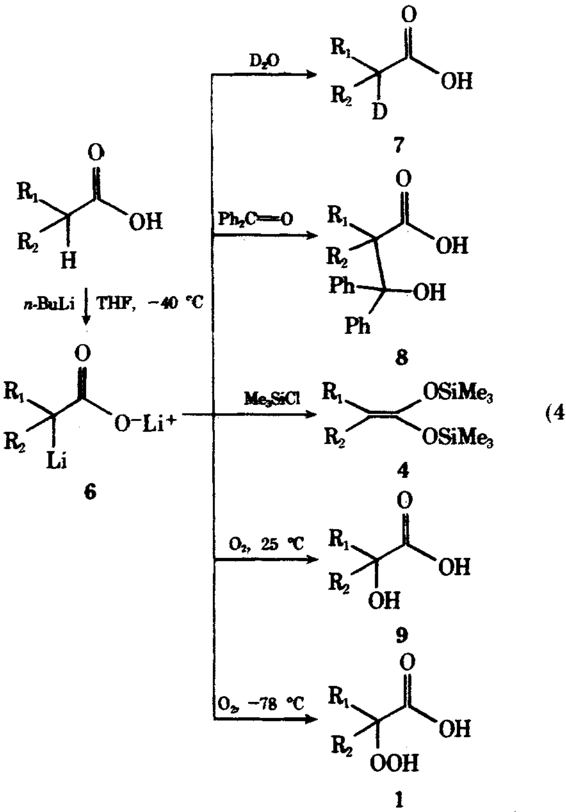
not improve the yield of α-lithiation; on the contrary, more carbonyl addition took place.

The various electrophilic substitution processes are summarized in eq 4. Deuterium oxide and trimethylsilyl chloride are excellent electrophiles for titrating the α-lithiocarboxylates. On the basis of NMR data, essentially quantitative deuteration and trimethylsilylation takes place. Since both are hard electrophiles, the attack takes place on oxygen rather than carbon and steric factors are minimized. For example, the significance of steric factors is dramatically exposed in the reaction of the α-lithiocarboxylates with benzophenone. Not even traces of the α-hydroxy acids **8b** and **8c** could be detected and only low yields of **8d** and **8e** could be isolated. Hydroxymethylation with ketones or aldehydes is not recommended for the titration of α-lithiocarboxylates.



(4)

Molecular oxygen, a soft electrophile, as expected affords high yields of the desired α-hydroxy and α-hydroperoxy acids, depending on the reaction conditions. Since the oxygen molecule is a relatively small electrophile, α-attack is unobstructed. Although this direct α-peroxylation of α-lithiocarboxylates is a convenient and efficient preparation of α-hydroperoxy acids derived from arylacetic acids, great care must be exercised in their isolation in view of their labile nature toward thermal, acid-, and base-catalyzed decarboxylation. Presently we are extending this method to other hitherto unavailable α-hydroperoxy acids which are of interest in biological oxidations.

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Registry No.—**1a**, 60538-67-2; **1b**, 60538-68-3; **1c**, 60538-69-4; **6a**, 60538-70-7; **6b**, 60538-71-8; **6c**, 60538-72-9; benzeneacetic acid, 103-82-2; α-phenylbenzeneacetic acid, 117-34-0; 9*H*-fluorene-9-carboxylic acid, 1989-33-9; *n*-butyllithium, 109-72-8.

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Chemiluminescence from Base-Catalyzed Decomposition of α-Hydroperoxy Esters. Dioxetanone Mechanism[1]

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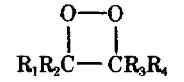
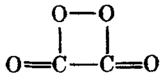
Chemiluminescence (CL) was observed from the methoxide-catalyzed decomposition of six α-hydroperoxy esters **4a–f** in the presence of fluorescein in MeOH. The quantum yields (Φ) of the CL were in the range of 5×10^{-6} to 3×10^{-4} and increased linearly with increasing concentration of fluorescein. Although the decomposition of **4** was dramatically accelerated by addition of water, the CL intensity remained constant, and hence Φ was significantly reduced. This suggests that the major reaction is the hydrolytic decomposition and the CL comes from a minor reaction involving no HO^- ion. The efficiency of fluorescers was in the order of fluorescein $\simeq$ eosin $\gg$ diphenylanthracene > dibromoanthracene. These results were discussed in connection with a mechanism of CL involving a charge-transfer complex between dioxetanone (**3**) and fluorescers. This mechanism differs from the reported CL from the spontaneous decomposition of **3** producing a triplet ketone.

