January, 1991] *Bull. Chem. Soc. Jpn., 64, 259—265 (1991)*

Substituent Effects in the Decomposition of *t*-Alkyl *t*-Butyl Peroxides

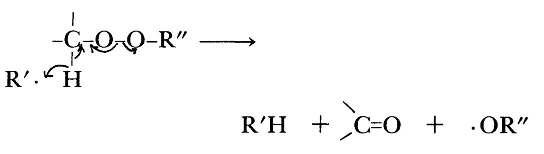
Kazuo Matsuyama* and Yoshiki Higuchi
Chemicals & Explosives Research Laboratory, Nippon Oil & Fats Co., Ltd.,
Taketoyo-cho, Chita-gun, Aichi 470-23

(Received August 2, 1990)

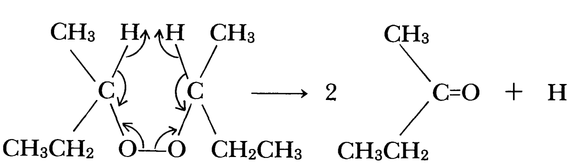
The decomposition rates and products of various *t*-alkyl *t*-butyl peroxides were examined in cumene at several temperatures. The decomposition of these peroxides took place homolytically, depending on the structure of the *t*-alkoxyl moieties ($RC(CH_3)_2$–O), and was retarded in the order: R=$(CH_3)_3CCH_2$>$(CH_3)_2CH$>$CH_3CH_2CH_2$>$PhCH_2$>CH_3CH_2>$ClCH_2$>CH_3. The rate constants for the electron-donating alkyl substitutents at 150 °C are correlated very well to a Taft equation ($\log k_d=-10.93\sum\sigma^*-6.61$ (correlation coefficient of 0.9501)), which is fairly different from the equation $\log k_d=-0.131\sum\sigma^*-3.422$ for electorn-withdrawing polar substituents. From this correlation and a product analysis, the nature of the polar character at the transition state of the decomposition is discussed.

Dialkyl peroxides have received considerable attention as clean sources of alkoxyl radicals and important intermediates in the oxidation or combustion of hydrocarbons. So far, many studies concerning the decomposition of dialkyl peroxides have been carried out.[1] The decomposition of di-*t*-butyl peroxide, which is probably one of the best-studied reaction in chemical kinetics, is accompanied by a slight radical-induced decomposition in most cases. However, the substituent effect correlation on the decomposition of dialkyl peroxides has not yet been made sufficiently clear, though it is believed that the decomposition rates are accelerated by electron-donating alkyl substituents.

Richardson et al. found a linear free-energy correlation concerning the decomposition of di-*t*-alkyl peroxides (*t*-alkyl denotes 1,1-dimethylalkyl through this paper) having electron-withdrawing polar substituents, where there was a very small change in the rates (ca. 1.5 times with 1.0 σ^* unit variation of the substituents studied).[2] On the other hand, the substituent effect correlation regarding the decomposition of dialkyl peroxides having electron-donating alkyl substituents was unsuccessful, because they contained primary and secondary dialkyl peroxides. Probably, the decomposition rates of bis(primary and secondary alkyl) peroxides were somewhat enhanced by an induced decomposition (Eq. 1) and a concerted decomposition (Eq. 2):[1b]

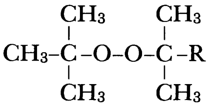


(1)



(2)

Di-*t*-alkyl peroxides, having a smaller possibility for induced decomposition, are most suitable for studying the substituent effect on O–O bond homolysis. In this work we studied the decomposition rates and products in the homolytic decomposition of *t*-alkyl *t*-butyl peroxides (**1**) in cumene in order to clearify the substituent effect. Cumene is a good solvent for investigating the homolytic reaction due to the formation of simple decomposition products:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-R$$

