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# Homolytic Decomposition of *t*-Alkyl 2,2-Dimethylperoxypropionates

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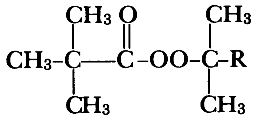
Decomposition rates and products of *t*-alkyl 2,2-dimethylperoxypropionates were measured in cumene at several temperatures. The peroxyesters decomposed homolytically, depending on the structure of the *t*-alkyl moiety. The relative rates of the *t*-alkyl moieties to the 1,1-dimethylethyl one were: 1,1-dimethylbutyl (1.14), 1,1-dimethylpropyl (1.19), 1,1,2-trimethylpropyl (1.85), 1,1,3,3-tetramethylbutyl (2.10), and 1,1-dimethyl-2-phenylethyl (2.34). The decomposition showed an isokinetic relationship and the importance of stabilization by hyperconjugation. Based on these data, the decomposition mechanism, which contains a slight stretching of the $C_\alpha$–$C_\beta$ bond to the peroxyl oxygen at the transition state is, discussed.

A large number of investigations concerning the decomposition mechanism of *t*-alkyl peroxyesters have been concerned with the relationship between the structure of the peroxyesters and the mode of decomposition.[1] However changes in the structure have been restricted to the acyl moiety. Only a few reports concerning the structure of the *t*-alkylperoxyl group exist.[2] Sheldon and Kochi indicated that there is a small influence of the *t*-alkylperoxyl group on the decomposition of di-*t*-alkyl diperoxyoxalates, and the variation of the solvent from pentane to acetonitrile enhances the rate and the formation of heterolytic decomposition products.[2a] Difficulties in studying the influence of the *t*-alkylperoxyl moiety can be attributed to the possibility that radical decompositions are accompanied by heterolytic ones.[3] It has also been known that peroxyesters are acceptable to heterolytic decompositions when the acidity of the parent acid is large.[4]

We have studied the homolytic decomposition of *t*-alkyl 2,2-dimethylperoxypropionates (**1**) which could be expected to decompose more homolytically because of the slight acidity of the parent acid. One of the compounds studied, 1,1-dimethylethyl 2,2-dimethylperoxypropionate (**1a**) has been used as a standard compound.



$$CH_3\text{-}C(CH_3)_2\text{-}C(=O)\text{-}OO\text{-}C(CH_3)_2\text{-}R$$

**1a**; R = $CH_3$, **1b**; R = $CH_3CH_2$, **1c**; R = $CH_3CH_2CH_2$, **1d**; R = $(CH_3)_2CHCH_2$, **1e**; R = $(CH_3)_2CH$, **1f**; R = $PhCH_2$

## Results and Discussion

The peroxyesters were synthesized by the acylation

Table 1. Rate Constants and Activation Parameters for Decomposition of *t*-Alkyl 2,2-Dimethylpropionates at Concentration of 0.05 mol dm$^{-3}$ in Cumene[a)]

| Peroxyester | Temperature | Rate constant | Activation parameter | |
|---|---|---|---|---|
| | °C | $10^5 k_d/s^{-1}$ | $\Delta H^*$/kJ mol$^{-1}$ | $\Delta S^*$/J K$^{-1}$ mol$^{-1}$ |
| **1a**[b)] | 60 | 2.95 | 118.0 | 23 |
| **1b** | 50 | 1.05 ±0.09 | 114.9±1.2 | 14±7 |
| | 60 | 3.51 ±0.08 | | |
| | 70 | 13.09 ±0.35 | | |
| | 80 | 42.39 ±3.61 | | |
| **1c** | 40 | 0.239±0.008 | 116.3±0.8 | 18±5 |
| | 50 | 0.883±0.031 | | |
| | 60 | 3.37 ±0.097 | | |
| | 70 | 12.26 ±0.51 | | |
| | 80 | 41.66 ±3.47 | | |
| **1d** | 40 | 0.480±0.011 | 112.4±1.3 | 12±8 |
| | 50 | 1.797±0.053 | | |
| | 60 | 6.18 ±0.32 | | |
| | 70 | 23.44 ±0.76 | | |
| **1e** | 40 | 0.36 ±0.11 | 114.2±1.5 | 15±9 |
| | 50 | 1.59 ±0.08 | | |
| | 60 | 5.14 ±0.40 | | |
| | 70 | 19.21 ±1.10 | | |
| **1f** | 40 | 0.456±0.017 | 116.5±0.5 | 24±3 |
| | 50 | 1.833±0.031 | | |
| | 60 | 6.91 ±0.20 | | |
| | 70 | 25.1 ±0.8 | | |

a) Rate constants and their standard deviations were calculated by the method of least squares. b) Ref. 19.

of the correspoding hydroperoxides with 2,2-dimethylpropionyl chloride in the presence of potassium hydroxide at low temperatures. The hydroperoxides were prepared from the corresponding alcohols or olefins by using 50% hydrogen peroxide in the presence of sulfuric acid.