1,2-Dioxetanes (**1**)[2] and 1,2-dioxetanedione (**2**)[3] are well known as intermediates or potent starting materials for chemiluminescence. 1,2-Dioxetanones (**3**) were synthesized[4b] from α-hydroperoxy acids and shown to be luminescent.[4–6]


$$\begin{array}{cc} O & O \\ | & | \\ R_1R_2C & CR_3R_4 \end{array}$$
1


$$\begin{array}{cc} O & O \\ | & | \\ O{=}C & C{=}O \end{array}$$
2

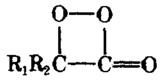
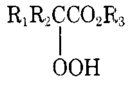

$$\begin{array}{cc} O & O \\ | & | \\ R_1R_2C & C{=}O \end{array}$$
3

Table I. Chemiluminescence from Base-Catalyzed Decomposition of α-Hydroperoxy Esters (4) at 40 °C[a]

Peroxide (R_2)	Solvent[b]	$10^5 k_{obsd}$,[c] s^{-1}	Fluorescer[d]	Rel I[e]	$10^6 \Phi_{obsd}$	$10^6 \Phi$[f]
		A. Effect of Fluorescers				
4a (Ph)	MeOH	5.72	Fl	20	4.2	280
	MeOH	5.72	Eosin	6.0	1.25	320
	MeOH	5.72	DPA	<0.1	<0.02	<0.02
	MeOH	5.72	DBA	0.0	0.00	0.00
4c (*i*-Pr)	MeOH	4.5	Fl	8.7	2.3	160
	MeOH	4.5	DPA	~0.7	~0.07	~0.08
	MeOH	4.5	DBA	0.0	0.00	0.00
		B. Effect of Solvents and Temperature				
4a (Ph)	MeOH	5.72	Fl	20	4.2	280
	90% MeOH	103[g]	Fl	20	0.23	15.5
	50% MeOH	612	Fl	~20	~0.039	~2.7
	MeOH (25 °C)	0.54	Fl	~2.0	~4.4	~300
4c (*i*-Pr)	MeOH	4.5	Fl	8.7	2.3	160
	50% MeOH	47.4	Fl	20.6	0.52	35
		C. Effect of Substituents				
4a (Ph)	MeOH	5.72	Fl	20	4.2	280
4c (*i*-Pr)	MeOH	4.5	Fl	8.7	2.3	160
4b (Ph)	MeOH	4.8	Fl	4.7	1.2	80
4f ($PhCH_2$)	MeOH	4.8	Fl	1.1	0.3	20
4d (Et)	MeOH	2.9	Fl	0.5	0.19	13
4e (Me)	MeOH	11.8	Fl	0.7	0.07	5

[a] Reaction with 0.01 M **4** and 0.25 M MeONa. [b] MeOH is pure MeOH and percent is volume percent of aqueous MeOH. [c] Rate constants of overall decomposition determined by iodometry. [d] Fluorescer of 0.0025 M concentration; Fl = fluorescein, DPA = diphenylanthracene, and DBA = dibromoanthracene. [e] Initial relative intensity of chemiluminescence. [f] $\Phi = \Phi_{obsd}/\Phi_F{}^A$; $\Phi_F{}^A = 0.0147$ with 0.0025 M Fl, 0.0039 with 0.0025 M eosin, and 0.85 with 0.0025 M DPA. [g] Rate constant from the CL decay was 1.1×10^{-3} s^{-1}, which is close to that by iodometry.