(**1**$_a$; R=CH_3, **1**$_b$; R=CH_3CH_2, **1**$_c$; R=$CH_3CH_2CH_2$, **1**$_d$; R=$(CH_3)_3CCH_2$, **1**$_e$; R=$(CH_3)_2CH$, **1**$_f$; R=$PhCH_2$, **1**$_g$; R=$ClCH_2$)

Results

The di-*t*-alkyl peroxides **1** were prepared mainly by the reaction of *t*-butyl hydroperoxide with the corresponding alcohols or olefins in the presence of sulfuric acid. The rates and products for the decomposition of **1** in cumene were determined with gas–liquid chromatography (GC) using alkanes as internal standards. Good first-order rate constants were obtained over 10—80% conversion in all cases. Decomposition rates and products data are given in Tables 1 and 2, respectively, together with calculated activation parameters. The rate constants had no appreciable change for a 10-fold increase in the concentration, thus seeming rule out any induced decomposition.

An isokinetic relationship was obtained for the decomposition of **1** in cumene (Fig. 1). Here, the steric interaction in the ground state was not important, since the values of the activation entropy decreased with those of the activation enthalpy.

Table 1 also includes a sum of the substituent constant for each peroxide. Where substituent constants were not reported, they were calculated by

Table 1. Rate Constants and Activation Parameters for Decomposition of *t*-Alkyl *t*-Butyl Peroxides in Cumene[a]

R in Peroxide, **1**	Temp	Conc	Rate const.	Activation parameter		$\Sigma\sigma^{*}$[b]
	°C	mol dm^{-3}	$10^6\,k_d/\mathrm{s}^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	
CH_3[c]	125		16	154.3	48.5	−0.600
(**1a**)	135		52			
	145		156			
CH_3CH_2	110	0.05	3.86±0.04	154.1±0.8	51.5±4.2	−0.615
(**1b**)	120	0.02	12.87±0.14			
		0.05	13.20±0.10			
		0.20	14.48±0.18			
	130	0.05	43.0 ±0.4			
	140	0.05	140.6 ±1.3			
$CH_3CH_2CH_2$	110	0.05	4.38±0.04	152.9±0.1	49.4±0.8	−0.630
(**1c**)	120	0.02	15.37±0.07			
		0.05	15.37±0.19			
		0.20	15.67±0.15			
	130	0.05	49.9 ±0.4			
	140	0.05	154.4 ±1.0			
$(CH_3)_3CCH_2$	110	0.05	10.85±0.05	147.6±0.3	43.1±1.7	−0.644
(**1d**)	120	0.02	37.3 ±0.5			
		0.05	37.0 ±0.5			
		0.20	36.7 ±0.2			
	130	0.05	114.1 ±1.1			
	140	0.05	340 ±2			
$(CH_3)_2CH$	110	0.05	7.07±0.08	149.7±0.1	45.2±0.4	−0.640
(**1e**)	120	0.02	23.74±0.21			
		0.05	23.80±0.10			
		0.20	23.92±0.12			
	130	0.05	76.2 ±0.4			
	140	0.05	230.8 ±2.5			
$PhCH_2$	110	0.05	4.35±0.01	151.7±0.3	46.0±1.3	−0.420
(**1f**)	120	0.02	14.58±0.15			
		0.05	14.63±0.06			
		0.20	14.76±0.09			
	130	0.05	47.0 ±0.3			
	140	0.05	146.3 ±0.7			
$ClCH_2$	120	0.05	8.82±0.05	155.9±0.3	52.3±1.3	−0.115
(**1g**)	130	0.02	28.0 ±0.6			
		0.05	29.0 ±0.2			
		0.20	29.9 ±0.6			
	140	0.05	92.6 ±0.6			
	150	0.05	278 ±4			

a) Rate constants and their standard deviations were calculated by the method of least squares. b) See Ref. 2. c) See Ref. 1e.