The rates for the decomposition of the peroxyesters were measured by iodometric titration of the active oxygen. Good first-order rate constants were obtained over 10—80% conversion in all cases. Rate data concerning cumene are given in Table 1 together with calculated activation parameters; data concerning acetonitrile are given in Table 2. The decomposition products formed from the *t*-alkylperoxyl moiety in cumene were analyzed with GC and are shown in Table 3, together with the relative rates of $\beta$-scission of the corresponding alkoxyl radicals.[4,5] The total yields of the corresponding alcohol and the acetone were upper 90%. The inversion product ($C(CH_3)_3CO_2$–$C(CH_3)_2$–OR) and the hydrolysis product (ROH) from the heterolyic decomposition could not be recognized with detectable amounts. The solvent effect in cumene and acetonitrile was similar to that of *p*-substituted 1,1-dimethylethyl 2-methyl-2-phenylperoxypropionates.[1f] These facts indicate that the decomposition of **1** in cumene proceeds mainly by a homolytic path. The formation ratio of the acetone to the corresponding alcohol in Table 3 changes with the alkyl group (R), and the order of these ratios is similar to those in the decomposition of di-*t*-alkyl diperoxyoxalates and in $\beta$-scission of the corresponding alkoxyl radicals (Table 3). However, the ratios of **1d** and **1e** are considerably different in the order and size from those of the relative rate ($k_\beta/k'_A$) in the $\beta$-scission. The ratio of **1d** increases regardless of whether there is less $\beta$-scission, and the ratio of **1e** is very small, compared with the remarkable $\beta$-scission. The decomposition rates of **1** change with the *t*-alkyl group, of which the effect is not large. The ratio of the rate constant for the slowest **1a** against the fastest **1f** is 0.43 at 60 °C. This corresponds to that reported for the decomposition of di-*t*-alkyl diperoxyoxalates in pentane.

Table 2. Rate Constants in Acetonitrile and Relative Rates with Variation of Solvent at 60 °C[a)]

| Peroxyester | Rate constant $10^5\,k_d/s^{-1}$ | Relative rate[b)] |
|---|---|---|
| **1a** | 5.18±0.04 | 1.76 |
| **1c** | 7.39±0.14 | 2.19 |
| **1d** | 11.43±0.13 | 1.85 |

a) Initial concentration of peroxyester is 0.05 mol dm$^{-3}$.
b) Relative rate of acetonitrile against cumene.

Figure 1 shows an isokinetic relationship for the decomposition of **1** in cumene. A good linear free-energy relation exists for five electron-donating alkyl substituents, except **1f** (electron-withdrawing one). This suggests that the difference of decomposition rates except **1f** (discussed later) takes place with a single interaction mechanism of the substituents.[6]

The relative rates in the decomposition of **1** in cumene are found to depend on the nature of the substituents and follow the order: **1a<1c<1b<1e<1d<1f** (Table 1). The data in Table I could be analyzed by the following Taft equation:[7]

$$\log(k_d/k_{d0}) = \rho^*\sigma^* + (\Delta n)h, \qquad (1)$$

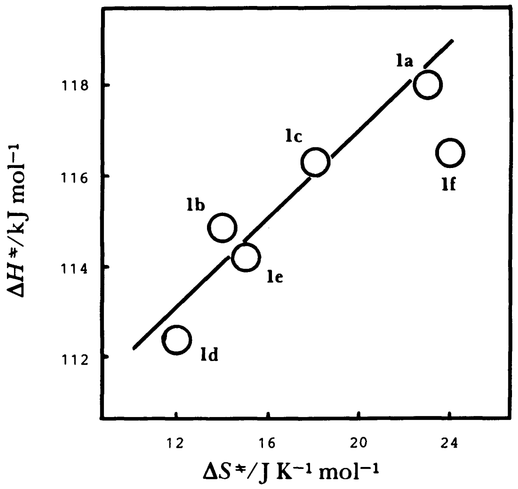


Fig. 1. Isokinetic relationship for the decomposition of *t*-alkyl 2,2-dimethylpropionates in cumene.