The decomposition of **3** is also interesting in relation to the chemi- and bioluminescence of luciferins.[7] Here we wish to report chemiluminescence from the base-catalyzed decomposition of simple α-hydroperoxy esters (**4**), where the luminescence is probably via a complex composed of **3** and an added fluorescer.



$R_1R_2C(OOH)CO_2R_3$

4

	R_1	R_2	R_3
a	Ph	Ph	Me
b	Ph	Ph	Et
c	Ph	*i*-Pr	Me
d	Ph	Et	Me
e	Ph	Me	Me
f	Ph	$PhCH_2$	Me

($Ph = C_6H_5$)

Results

α-Hydroperoxy esters (**4**) decompose gradually on addition of sodium methoxide in MeOH to give ketones and the pseudo-first-order rate constants k_{obsd} were determined by iodometry.

$$v = k_{obsd}[\mathbf{4}]_s \qquad (1)$$

Here, $[\ ]_s$ denotes stoichiometric concentration. The validity of eq 1 was confirmed for the case of **4a**; the k_{obsd} values were constant up to 80% conversion and at various initial concentrations of 0.005, 0.01, and 0.02 M. The rate constant of decomposition was not altered by addition of EDTA.

The addition of water to the MeOH solution greatly increased the rate (Table IB). This hydrolytic decomposition is known to proceed via hydrolysis of α-peroxy esters leading eventually to ketones and carbon dioxide.[8]

Effect of Fluorescers. Although the reaction of **4** with MeONa is nonluminescent, the addition of fluorescers led to chemiluminescence (CL) as shown in Table IA. The CL with xanthene dyes (fluorescein and eosin) was considerably strong, while the CL with diphenylanthracene (DPA) and dibromoanthracene (DBA) were weak or undetectable. Bubbling of nitrogen had no effect.

Quantum yield of the CL was calculated according to eq 2 and 3 (reaction volume is always 3 ml in a quartz cell 1 cm long):

$$\Phi_{obsd} = \frac{I}{k_{obsd}[\mathbf{4}]_s \times 6 \times 10^{23}} \qquad (2)$$

$$\Phi = \Phi_{obsd}/\Phi_F{}^A \qquad (3)$$

Here, *I* is the number of photons produced per second and $\Phi_F{}^A$ is the apparent fluorescence quantum yield of a fluorescer at the experimental concentrations (see the Experimental Section for details). The Φ value thus obtained is ca. 3×10^{-4} (i.e., 0.03%) for the case of **4a** and fluorescein or eosin at 40 °C (Table IA and B).

The relative intensity of the CL (rel I) from **4a** with 0.025 M fluorescein (Fl) is proportional to $[\mathbf{4a}]_s$ at the concentrations of 5–20 mM. On the other hand, rel I increased with increasing [Fl] up to ca. 2 mM and then decreased. But the resulting Φ increased with increasing [Fl] after correcting the fluorescence efficiency of Fl according to eq 3 (Table II).

The use of eq 2 was justified by the proportionality of rel I vs. [**4**] and also by the identity of the rate constant from rel I with that from iodometry (see Table IB).

Effect of Solvents and Substituents. The decomposition rate (k_{obsd}) of **4** in aqueous MeOH is much faster than that in MeOH, while the CL intensity remains constant (Table IB). This leads to a considerable decrease in the Φ value in aqueous MeOH. The decay curve of rel I in aqueous MeOH was identical with the one by iodometry.