Table 2. Decomposition Products of *t*-Alkyl *t*-Butyl Peroxides (**1**) in Cumene at 130 °C

Substituent, R in **1**	Decomposition products[a]/mol mol^{-1}				Ratio[b]
	$[(CH_3)_3COH]$	$[CH_3COCH_3]$	$[RC(CH_3)_2OH]$	$[(PhC(CH_3)_2)_2]$	
CH_3	1.57	0.39	—	0.99	0.25
CH_3CH_2	0.78	0.95	0.13	0.91	5.77
$CH_3CH_2CH_2$	0.83	0.86	0.29	0.96	2.28
$(CH_3)_3CCH_2$	0.77	1.02	0.12	0.94	6.83
$(CH_3)_2CH$	0.84	1.16	Not detected	0.89	Infinite
$PhCH_2$	0.73	1.11	Not detected	0.53[c]	Infinite

a) The amount of decomposition products formed per the decomposed peroxide, **1**. b) The ratio of yield of acetone against that of the corresponding alcohol formed from a *t*-alkoxyl moiety. c) In addition to this compound, toluene (0.45), 1,2-diphenylethane (0.05), and 1,2-diphenyl-2-methylpropane (0.23) were detected by GC.

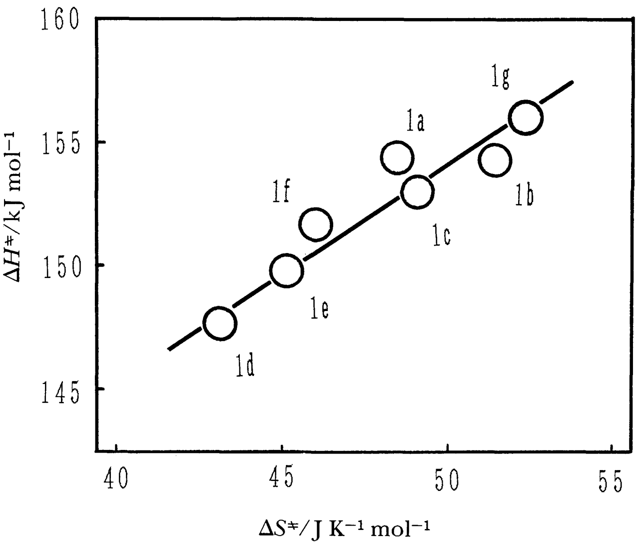


Fig. 1. An isokinetic relationship in the decomposition of *t*-alkyl *t*-butyl peroxides in cumene.

Table 3. Results of Taft Equation in Decomposition of *t*-Alkyl *t*-Butyl Peroxides[a)]

Temp	ρ^* Value	Intercept	Correlation coefficient
110	−12.57	−13.16	0.9434
120	−12.28	−12.44	0.9441
130	−11.74	−11.60	0.9474
140	−11.16	−10.74	0.9453
150[b)]	−10.99	−6.61	0.9501

a) The data were calculated by the method of least squares. b) The values were estimated by extrapolation using Arrhenius equation.

the known method.[2)] With the exception of $\mathbf{1}_\mathrm{f}$ and $\mathbf{1}_\mathrm{g}$, the data in Table 1 satisfy the Taft equation as follows:

$$\log k_\mathrm{d} = \rho^* \sum \sigma^* + c \qquad (3)$$

Here, k_d is the rate constant for the decomposition of **1**, $\sum\sigma^*$ is the sum of the substituent constants by Taft, ρ^* is a reaction constant and c is an intercept, respectively. The calculated ρ^* values are shown in Table 3, together with the intercepts and correlation coefficients.