Table 3. Decomposition Products Formed from *t*-Alkyl Moiety at 60 °C

| Peroxyester | Product/mol Acetone | Product/mol Corresponding alcohol | Ratio[a)] | Ratio in peroxyoxalate[b)] | $k_\beta/k'_A$ in $\beta$-scission[c)] |
|---|---|---|---|---|---|
| **1a** | 0 | 0.88 | 0 | <0.02 | 0.053 |
| **1b** | 0.28 | 0.66 | 0.42 | 0.09 | 2.9 |
| **1c** | 0.17 | 0.76 | 0.22 | — | 2.4 |
| **1d** | 0.43 | 0.59 | 0.73 | — | 1.4 |
| **1e** | 0.54 | 0.38 | 1.42 | 2.92 | 96 |
| **1f** | 0.54 | 0.40 | 1.35 | 1.25 | 2.2 |

a) Ratio of acetone to the corresponding alcohol formed per the decomposed peroxyester **1** (mol/mol) in cumene. b) In pentane at 40 °C.[2a)] c) Relative rate of $\beta$-scission to hydrogen abstraction with cyclohexane of alkoxyl radical.[5)] These values were calculated by using data in Ref. 4.

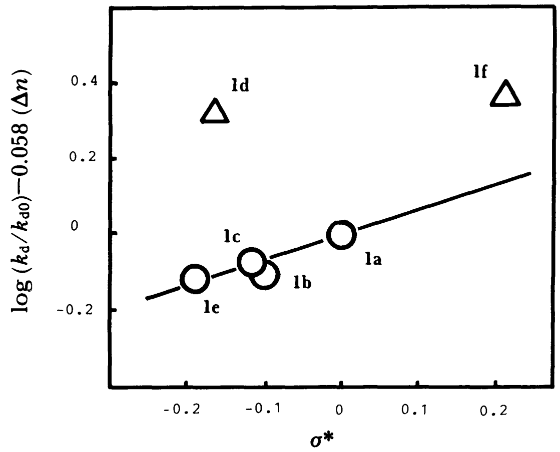


Fig. 2. A plot of [log ($k_d/k_{d0}$)=0.058 ($\Delta n$)] against $\sigma^*$ in the decomposition of *t*-alkyl 2,2-dimethylpropionates in cumene at 60°.

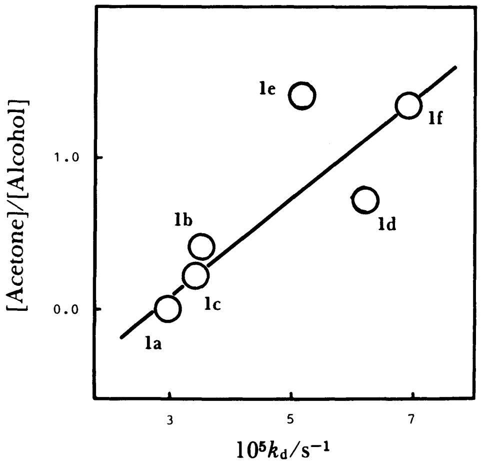
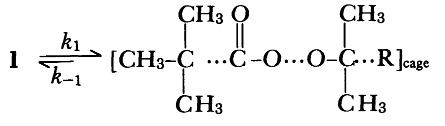


Fig. 3. A plot of [Acetone]/[Alcohol] against $k_d$ in the decomposition of *t*-alkyl 2,2-dimethylpropionates in cumene at 60°C.

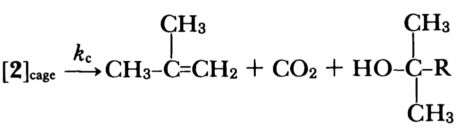
where $k_d/k_{d0}$ is relative rate of the related peroxyester to **la**, $\sigma^*$, the polar substituent constant by Taft, $\rho^*$, reaction constant, ($\Delta n$), the difference between the related peroxyester and **la** for the number of the hydrogen atoms participating in C–H hyperconjugation, and *h*, an emperical constant. A plot of [log ($k_d/k_{d0}$)−($\Delta n$)*h*] vs. $\sigma^*$ in Fig. 2 shows good linearity for **la**, **lb**, **lc**, and **le**, and the values of $\rho^*$= 0.67 and *h*=0.058 are estimated by using a least-squares method. These are interpreted in terms of C–H hyperconjugative and inductive stabilizing effects of the substituents at the transition state.

On the basis of the decomposition rates and products, the isokinetic relationship and the importance of the hyperconjugation, the following scheme for the main reactions may be considered as a decomposition mechanism of **1**:

 (2)

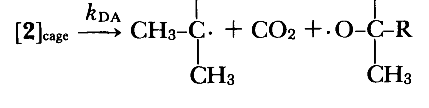
$$1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdots\overset{O}{\overset{\|}{C}}\text{-}O\cdots O\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdots R]_{cage} \quad (2)$$

**2**

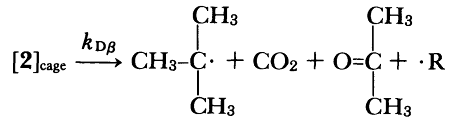
 (3)

$$[2]_{cage} \xrightarrow{k_c} CH_3\text{-}\overset{CH_3}{C}{=}CH_2 + CO_2 + HO\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}R \quad (3)$$