Similar luminescence is observed for other α-hydroperoxy esters. Although the overall decomposition rate constants

Table II. Effect of [Fl] on the CL of 4a in MeOH at 40 °C [a]

[Fl], 10^3 M	$\Phi_F{}^A$ [b]	Rel I [c]	$10^6\ \Phi_{obsd}$	$10^4\ \Phi$ [d]
0.322	0.45	4.30	0.90	0.020
0.625	0.101	7.85	1.64	0.162
0.910	0.027	10.5	2.20	0.81
1.18	0.026	12.7	2.65	1.02
1.43	0.023	14.5	3.02	1.32
2.00	0.0175	16.3	3.40	1.95
2.50	0.0147	19.6	4.10	2.8
5.0	~0.011	20.0	4.17	~3.8
12.5		12.4	2.58	

[a] Reaction with [**4a**] = 0.01 M, [MeONa] = 0.25 M, and Fl = fluorescein. [b] Fluorescence yield of fluorescein at the concentration indicated. [c] Relative intensity of the initial CL. [d] $\Phi = \Phi_{obsd}/\Phi_F{}^A$.

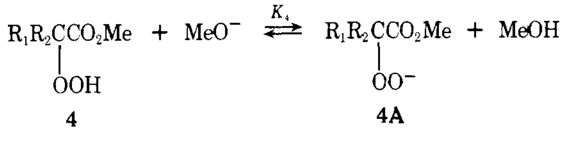
(k_{obsd}) are of the same order, the quantum yields are in the range of 10^{-4}–10^{-6}, the order being **4a** > **4c** > **4b** > **4f** > **4d** > **4e** (Table IC).

Effect of [MeONa]. The Cl was affected by base concentrations; the rel I of **4a** increased and then decreased with increasing [MeONa], resulting in a maximum intensity at ca. 50 mM MeONa (Table III). This relationship is in contrast with that for α-hydroperoxy ketones, which has no maximum.[9,10]

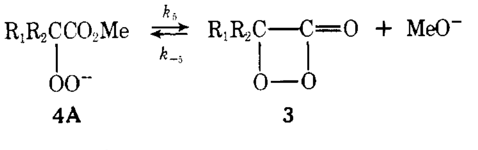
Discussion

Hydrolysis and a Dioxetanone Mechanism. The base-catalyzed decomposition of α-peroxy esters to ketones and carbon dioxide in aqueous solution proceeds via the hydrolysis of the esters,[8] and the reaction with alkoxide ion in alcohol-benzene exhibits a preliminary transesterification without the decomposition of the peroxy group.[11] The latter fact together with the facile decomposition in aqueous MeOH suggests that the base-catalyzed decomposition of **4** proceeds predominantly via the hydrolyzed α-peroxy acid (**5**) (eq 7). Since methanol contains a trace amount of water, the decomposition in MeOH also proceeds mainly via eq 7.

No luminescence was observed with α-alkylperoxy esters.[8a] In contrast, the observation of CL from α-hydroperoxy esters suggests an intervention of a dioxetane intermediate. In spite of the acceleration in the decomposition of **4** by the addition of water, i.e., HO⁻, the initial CL intensity remains constant. This indicates that the luminescence (eq 5 and 6) is competitive with the nonluminescent decomposition via hydrolysis (eq 7). These facts and the appearance of a maximum in the plot of rel I vs. [MeONa] (curve A in Figure 1) can be explained by the following sequences and considerations.

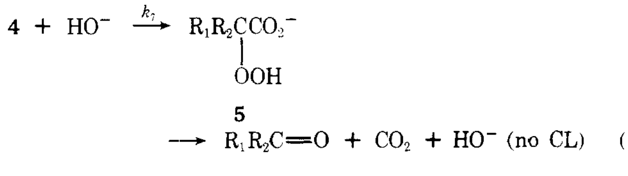


$$\underset{\underset{\textbf{4}}{OOH}}{R_1R_2CCO_2Me} + MeO^- \overset{K_4}{\rightleftarrows} \underset{\underset{\textbf{4A}}{OO^-}}{R_1R_2CCO_2Me} + MeOH \quad (4)$$



$$\underset{\underset{\textbf{4A}}{OO^-}}{R_1R_2CCO_2Me} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \underset{\textbf{3}}{R_1R_2C(-O-O-)C{=}O} + MeO^- \quad (5)$$

$$\textbf{3} + Fl \xrightarrow{k_6} R_1R_2C{=}O + CO_2 + Fl^*\ (CL) \quad (6)$$



$$\textbf{4} + HO^- \xrightarrow{k_7} \underset{\underset{\textbf{5}}{OOH}}{R_1R_2CCO_2{}^-} \longrightarrow R_1R_2C{=}O + CO_2 + HO^-\ (no\ CL) \quad (7)$$