The yields of acetone and alcohols formed from **1**, and 2,3-dimethyl-2, 3-diphenylbutane (**2**) from cumene are given in Table 2, respectively. The alcohols corresponding to the *t*-alkoxyl moieties were not detected for $\mathbf{1}_\mathrm{e}$ and $\mathbf{1}_\mathrm{f}$. The yields of **2** were over ca. 90 %, with the exception of $\mathbf{1}_\mathrm{f}$. The decomposition of $\mathbf{1}_\mathrm{f}$ gave, in addition to **2** (53%), 2-methyl-2-propanol (73%), acetone (111%), toluene (45%), 1,2-diphenylethane (5%), and 1,2-diphenyl-2-methylpropane (23%). The products from the benzyl segment of $\mathbf{1}_\mathrm{f}$ were detected in 78% yield. All of these products were formed by radical reactions. These facts suggest that **1** decomposes homolytically to follow a radical reaction outside of the solvent cage. The yield of the β-scission product, acetone from the *t*-butoxyl moiety for each peroxide of $\mathbf{1}_\mathrm{b}$—$\mathbf{1}_\mathrm{f}$, is equal to half that for $\mathbf{1}_\mathrm{a}$. The acetone is obtained indpendently from the *t*-alkoxyl ($RC(CH_3)_2$-O) and *t*-butoxyl ($C(CH_3)_3$-O) moieties in each peroxide, respectively. Accoordingly, the yield of the acetone from a *t*-alkoxyl moiety can be estimated by subtracting 0.39/2 (cf. $\mathbf{1}_\mathrm{a}$) from the total acetone obtained by the decomposition of each peroxide. The ratio of the yield of the acetone against that of the corresponding alcohol formed from the *t*-alkoxyl moiety is shown in Table 2.[2)]

Discussion

The effects of electron-withdrawing polar substituents on the decomposition were reported to be small. For example, Richardson et al. found the following Taft equation:

$$\log k_\mathrm{d} = -0.131 \sum \sigma^* - 3.422 \qquad (4)$$

This equation is for the decomposition of the di-*t*-alkyl peroxides with polar substituents in chlorobenzene at 150 °C.[2)] Similarly, kinetic data regarding the decomposition of bis(trifluoromethyl) peroxide in the gas phase were within the experiment error of those measured for $\mathbf{1}_\mathrm{a}$, and the expected inductive effect of the electronegatively substituted fluorine atoms ($\sum\sigma^* > +2.65$) was not found.[3)]

However, the electron-donating alkyl substituents considerably accelerated the decomposition of **1** in this work. Table 4 shows the relative rates ($k_\mathrm{d}/k_\mathrm{d0}$) of **1** against $\mathbf{1}_\mathrm{a}$ at 150 °C, together with the data of Richardson et al. A plot of $\log(k_\mathrm{d}/k_\mathrm{d0})$ vs. $\sum\sigma^*$ consists of two straight lines intersecting each other at the point of $\mathbf{1}_\mathrm{a}$ (Fig. 2). One is for the electron-donating alkyl substituents with a large slop of $\rho^* = -10.99$; the other is for the electron-withdrawing polar substituents with a small slope of $\rho^* = -0.131$. The considerable rate acceleration by the electron-donating alkyl substituents suggests that the polar character of an activation complex seems to stabilize the transition state much more. Huyser and Van Scoy investigated the effects of solvents on the unimolecular decomposition of $\mathbf{1}_\mathrm{a}$, and indicated the dipolar character in the C–O bond of the *t*-butoxyl moiety at the transition state.[4)] Similarly, the polar character of the *t*-alkoxyl moiety at the transition state was pointed out in the decomposition of *t*-alkyl 2,2-dimethylperoxypropionates,[5)] which showed a similar substituent effect as that of **1**, though not sufficiently correlated with $\sum\sigma^*$ (correlation coefficient of 0.3890 in Table 4).

The O–O bond may be polarized when stretched at the transition state of the decomposition. That is to say, the activation complexes of **3** and **4** are stabilized by the electron-donating alkyl and electron-with-

Table 4. Influence of Substituents on Rates in Decomposition of Di-*t*-Alkyl Peroxides and Peroxy Esters in Cumene[a]