**3**

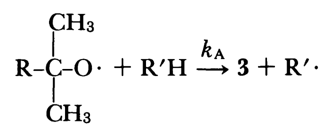
 (4)

$$[2]_{cage} \xrightarrow{k_{DA}} CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot + CO_2 + \cdot O\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}R \quad (4)$$

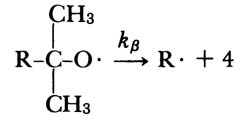
 (5)

$$[2]_{cage} \xrightarrow{k_{D\beta}} CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot + CO_2 + O{=}\overset{CH_3}{\underset{CH_3}{C}} + \cdot R \quad (5)$$

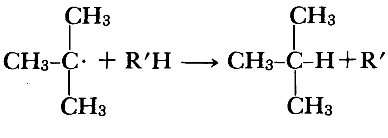
**4**

 (6)

$$R\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\cdot + R'H \xrightarrow{k_A} 3 + R'\cdot \quad (6)$$

 (7)

$$R\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\cdot \xrightarrow{k_\beta} R\cdot + 4 \quad (7)$$

 (8)

$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot + R'H \longrightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}H + R'\cdot \quad (8)$$

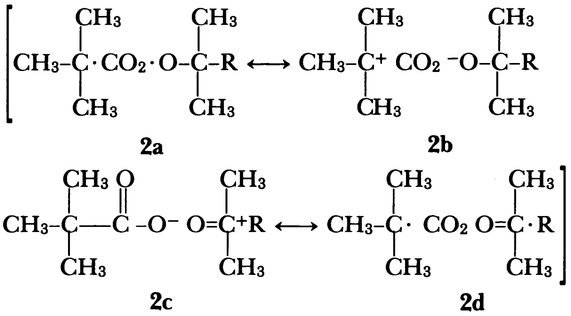
$$2R'\cdot \longrightarrow R'\text{-}R' \quad (9)$$

Here, $k_1$ is the rate constant for the bond homolysis, $k_{-1}$ the rate constant for the cage return, **2** a reaction intermediate, $k_c$ the rate constant for the disproportionation between the 1,1-dimethylethyl and the alkoxyl radicals within a solvent cage, $k_{DA}$ the rate constant for the diffusion of the alkoxyl radical out of the solvent cage, $k_{D\beta}$ the rate constant for the outwared diffusion of the acetone formed within the solvent cage, $k_A$ the rate constant for hydrogen abstraction of the alkoxyl radical with cumene (R'H), and $k_\beta$ the rate constant for $\beta$-scission of the alkoxyl radical outside the solvent cage, respectively.

The decomposition prcducts of **la** in cumene included isobutylene and isobutane in approximately equal amounts;[8] most of them may be considered from the amount of 2,3-dimethyl-2,3-diphenylbutane to be formed exclusively within (Eq. 3) and outside the solvent cage (Eq. 8), respectively. The coupling products between the 1,1-dimethylethyl and the alkoxyl radicals within the solvent cage, and between these radical species outside it were negligibly small in the photodecomposition of **1**.[2c] Since the cage return (Eq. 2) can be neglected in a concerted decomposition ($k_1 \gg k_{-1}$)[9] the observed rate constant of the decomposition, $k_d$, is as follows:

$$k_d = k_1(k_{DA} + k_{D\beta} + k_c)/(k_{-1} + k_{DA} + k_{D\beta} + k_c) \simeq k_1, \quad (10)$$

The formation ratio of the acetone to the corresponding alcohol ([**4**]/[**3**]) in Table 3 is plotted against the decomposition rate constant, $k_d$, shown in Fig. 3. The decomposition of **1d** yield much more acetone than that estimated from the $\beta$-scission, compared with those of **1b** and **1c**. This can be explained by the fact that a part of the acetone is formed by the $\beta$-scission within the solvent cage or directly from the intermediate 2 (Eq. 5). Figure 3 suggests that the formation of acetone is apt to increase with the decomposition rate of **1** and is based on the direct one from the intermediate **2**. The points of **1e** and **1d** in Fig. 3 deviate greatly from a linear line (correlation coefficient=0.8676)[10] which passes through the points of **1c** and **1f**, and the corresponding alkoxyl radicals to **1c** and **1f** have the similar values of $k_\beta/k'_A$ with each other (Table 3). These deviations may be understood by the difference of the $\beta$-scission outside the solvent cage.[10]



$$\left[ CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot CO_2\cdot O\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}R \longleftrightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}{}^+\ CO_2{}^-\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}R \right.$$

**2a** **2b**

$$\left. CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{-}O^-\ O{=}\overset{CH_3}{\underset{CH_3}{C}}{}^+R \longleftrightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot\ CO_2\ O{=}\overset{CH_3}{\underset{CH_3}{C}}\cdot R \right] \quad (11)$$