Table III. Effect of [MeONa] on the CL of 4a in MeOH at 40 °C [a]

[MeONa], M	Rel I [b]	[MeONa], M	Rel I [b]
0.0084	10.1	0.054	25.7
0.0140	17.7	0.125	23.4
0.0196	22.3	0.250	20.4
0.028	23.8	0.500	10.6

[a] Reaction with 0.005 M **4a** and 0.0025 M fluorescein. [b] Relative intensity of the initial CL.

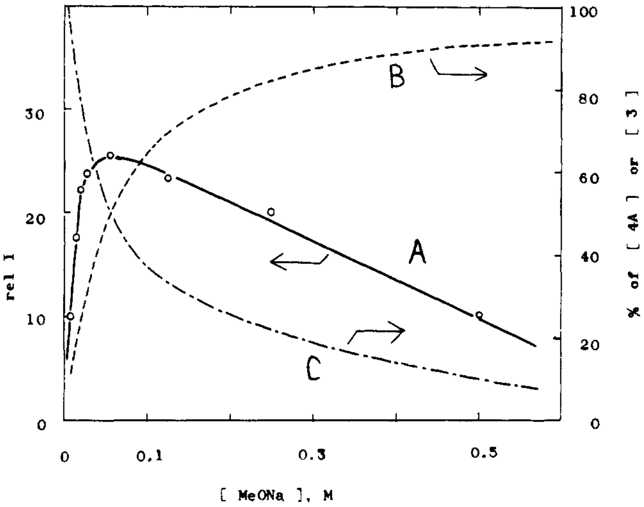


Figure 1. Effect of [MeONa] on the CL from the basic decomposition of **4a** (see Table III for the conditions); A, initial rel I vs. [MeONa]; B, % of [**4A**] vs. $[4]_s$; C, % of [**3**] vs. $[3]_0$ at [MeONa] = 0 (see text, eq 9 and 10).

From a steady-state assumption of dioxetanone **3** the concentration of **3** is expressed as

$$[3] = \frac{k_5[4A]}{k_{-5}[MeO^-] + k_6[Fl]} = \frac{k_5K_4[MeO^-][4]_s}{(k_{-5}[MeO^-] + k_6[Fl])(K_4[MeO^-] + 1)} \quad (8)$$

Here, $K_4[4][MeO^-] = [4A]$ and the K_4 value is 18 M^{-1} in MeOH and 26 M^{-1} in 75% MeOH at 20 °C.[12] If $k_{-5}[MeO^-] \ll k_6[Fl]$ at low $[MeO^-]$ (i.e., equilibrium 5 is not established),

$$[3] = \frac{k_5K_4[MeO^-][4]_s}{k_6[Fl](K_4[MeO^-] + 1)} \quad (9)$$

Since the CL intensity is proportional to [3] (i.e., rel I ∝ $k_6[3]$), eq 9 can explain the increasing CL at lower $[MeO^-]$ (i.e., curve B in Figure 1). If $k_{-5}[MeO^-] \gg k_6[Fl]$ at higher $[MeO^-]$,

$$[3] = \frac{K_4K_5[4]_s}{K_4[MeO^-] + 1} \quad (10)$$

The observed decrease of rel I at higher concentrations of base (curve C in Figure 1) can be explained by eq 10, where K_4 = 18 M^{-1} [12] and $K_5 = k_5/k_{-5}$.