Substituent, R	Relative rate	
	$RC(CH_3)_2OOC(CH_3)_3$ at 150 °C[b]	$C(CH_3)_3CO_3C(CH_3)_2R$ at 60 °C[c]
CH_3	1.00	1.00
CH_3CH_2	1.52	1.19
$CH_3CH_2CH_2$	1.69	1.14
$(CH_3)_3CCH_2$	3.59	2.10
$(CH_3)_2CH$	2.46	1.74
ρ^* Value	−10.99	−6.55
Correlation coefficient	0.9051	0.3890
$PhCH_2$	1.58	2.34
$BrCH_2$[d]	(0.82)[e]	—
$ClCH_2$	1.03 (0.93)[e]	—
ρ^* Value	−0.25	—
Correlation coefficient	0.4876	—

a) The values in the table show the relative rates against $R=CH_3$ for decomposition rates of di-*t*-alkyl peroxides and peroxy esters. b) The extrapolated values to 150 °C in this work. c) See Ref. 5. d) The sum of the substituent constant is −0.133. e) The values in parentheses is the data in chlorobenzene of Ref. 2.

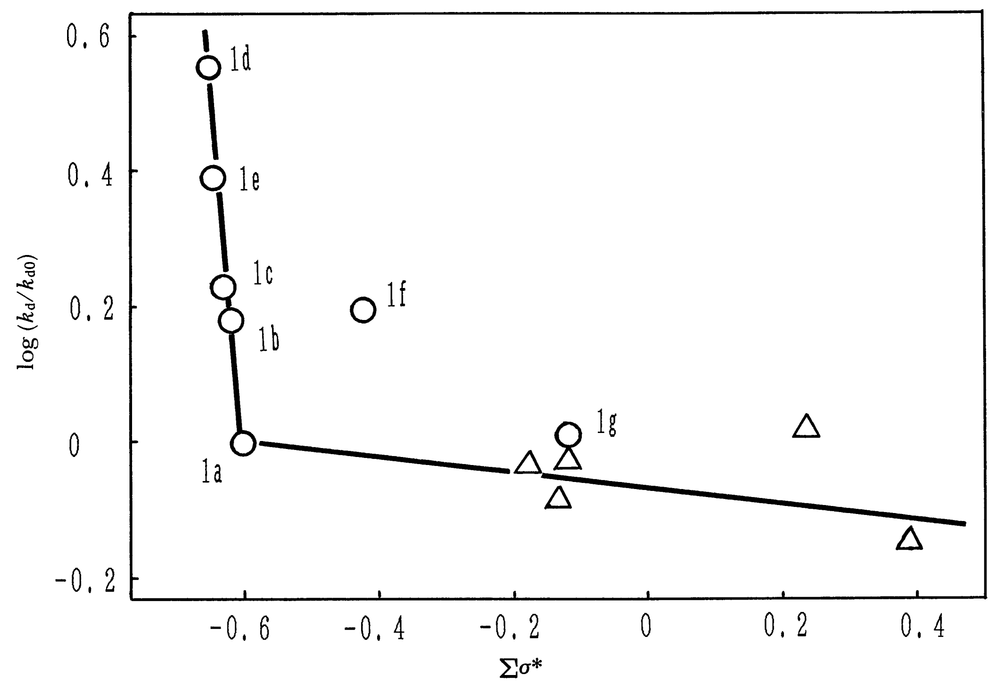
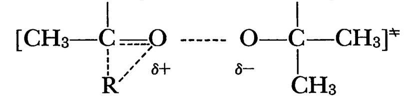
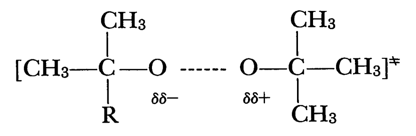


Fig. 2. A plot of log (k_d/k_{d0}) vs. $\sum\sigma^*$ in the decomposition of dialkyl peroxides at 150 °C; ○, this work; △, the data of Richardson et al.[2]


$[CH_3-\overset{CH_3}{\underset{R}{C}}\overset{\delta+}{\cdots}O \text{ ------ } \overset{\delta-}{O}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3]^{\ddagger}$

(**3**)