**2c** **2d**

The intermediates of **2a** and **2b** at the transition state had been confirmed by the relationships between the structure of the acyl group and the reactivity.[1] The positive value of $\rho^*$ in the Taft equation (Eq. 1) shows an inductive stabilizing effect more by an electron-withdrawing substituent on the intermediate **2**. The importance of the hyperconjugation (Eq. 1) and the formation of the $\beta$-scission product from the intermediate **2** (Eq. 5) indicate that, in addition to **2a** and **2b**, there exist intermediates of **2c** and **2d** at the transition state. The intermediate of **2c** is correlated to that in the heterolytic decomposition of *t*-alkyl *p*-nitroperbenzoates.[3] Walling et al. had proposed that all of radical and ionic decomposition products arise from a common rate-determining transition state to partition into radical and ionic pairs occurring at a later stage in the decomposition of diacyl peroxides.[11] The decompositions of 1-methyl-1-phenylethyl peracetate and di-*t*-alkyl diperoxyoxalates follow heterolytic, homolytic, or their mixed pathways, depending on the polarity of the solvent and the presence of acid catalysis.[12] The similarities between the homolytic and the heterolytic decompositions (as shown in this work) support the Walling hypothesis in the same manner as diacyl peroxides. Deviations of **1f** from the isokinetic relationship and the Taft equation (Figs. 1 and 2) may probably result from the stabilization of the intermediate **2d** of which the benzyl radical is the most stable. The deviation of **1d** from the Taft equation (Fig. 2) may be understood to be similar to the rate enhancement in neopentyl solvolysis, in which $\gamma$-carbon atoms to the cationic center participate in the stabilization at the transition state.[13] Thus, the influence of the *t*-alkylperoxyl moiety could be explained by inductive and resonance effects without any consideration of steric effects. In conclution, it may be suggested that the $C_\alpha$–$C_\beta$ bond to the peroxyl oxygen is only slightly streched, together with the $C_\alpha$–CO and O–O bonds at the transition state.

## Experimental

IR and NMR spectra were recorded on JASCO A-3 and JEOL JNM-MH-100 spectrometers, respectively. GC analysis was carried out using Shimadzu GC-6A and GC-2D gas chromatography using five columns: (A), Silicone GE-30 on Shimalite (NAW), 2.4 m; (B), PEG 20M 25% on Shimalite (NAW), 2 m; (C), PEG 20M 5% on Shimalite (NAW), 2 m; (D), Sorbitol 30% on Shimalite (NAW), 3 m; (E), PEG 20 M 25% on Shimalite (NAW), 3 m.

**Materials.** 2,2-Dimethylpropionyl chloride was purified by the distillation (bp 103 °C) of a commercial product. Sixty-nine per cent 1,1-dimethylethyl, 90% 1,1-dimethylbutyl, and 86% 1,1,3,3-tetramethyl-butyl hydroperoxides were the products of Nippon Oil & Fats Co., Ltd. 1,1-Dimethylpropyl alcohol was prepared by the reaction of 2-methyl-1-pentene with an excess of 65% $H_2O_2$ for 30 min at 0—5 °C and the hydrolysis of the reaction mixture with an aqueous solution of 5% NaCl under a temperature of 10 °C. The alcohol was distilled after drying over anhydrous $MgSO_4$ (bp 66 °C/76 mmHg (1mmHg=133.322 Pa)).[14] In a similar method 1,1,3,3-tetramethylbutyl alcohol was prepared (bp 54 °C/16 mmHg).[14]

**Preparation of Hydroperoxides.** The purities of hydroperoxides were checked by iodometric titration and GC. The titration procedure involved the use of a mixture (20:2) of isopropyl alcohol and acetic acid as the solvent, and saturated potassium iodide as the source of iodide.[15]

**1,1-Dimethylpropyl hydroperoxide** was prepared from a reaction of the corresponding alcohol with 50% $H_2O_2$ by the method of Milas and Surgenor[16] and the purification by distillation (bp 50 °C/20 mmHg).[17] **1,1-Dimethylbutyl hydroperoxide** was purified by distillation (bp 41 °C/3 mmHg)[18] of the commercial product. **1,1,3,3-Tetramethylbutyl hydroperoxide** was purified from a commercial product by the isolation of sodium salt with sodium amide, regeneration of the hydroperoxide with carbon dioxide and vacuum distillation (bp 46 °C/1 mmHg).