The observed maximum in Figure 1 can thus be explained by eq 9 at lower base concentrations and by eq 10 at higher ones. A quantitative treatment is, however, impossible because of unknown values of k_5 and k_{-5}.[13]

The effect of substituents on Φ shows the order **4a** > **4c** > **4f** > **4d** > **4e,** which seems to reflect the bulkiness (e.g., Taft's E_s value) of R_2 group; i.e., E_s values being in the order Ph > *i*-Pr > $PhCH_2$ > Et > Me. The order in Φ can be explained by the competition between the major hydrolytic decomposition (eq 7) and the CL one (eq 5 + eq 6). That is, the intramolecular

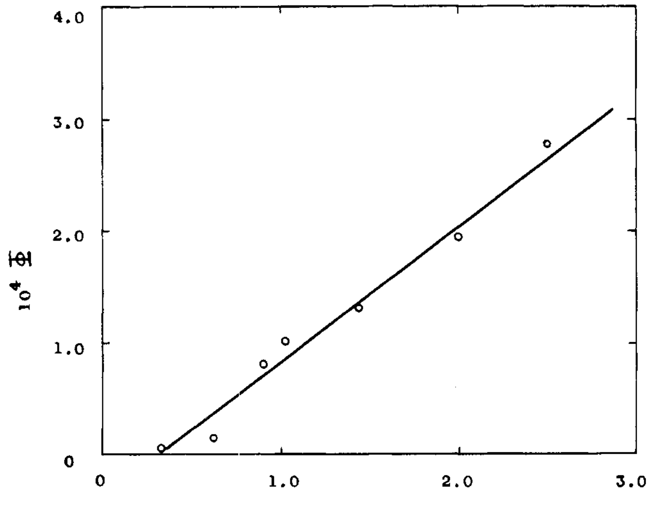


Figure 2. Dependence of the CL yields (Φ) on [Fl] from the basic decomposition of **4a** (see Table II for the reaction conditions; Fl = fluorescein).

C=O addition (k_5) is probably less sensitive to the steric hindrance than the intermolecular one (k_{-5} and/or k_7).[14] Thus the CL yields are higher for hydroperoxy esters bearing larger groups. A more quantitative argument is, however, is impossible at present because of the unknown values of k_5, k_{-5}, k_6, and the quantum yield for eq 6.

Chemiluminescence Precursor. The thermolysis of tetramethyldioxetane (**1**, $R_1 = R_2 = R_3 = R_4 = Me$)[2c] and dimethyldioxetanone (**3**, $R_1 = R_2 = Me$)[4c,5] yields mostly triplet acetone (over 95%), the overall Φ being 0.2 for the dioxetanone. The CL from the base-catalyzed decomposition of α-hydroperoxy ketones shows also a predominant formation of triplet acetone, the CL intensity with various fluorescers being in the order of DBA ≫ DPA ~ fluorescein;[10] the high efficiency of DBA suggests the formation of a triplet ketone.[5]

On the other hand, the present case of α-hydroperoxy esters showed the reverse order of fluorescein ≃ eosin ≫ DPA > DBA and the Φ values are 10^3–10^4 times less than the neutral thermolysis of **3**. No observation of the CL with DBA suggests that no triplet ketone ($^{T}C{=}O$) is formed. This indicates also no formation of singlet ketone ($^{S}C{=}O$), if any, for the present case of aromatic ketones, since the intersystem crossing from $^{S}C{=}O$ to $^{T}C{=}O$ is fast and efficient.[15]

When an energy transfer from a short-lived precursor to a fluorescer is concerned, a linear relationship is usually observed between 1/Φ and 1/[Fl].[16] But, for the present case of **4a** and fluorescein, the plot of 1/Φ vs. 1/[Fl] is not linear and a linear relationship is observed between Φ and [Fl] (Figure 2). The failure of the plot in Figure 2 to pass through 0.0 may be allowed in view of the experimental error (±20%) in Φ values. The relation in Figure 2 is explicable by assuming a charge-transfer (C-T) complex between dioxetanone **3** and fluorescer (Fl).[3]

$$3 + \mathrm{Fl} \rightleftarrows \text{C-T complex} \rightarrow R_1R_2C{=}O + CO_2 + \mathrm{Fl}^* \quad (11)$$

Thus, the rate of formation of Fl* (i.e., rel I) is proportional to the product of [**3**] and [Fl] as is the case.