$[CH_3-\overset{CH_3}{\underset{R}{C}}-\overset{\delta\delta-}{O} \text{ ------ } \overset{\delta\delta+}{O}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3]^{\ddagger}$

(**4**)

drawing polar substituents, respectively. The substituent effects of **3** and **4** are expepcted to be $\rho^*<0$ and $\rho^*>0$, respectively, but the absolute value of ρ^* in the former seems to be much larger than that in the later, by considering the difficulty that the *t*-butoxyl group is hardly able to stabilize the positive charge in **4**. On the other hand, the substituent effect in the ground state is expected to be $\rho^*<0$ on account of the stabilization by electron-withdrawing polar substituent.[2,6] Consequently, the experimental results in Fig. 2 can be understood in terms of the fact that

Table 5. Influence of Substituents on β-Scission Product Formation from *t*-Alkoxyl Moieties in Decomposition of Di-*t*-alkyl Peroxides, Peroxy Esters and Hypochlorites[a)]

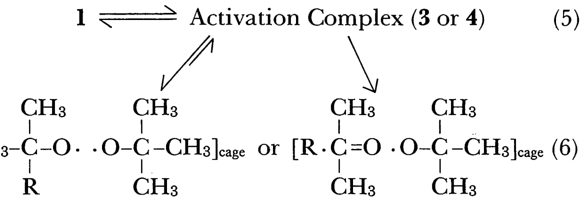
Substituent, R	Relative rate		
	$RC(CH_3)_2OOC(CH_3)_3$ at 130 °C	$C(CH_3)_3CO_3C(CH_3)_2R$ at 60 °C[b)]	RR′R″COCl at 40 °C[c)]
CH_3	0.037	0	0.01[d)]
CH_3CH_2	1.00	1.00	1.00
$CH_3CH_2CH_2$	0.33	0.52	0.78[d)]
$(CH_3)_3CCH_2$	1.01	1.74	0.44[d)]
$(CH_3)_2CH$	Infinite	3.38	27.1[e)]
$PhCH_2$	Infinite	3.19	2.72[e)]
$ClCH_2$	0.057[f)]	—	0.35[e)]

a) The values in the table show the relative rates against $R=CH_3CH_2$. b) See Ref. 5. c) The data of β-scission for *t*-alkyl hypochlorites with dirrect competition method. d) See Ref. 7b. e) See Ref. 7a. f) The data of Ref. 2 at 150 °C.

negatively large ρ^* value is due to an overlap of the substituent effects at the transition and ground states in the same direction, and that the negatively small ρ^* value is a compensation of those in the opposite direction.

The substituent effect on β-scission products from the *t*-alkoxyl moiety in the decomposition of **1** is shown in Table 5 as the relative rates of **1** against $\mathbf{1}_\mathrm{b}$ on the formation ratios of acetone against the corresponding alcohols and compared with those of *t*-alkyl 2,2-dimethylperoxypropinates[5)] and *t*-alkyl hypochlorites.[7)] The β-scission from **1** in this work was a nonchain decomposition, and reactions between radical pairs within a solvent cage were very few, as shown by high yields of **2**. The relative rate of **1** against $\mathbf{1}_\mathrm{b}$ on acetone formation decreased in the following order: $R=(CH_3)_2CH \approx PhCH_2 \gg CH_3CH_2 > CH_3CH_2CH_2 > ClCH_2 \approx CH_3$. These results seem to approximately correspond to those of the peroxy esters, through the both are a little different because acetone formation in the later was suppressed by disproportionation between the *t*-butyl and the *t*-alkoxyl radicals within a solvent cage. The difference from the hypochlorites (particularily, $R=PhCH_2$ and $(CH_3)_3CCH_2$) suggests that the acetone from **1** may be formed by β-scission within a solvent cage or directly from the activation complex at the transition state.

