B	50–51° (M)	I	79–82° (B–P)	95	3290	1685	8.60 (1 H)	(10 H)	CH_3, 1.93 (3 H, s)
l	Ph	Ph	Et	B	56–57° (M)	I	68–72° (B–P)	99	3290	1690	7.8 (1 H)	(10 H)	Et, 2.30 (2 H, q), 0.81 (3 H, t)
m	Ph	Ph	$PhCH_2$	F	120° (B–E)	I	157–158° (B–H)	100	3350	1670	Br[h]		CH_2, 3.32 (s)[h]
n	Ph	Me	Me	*i*	Bp 110–112° (22 mm)	I	Liq	60	3350	1680	6.74		CH_3, 1.60 (s)
o	*i*-Pr	Me	Me		Liq (commercial)	I	40–42°[j]	94					
p	Me	Ph	Ph	G	Bp 135–138° (1.5 mm)	I	Liq[k]	~50					
3a	MeO	Ph	Ph	*l*	58–59° (M)	I	73–74° (B–P)[m]	102	3430	1725	12.0[n]	7.2[n]	CH_3, 1.40 (s)[n]
3b	EtO	Ph	Ph	*l*	58–58.5° (M)	I	61–62° (B–P)	101	3390	1720			

[a] See the text for the methods and references. α-Hydroperoxy ketones **1a**, **d**–**n**,**p** and **3b** are new compounds. [b] M = MeOH; E = EtOH; H = *n*-hexane; B = benzene; P = petroleum ether. [c] Determined iodometrically (±3%). [d] In a Nujol mull for the crystal samples and in a neat form for the liquid ones (cm^{-1}). [e] In a ca. 5% $CDCl_3$ solution unless specified otherwise. Chemical shifts are on the δ scale (ppm) and the figures in parentheses are peak areas. Peroxidic proton (OOH) shows usually a broad singlet. Aromatic protons ranged at 7.0–8.0 for the most aromatics and only their areas are shown. [f] Chemical shift is 12.1 in DMSO. [g] Lit.[4b] mp 28–30°. [h] In DMSO-d_6. [i] Friedel-Crafts reaction. [j] Lit.[4b] mp 43–44°. [k] 1p was the most unstable peroxide and its half-life in benzene was about 2 days at room temperature. We could not obtain the pure sample and hence its spectra. [l] H_2SO_4-catalyzed esterification. [m] Lit.[11a] mp 69.5–70.5°. [n] Determined in DMSO and aromatic protons were singlets (δ 7.2).

cessful for the peroxides **1k–m,o**, and **3a,b**, since the starting ketones have poor crystallizability. For the case of **1a,d–f**, the purification by recrystallization was unsuccessful, the contamination being the starting ketone by GLC. For the peroxides **1c,g,i,j,n,p**, attempted crystallizations were unsuccessful, their impurities being starting ketones and/or ethyl benzoate by GLC. Another purification such as column chromatography was not appropriate for these labile peroxides.

Formation and structures of the new α-hydroperoxy ketones were ascertained by iodometry, GLC, ir, NMR, the reaction with alkoxide (eq 3), and the reduction with triphenyl phosphite or potassium iodide to the corresponding α-hydroxy ketones. Ir and NMR spectra are consistent with α-hydroperoxy ketone structure (Table VIII). That is, ir spectra (Nujol mull) characterized OOH at 3290–3380 cm^{-1} (broad) and C=O at 1660–1710 cm^{-1}. NMR spectra ($CDCl_3$) exhibited aromatic ortho protons (δ 7.7–7.8, $J \sim 7$ Hz) adjacent to C=O and a characteristic downfield shift (δ 6.7–9.4) of hydroperoxy proton.[39]

Base-catalyzed autoxidation of isobutyrophenone was said to give a cyclic peroxide (mp 153°),[40] but our conditions of low temperature afforded **1n**. Peroxide **1p** was too unstable to prepare a neat sample, but the iodometry, the reduction to the corresponding α-hydroxy ketone, and the basic or thermal (250°) decomposition to benzophenone prove its formation.

Generally, α-hydroperoxy ketones with higher melting points (mp > 100°) are stable at least for a year at room temperature. The peroxides with lower melting points or a neat liquid sample decompose gradually, but their dilute benzene solutions are stable for several months. We prepared the hydroperoxides in a small scale (usually 10 mmol) to avoid explosion, but no explosion was observed by hammering or during handling. However, precaution should be taken to avoid any accident.

Iodometry and Kinetics. Saturated KI aqueous (1 ml) and then the hydroperoxide were added into 20 ml of AcOH–H_2O–MeOH (1:1:2) and reacted at ~60° for 5 min, covering the flask with aluminum foil. While warm, liberated iodine was titrated with $Na_2S_2O_3$. The liberation of iodine in a blank test is negligible.

The basic decomposition of **1** was started by the final addition of alkoxide to the reaction mixture at a desired temperature. An aliquot was taken out and titrated iodometrically. The reproducibility was adequate (±5%) and the rate constants in tables are averages of two or three determinations. EDTA was not used because of its insolubility, but the rates in aqueous methanol were not affected by its presence.

Products. In general, products (ketones and esters) were identified and determined by GLC in comparison with an authentic sample. GLC analyses were carried out at 40–250° on four different columns (1 m) directly and/or after CH_3Cl extraction: (i) Apiezon grease L, 15% on Celite 545; (ii) Silicone SE30, 10% on Chromosorb; (iii) PEG 20M, 2% on Chamelite CK; (iv) PEG succinate, 13% on Chromosorb. Internal standards were propiophenone, biphenyl, naphthalene, or benzophenone. The results are summarized in Tables II, III, and IV. Benzophenone and acetone were isolated from **1a** and **1b** as 2,4-dinitrophenylhydrazone, mp 237–238° and 150–152°, respectively. Other esters and ketones were not isolated but identified by GLC retention times using four different columns. Authentic ketones and esters were obtained by routine procedures.

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(9) Benzoic acid was not determined but detected by GLC in a few runs, since a small amount of the acid was not accurately determined.

(10) The rate constants ($10^3 k_{obsd}$ = 0.0076 and 0.0101 sec^{-1}) increased to 0.0082 and 0.0108 sec^{-1} with 0.1 and 0.2 *M* MeONa, respectively, by addition of 1 *M* H_2O in benzene–methanol (1:1) at 25°.

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