The assumption of the C-T complex (eq 11) seems to explain the effective luminescence with the xanthene dyes. That is, the ionization potential (IP) of aromatics is correlated with σ^+ to give a negative ρ value,[17a] and hence the IP of xanthene dyes with a strongly electron-donating group ($-O^-$) is considerably low.[17b] A similar C-T complex mechanism has been suggested for the luminescence from dioxetanedione **2**[3] and dioxetanone **3**.[4a] Since such a complex was not detected for the case of dioxetane **1**,[18] the attachment of the electron-attracting carbonyl group seems to be necessary for the formation of the C-T complex as is the case of **2** and **3**. In conclusion, the present CL can well be rationalized by the sequences of eq 4, 5, and 11.

A reason follows for the operation of the C-T complex mechanism, while dioxetanones have an energy transfer mechanism via triplet ketone formed in the high yield by the thermolysis of **3** at room temperature.[4,5] Although the lifetimes of dioxetanones are several minutes or longer in neutral solvents,[4,6] the steady-state concentration of **3** under the basic condition is probably reduced by its facile reverse reaction with MeO^- (k_{-5} in eq 5). This makes the C-T mechanism (eq 4, 5, and 11) an only effective CL scheme and reduces the spontaneous decomposition of **3** to produce $^{T}C{=}O$, which is contrary to the reported case.[5]

Experimental Section[19]

Materials. Starting esters, $R_1R_2CHCO_2Me$, were rectified after the reaction of methyl phenylacetate, alkyl halide, and *t*-BuOK (molar ratio of 1:1:1.2) in *t*-BuOH-DMF (1:5) under nitrogen (30 min at room temperature). Alkyl halides, MeI, EtBr, *i*-PrBr, and $PhCH_2Cl$, gave 60–90% yields of the esters, boiling points being 118–121 °C (25 mm) [lit.[20] 115 °C (24 mm)], 110–112 °C (12 mm) (lit.[21] 225–226 °C), 113–116 °C (14 mm),[22] and 147–150 °C (1.5 mm) [lit.[24] 123–124 °C (0.2 mm)], respectively.

α-Hydroperoxy esters, **4a** and **4b**, are reported previously.[11] The other peroxides, **4c–f**, were synthesized by method I in the previous report[11] in 30–70% yields. Peroxide **4f** was recrystallized from benzene–petroleum ether (2:1), melting point 107–108 °C (lit.[8b] 109 °C). Liquid peroxides, **4c–e**, were purified by passing through a column of Florisil using *n*-hexane–dichloromethane as an eluent.

Iodometry[11] showed over 95% purity of the peroxides. The structures of α-hydroperoxy esters were supported by the following NMR spectra (δ, CCl_4): for **4e** ($R_2 = Me$), 1.83 (s, 3 H), 3.06 (s, 3 H), 7.1–7.4 (m, 5 H), 9.28 (s, 1 H); for **4d** ($R_2 = Et$), 0.80 (t, 3 H, $J = 7.5$ Hz), 2.21 and 2.26 (two q, 2 H, $J = 7.5$ Hz), 3.65 (s, 3 H), 7.1–7.4 (m, 5 H), 8.63 (broad s, 1 H); for **4c** ($R_2 = i$-Pr), 0.80 and 0.95 (two d, 6 H, $J = 6$ Hz), 2.34 (septet, 1 H, $J = 6$ Hz), 7.1–7.6 (m, 5 H), 9.61 (s, 1 H). A characteristic downfield shift (δ 7–10) of the hydroperoxy proton has already been mentioned.[11]

Chemiluminescence. The CL was monitored by a Hitachi MPF-2A fluresecence spectrophotometer using a 4-ml quartz cell (1-cm path length). Usually, the decomposition of **4** was moderate at 40 °C and then the CL intensity was practically constant for several minutes. When the decomposition was fast as was the case in aqueous MeOH, the initial I at time zero was determined from the plot of I vs. time. Reproducibility of the CL intensity was adequate (within ±20%) and the CL spectrum with fluorescein (E_{max} = 540 nm) recorded with slit width of 40 nm was identical with the fluorescence spectrum of the fluorescer under the same conditions.