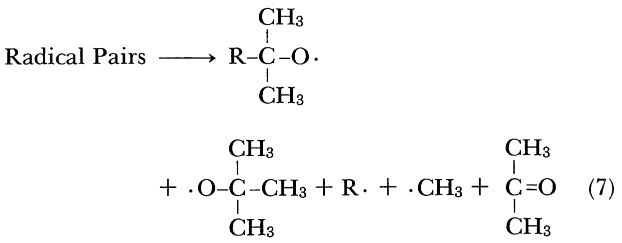
Based on these facts, it is speculated that the C_α–C_β bond neighbouring the peroxyl oxygen atom in the di-*t*-alkyl peroxides may be slightly stretched, together with the homolytic scission of the O–O bond at the transition state.[8)] Consequently, the decomposition of **1** proceeds mainly as follows:



$$\mathbf{1} \rightleftharpoons \text{Activation Complex } (\mathbf{3} \text{ or } \mathbf{4}) \qquad (5)$$

$$[CH_3-\overset{CH_3}{\underset{R}{C}}-O\cdot\ \cdot O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3]_{cage} \text{ or } [R\cdot\overset{CH_3}{\underset{CH_3}{C}}=O\ \cdot O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3]_{cage} \qquad (6)$$

(Radical Pairs)

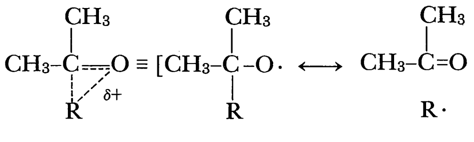


$$\text{Radical Pairs} \longrightarrow R-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot$$

$$+\ \cdot O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + R\cdot + \cdot CH_3 + \overset{CH_3}{\underset{CH_3}{C}}=O \qquad (7)$$

The β-scission of *t*-alkoxyl radicals out of a solvent cage competes with hydrogen abstraction from cumene. The various radicals produced in these ways easily abstract the hydrogen of cumene to form the 1-methyl-1-phenylethyl radical which couples mainly with each other to give **2**.

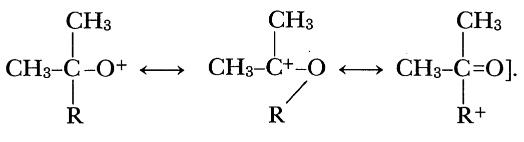
A positively charged partner, **5**, of the activation complex, **3**, may be written as a resonance hybrid of the following limiting formulas:



$$CH_3-\overset{CH_3}{\underset{R}{C}}\overset{\delta+}{=\!=}O \equiv [CH_3-\overset{CH_3}{\underset{R}{C}}-O\cdot \longleftrightarrow CH_3-\overset{CH_3}{C}=O\quad R\cdot$$

(**5**) (**5**$_\mathrm{a}$) (**5**$_\mathrm{b}$)

and

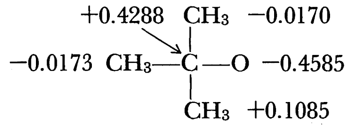


$$CH_3-\overset{CH_3}{\underset{R}{C}}-O^+ \longleftrightarrow CH_3-\overset{CH_3}{\underset{R}{C^+}}-O \longleftrightarrow CH_3-\overset{CH_3}{\underset{R^+}{C}}=O].$$

(**5**$_\mathrm{c}$) (**5**$_\mathrm{d}$) (**5**$_\mathrm{e}$)

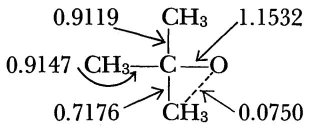
It can well explain the substituent effects on the decomposition rates and products of **1**. These structures are supported by data regarding the *t*-butoxyl radical optimalized energetically by the MINDO/3-RHF method using the MOPAC program to give both atomic charges and bond orders as follows:

Atomic charge:



and

Bond order:



The deviation from the Taft equation and the formation of an additional β-scission product for $\mathbf{1}_f$ may be understood in terms of stabilization by a resonance effect of the $PhCH_2$ radical ($\mathbf{5}_b$).