**1,1,2-Trimethylpropyl hydroperoxide** was prepared by the reaction of olefin with $H_2O_2$ in the presence of $H_2SO_4$ and acetonitrile. To an aqueous solution of 44% $H_2O_2$ (115.0 g, 1.50 mol) there was added dropwise concd $H_2SO_4$ (80.0 g, 0.82 mol) for 30 min at 0 °C and added continuously acetonitrile (32.8 g, 0.80 mol) and chloroform (50 g). Then, to the mixture there was added dropwise 2,3-dimethyl-2-butene (67.4 g, 0.80 mol) for 30 min at 0—5 °C. The mixture was stirred for 30 min at 5 °C and continuously for 30 min at 10 °C in order to complete the reaction. After the reaction mixture was added by petroleum ether (50 g) and washed three times with an aquous solution of 40% $(NH_4)_2SO_4$, a crude product was obtained by the evaporation of the solvent at reduced pressure. Because dangerous materials (ketone peroxides) were contained in the crude product,[3] they were eliminated by a separation of the oily material from the crude product (32.2 g), which was added by petroleum ether (6.0 g) after the neutralization with 35% KOH (45.0 g) and methanol (30 cm$^3$). After regeneration of the hydroperoxide by carbon dioxide and washing with an aqueous solution of 40% $(NH_4)_2SO_4$, the crude product was distilled (bp 30—33 °C/2 mmHg) in the presence of polyethylene glycol oligomer ($\bar{n}$=300) to give 1,1,2-trimethylpropyl hydroperoxide (6.2 g) of 82.0% purity analyzed by GC using column A. IR (neat): $\nu_{O-H}$ 3400 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=1.00 (6H, d, >C$(CH_3)_2$), 1.13 (6H, s, -C$(CH_3)_2$-), and 2.02 (H, m, >CH-).

**1,1-Dimethyl-2-phenylethyl hydroperoxide** was prepared by a reaction of the corresponding alcohol with 50% $H_2O_2$. A mixture of 1,1-dimethyl-2-phenylethyl alcohol (300.4 g, 2.0 mol) and THF (100 cm$^3$) was added dropwise to 72% $H_2SO_4$ (272.6 g, 2.0 mol) under a temperature of 10 °C to give the sulfonate. Then after the addition of 50% $H_2O_2$ (272.0 g, 4.0 mol) for 90 min under a temperature of 10 °C, the mixture was stirred for 3 h at 40 °C and for 2 h at 30 °C. The 15.4% crude material (623.0 g, containing 0.57 mol of the hydroperoxide) was obtained by washing with water after the addition of petroleum ether (300 g), and drying over anhydrous $MgSO_4$. The hydroperoxide (29.6 g) of 97.0% purity was obtained by the isolation of the sodium salt with sodium amide, regeneration of the hydroperoxide by carbon dioxide and recrystallization from petroleum ether. Mp 40—41 °C (lit,[3] mp 44 °C); IR ($CCl_4$): $\nu_{O-H}$ 3400 cm$^{-1}$, phenyl 1600 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=1.16 (6H, s, -C$(CH_3)_2$-), 2.83 (2H, s, -$CH_2$-), 7.20 (5H, s, phenyl), and 8.02 (1H, s, -OOH).

**Preparation of Peroxyesters.** Purities of peroxyesters were checked by iodometric titration which involved the use of an acetic acid solution containing a saturated aqueous solution of NaI and a small amount of iron(III) chloride.[19]

**Peroxyester 1a** was prepared by a Schotten–Baumann reaction of 2,2-dimethylpropionyl chloride with the corresponding hydroperoxide. To a mixture of 69% 1,1-dimethylethyl hydroperoxide (20.9 g, 0.16 mol) and 30% KOH (30.0 g, 0.16 mol) there was added dropwise the acid chloride (16.1 g, 0.13 mol) for 30 min at 2 °C; the mixture was then stirred for 30 min to complete the reaction. After the reaction mixture was washed twice with 5% NaOH for 5 min at 0 °C, three times with water and dried with anhydrous $MgSO_4$, the peroxyester (18.5 g, yield 76.9%) of 93.8% purity was obtained. The distilled material (bp 50.5 °C/5 mmHg) was shown to be 97.0% purity. IR ($CCl_4$): $\nu_{C=O}$ 1762 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=1.24 (9H, s, acyl *t*-Bu) and 1.20 (9H, s, peroxyl *t*-Bu).

**Peroxyester 1b** was prepared by a Schotten–Baumann reaction of the acid chloride with the corresponding hydroperoxide. To a mixture of 95.0% 1,1-dimethylpropyl hydroperoxide (7.7 g, 0.07 mol) and 20% KOH (25.3 g, 0.09 mol) there was added dropwise acid chloride (10.9 g, 0.07 mol) containing petroleum ether (2.5 g) for 30 min at 0—5 °C and stirred for 30 min to complete the reaction. Then, the reaction mixture was washed once with 5% NaOH, once with an aqueous solution which contained $Na_2SO_4$ (4.2%), sodium acetate (8.3%) and acetic acid (4.2%), and twice with water. After drying over anhydrous $MgSO_4$ and evaporation of the solvent, the crude product of 11.5 g (yield 83.0%) was obtained and further purified by distillation (bp 51 °C/3 mmHg) to give the peroxyester of 95.8% purity. IR ($CCl_4$): $\nu_{C=O}$ 1765 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=0.94 (3H, m, peroxyl -$CH_3$), 1.24 (15H, s, acyl *t*-Bu and peroxyl *t*-Bu) and 1.53 (2H, q, -$CH_2$-).