The quantum yield was measured according to the literature method[25] using DPA and fluorescein. The incident light from Xe arc was determined by the ferrioxalate actinometry.[26] The quantum yield Φ was calculated from eq 2 and 3 using 3 ml of solution for all determinations.

Products. The methoxide-catalyzed decomposition of **4** in MeOH afforded 60–95% yields of ketones ($R_1R_2C{=}O$) by GLC analysis. Since further reactions (e.g., autoxidation) of the ketones produced also occurred, the yields were significantly lowered except for the case of benzophenone. Carbon dioxide was not determined since its formation is already reported.[8b]

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Registry No.—**4a**, 57272-44-3; **4b**, 25818-61-5; **4c**, 60538-63-8; **4d**, 60538-64-9; **4e**, 60538-65-0; **4f**, 60538-66-1.

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Steric Effects in Homogeneous Gas-Phase Reactions. Pyrolysis of Isopropyl Esters

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Absolute reaction rate constants have been determined in the pyrolysis of 18 isopropyl alkanoates to acids and propene in a very carefully deactivated stainless steel static reactor. Trisubstitution by alkyl groups at the α position of the acid moiety showed a small, but readily measurable, rate of acceleration. Substitution at the β position had no effect on the rate of pyrolysis. This rate acceleration was reflected in the entropy of activation. α-Phenyl and α-chloro substituents influence pyrolysis rates more than α-alkyl substituents and at least with the chloro substituent the effects are a combination of both steric and electronic.

The pyrolysis of esters, when studied in a very carefully deactivated reactor, has been demonstrated to be a homogeneous, first order, unimolecular reaction proceeding through a converted cyclic transition with a degree of charge separation between the oxygen and carbon. Removal of the β hydrogen is also part of the rate-determining step. The mechanism which has been proposed[2] explained all available data excepting some rearrangements which likely were not gas-phase reactions but surface-catalyzed reactions. Refinements to this mechanism have been presented by others.[3] There are, no doubt, many studies on ester pyrolysis which were thought to be gas-phase reactions but were carried out in unseasoned reactors, e.g., dropping the ester through a clean glass tube, which most likely were not homogeneous gas-phase reactions but rather were surface-catalyzed reactions resulting in different product ratios, rearrangements, and faster reaction rates than are found under strictly gas-phase reactions conditions.

There have been many studies dealing with the electron influences on the rate of pyrolysis,[4a] but only a very few which have dealt specifically with steric influences on pyrolysis rates. Studies of steric effects in the acid moiety are very limited. Tinkelenberg et al. included some steric effect studies in their paper on the polar nature of β-elimination reactions.[4b] Effects of electronic changes in the acid portion are known to be not nearly as influential as they are in the alkyl portion. This paper reports a study of changes in steric effects in the acid portion on the ease of ester pyrolysis and a report of some electronic effects studies.

Steric effects in unimolecular homogeneous gas-phase pyrolysis of esters are not expected to be pronounced and certainly not as great as found in bimolecular reactions such as found in mineral acid catalyzed esterification of carboxylic acids. However, a measure of the effects, if present, would reveal some interesting aspects about gas-phase pyrolysis mechanisms and the nature of steric interactions as well. In homogeneous gas-phase reactions, all solvent effects are excluded.

The absolute rate constants have been determined for 18 isopropyl esters in which the extent of substitutions at the α and β positions have been varied. The electronic effects by different alkyl groups are very similar. Therefore, any change in rate will reflect steric interactions. Although the high temperatures used in pyrolysis of esters (~378 °C) minimize substituent effects, small effects are readily detectable within experimental error when studies are made in a carefully deactivated reactor. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were determined for the two esters (VII and VIII, Table I)