**Peroxyester 1c** was prepared by the method according to 1,1-dimethylpropyl peroxyester. Yield 81.4%; purity 96.1%; IR ($CCl_4$): $\nu_{C=O}$ 1765 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=0.95 (3H, m, peroxyl-$CH_3$), 1.24 (15H, s, acyl *t*-Bu and peroxyl -C$(CH_3)_2$-O), and 1.52 (4H, m, -$CH_2CH_2$-).

**Peroxyester 1a** was prepared by the method according to 1,1-dimethylpropyl peroxyester. The purity and yield of the crude product were 83.7 and 65.0%, respectively. The crude product was purified by flash chromatography on Merck Kieselgel 60 using hexane–ethyl acetate (95:5) as the eluent to give 93.1% purity. IR ($CCl_4$): $\nu_{C=O}$ 1765 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=0.96 (6H, d, peroxyl >C$(CH_3)_2$), 1.20 (6H, s, peroxyl -C$(CH_3)_2$-O), 1.24 (9H, s, acyl *t*-Bu), and 1.88 (1H, m, >CH-).

**Peroxyester 1d** was prepared by a Schotten–Baumann reaction of the acid chloride with the corresponding hydroperoxide. To a mixture of 98.0% 1,1,3,3-tetramethylbutyl hydroperoxide (22.3 g, 0.15 mol) and 35% KOH (31 g, 0.23 mol) there was added dropwise the acid chloride (21.7 g, 0.18 mol) for 35 min at 0—5 °C to complete the reaction. The reaction mixture was washed once with 5% NaOH, once with an aqueous solution which contained $Na_2SO_4$ (4.2%), sodium acetate (8.3%) and acetic acid (4.2%), twice with water, and dried over anhydrous $MgSO_4$ to give the peroxyester of 94.7% purity (21.0 g, yield 48.9%). IR ($CCl_4$): $\nu_{C=O}$ 1765 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=1.03 (9H, s, peroxyl *t*-Bu), 1.22 (9H, s, acyl *t*-Bu), 1.32 (6H, s, -C$(CH_3)_2$-O), and 1.60 (2H, s, -$CH_2$-).

**Peroxyester 1f** was prepared by a Schotten–Baumann reaction of the acid chloride with the corresponding hydroperoxide. To a mixture of 97.0% 1,1-dimethyl-2-phenylethyl hydroperoxide (17.1 g, 0.10 mol) there was added dropwise the acid chloride (14.5 g, 0.12 mol) for 15 min at 25 °C, and stirred for 10 min at 10 °C to complete the reaction. The reaction mixture was washed once with 5% NaOH, three times with water and dried over anhydrous $MgSO_4$. After the evaporation of the solvent under vacuum, a crude product of 90.0% purity (24.0 g, yield 72.0%) was obtained and purified by flash chromatography on Merck Kieselgel 60 using hexane–ethyl acetate (95:5) as the eluent to give the peroxyester of 94.0% purity. IR ($CCl_4$): $\nu_{C=O}$

1762 cm$^{-1}$; phenyl 1600 cm$^{-1}$; $^1$H NMR ($CCl_4$): $\delta$=1.25 (9H, s, acyl *t*-Bu), 2.83 (2H, s, $PhCH_2$–), and 7.12 (5H, s, phenyl).

**Kinetic Procedure.** A dilute solution of peroxyester in cumene or acetonitrile was placed in sealed tubes under vacuum and heated in a constant-temperature bath. The remaining amount of peroxyester was determined by the above-mentioned iodometric titration for peroxyester, in which the sample solutions were allowed to stand at room temperature for 15—30 min. The reaction was followed up to 70—80% decomposition and exhibited first-order kinetics.

**Decomposition Products.** Peroxyester at the concentration of 0.05 mol dm$^{-3}$ in cumene was decomposed completely at 60 °C over 50 h and the solution were analyzed by GC using nonane and decane as internal standards. The following are the conditions used in determining yield of products (product, column): acetone, 1,1-dimehylethyl alcohol, 1,1-dimethylpropyl alcohol, 1,1-dimethylbutyl alcohol and 1,1,2-trimethylpropyl alcohol for **1a**, **1b**, **1c**, and **1e**, column B; acetone and 1,1-dimethyl-2-phenylethyl alcohol for **1f**, column C; 1,1,3,3-tetramethylbutyl alcohol for **1d**, column D; acetone for **1d**, column E.

## References

1) a) T. Koenig, "Free Radicals, Vol. I", ed by J. K. Kochi, Wiley-Interscience, Chap. 3 (1973); b) L. A. Singer, "Organic Peroxides, Vol. I," ed. by D. Swern, Wiley-Interscience, Chap. V (1970); c) R. L. Friedman, R. N. Lewis, and R. L. Pstorio, *Mod. Plast.*, **48**, 66 (1971); d) C. Ruchardt, *Angew. Chem., Ent. Ed. Engl.*, **9**, 830 (1970); e) C. Ruchardt "23rd Int. Congress of Pure and Applied Chemistry 4," 223 (1971); f) J. P. Engstrom and J. C. DuBose, *J. Org. Chem.*, **38**, 3817 (1973); g) D. D. Tanner, H. Yabuuchi, and H. Lutzer, *Can. J. Chem.*, **55**, 612 (1977); h) T. Yamamoto, Y. Nakashio, H. Onishi, and M. Hirota, *Nippon Kagaku Kaishi*, **1986**, 224.

2) a) R. A. Sheldon and J. K. Kochi, *J. Org. Chem.*, **35**, 1223 (1970); b) R. R. Hiatt and W. M. J. Strachan, *J. Org. Chem.*, **28**, 1893 (1963); c) R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 5175 (1970); d) A. S. Nazran and J. Warkentin, *J. Am. Chem. Soc.*, **104**, 6405 (1982).

3) E. Hedaya and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1661 (1967).

4) a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963); b) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

5) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", John Wiley & Sons (1963).

7) M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77**, 5590 (1955).

8) J. P. Lorand, S. D. Chodroff, and R. W. Wallance, *J. Am. Chem. Soc.*, **90**, 526 (1968); The decomposition products of **1a** in cumene were $CO_2$ (98%), 1,1-dimethylethyl alcohol (79%), isobutylene (40%), isobutane (30%), 2,3-dimethyl-2,3-diphenylbutane (68%) and bis(1,1-dimethylethyl) ether(2%) in the reference.

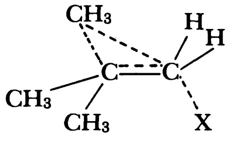
9) W. A. Pryor, E. H. Morkved, and H. T. Bickley, *J. Org. Chem.*, **77**, 1999 (1972).

10) If we can assume $k_c = k_{DA}$ from the decomposition products of **1a**,8) the steady-state approximation in the reaction of Eqs. 2—7 leads to the following equation: $k_{D\beta}/k_{DA}=\{(2+k_\beta/k_A[R'H])[\mathbf{4}]/[\mathbf{3}]-k_\beta/k_A[R'H]/(1+k_\beta/k_A[R'H])\}$, where $k_\beta/k_A[R'H]=k_\beta/k'_A \times (1/[\text{Cyclohexane}]) \times (k'_A[\text{Cyclohexane}]/k_A[R'H])$.5) A relationship between $k_{D\beta}/(k_{DA}+k_{D\beta})$ and $k_d$ has a good linearity with correlation coefficient of 0.9529. This can support the existence of Eq. 5.

11) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiannou, *J. Am. Chem. Soc.*, **92**, 4927 (1970).

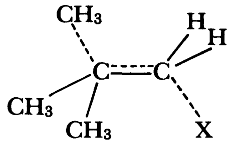
12) a) J. E. Leffler and F. E. Scrivener, Jr., *J. Org. Chem.*, **37**, 1974 (1972); b) J. T. Barbas and J. E. Leffler, *J. Org. Chem.*, **50**, 705 (1985); c) Ref. 2c.

13) a) I. L. Reich, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5635 (1969); b) T. Ando, H. Yamataka. H. Morisaki, J. Yamawaki, J. Kuramochi, and Y. Yukawa, *J. Am. Chem. Soc.*, **103**, 430 (1981): in this reference, it was suggested that the rate enhancement may be due to a small $\alpha$–$\gamma$ bond interaction (intermediate **3a**) or lenghthening of the $\beta$–$\gamma$ bond to the cationic center (intermediate **3b**).



**3a**

or



**3b**

14) J. J. Ritter, *J. Am. Chem. Soc.*, **70**, 4253 (1948).

15) T. Komai and K. Matsuyama, *Bull. Chem. Soc. Jpn.*, **58**, 2207 (1985).

16) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 643 (1946).

17) M. R. Vilenskaya and T. I. Yurzhenko, *Chem. Abstr.*, **60**, 15723 (1964).

18) A. W. White, *J. Chem. Soc.*, **1953**, 1541.

19) T. Komai, H. Ishigaki, and K. Matsuyama, *Bull. Chem. Soc. Jpn.*, **58**, 2431 (1985).