Experimental

IR, NMR and UV spectra were recorded on JASCO A-3, JEOL JNM-MH-100 and Shimadzu UV-200S spectrometers, respectively. GC-MS spectra were recorded on a JEOL JMS-D 300 mass spectrometer. GC analysis was carried out using Shimadzu GC-2D gas chromatography with columns: SE-30 (5%) and PEG-20M (25%) on Shimalite W (QW-DMCS). A LC analysis was carried out using a JASCO TRIROTAR-V with a column: JASCO Finepak SIL C_{18} and an eluent ($MeOH$:H_2O=9:1). A TLC analysis was carried out using columns with a Merck Kieselgel 60 F_{254} and a Kieselgel 60. The products were purified by flash chromatography on a Merck Kieselgel (40 and 60). The purities of the dialkyl peroxides were determined by GC.

Materials. *t*-Butyl, 1,1-dimethylbutyl, and 1,1,3,3-tetramethylbutyl hydroperoxides were the products of Nippon Oil & Fats Co., Ltd. 2-Methyl-2-butanol, 2-methyl-1-pentene, 2-methyl-2-pentanol, 2-methyl-1-phenyl-2-propanol, and 2-methyl-2-propanol were the products of Wako Pure Chemical Ind., Co. Cumene was stirred for several hours with concentrated sulfuric acid, washed with 10% NaOH aqueous solution and distilled H_2O, dried with drying agents and distilled through a 24-in Vigreaux column.

Preparation of Di-*t*-Alkyl Peroxides. Di-*t*-butyl peroxide ($\mathbf{1}_a$) was purified to 99.2% by distillation (62—63 °C/58 mmHg, 1 mmHg=133.322 Pa) of a commercial product of Nippon Oil & Fats Co., Ltd.

***t*-Butyl *t*-Pentyl Peroxide ($\mathbf{1}_b$).** To an aquous solution of 80% H_2SO_4 (59.0 g, 0.48 mol) there was added dropwise 2-methyl-2-butanol (35.5 g, 0.40 mol) below 10 °C. Then, the solution was kept at 0 °C for 15 min, added dropwise for 5 min by 70% *t*-butyl hydroperoxide (53.0 g, 0.41 mol), and stirred for 2 h at 20 °C to complete the reaction. The oil layer was separated from the reaction mixture, washed with 10% NaOH and H_2O, dried with anhydrous $MgSO_4$ and distilled at reduced pressure (62—63 °C/58 mmHg) to give $\mathbf{1}_b$ of 53.7 g (purity 95.5%, yield 80.0%). IR $\nu_{O\text{-}O}$ 880 cm^{-1}; ^{1}H NMR δ=0.99 [3H, t, $-CH_2CH_3$], 1.44 [6H, s, $-OO-C(CH_3)_2-CH_2-$], 1.21 [9H, s, $-OO-C(CH_3)_2$], and 1.53 [2H, q, $-CH_2-CH_3$]; MS (m/z) 160 [M$^+$].

***t*-Butyl 1,1-Dimethylbutyl Peroxide ($\mathbf{1}_c$).** To an aquous solution of 65% H_2SO_4 (90.6 g, 0.60 mol) there was added dropwise 2-methyl-1-penten (42.1 g, 0.50 mol) below 10 °C. Then, the solution was kept for 10 min at 0 °C, added dropwise for 5 min by 70% *t*-butyl hydroperoxide (64.4 g, 0.50 mol), and stirred for 2 hr at 20 °C to complete the reaction. The oil layer was separated from the reaction mixture, washed with 10% NaOH and H_2O, dried with anhydrous $MgSO_4$ and distilled at reduced pressure (75—76 °C/57 mmHg) to give $\mathbf{1}_c$ of 69.5 g (purity 96.9%, yield 77.3%). IR $\nu_{O\text{-}O}$ 880 cm^{-1}; ^{1}H NMR δ=0.98 [3H, t, $-CH_2-CH_3$], 1.16 [6H, s, $-OO-C(CH_3)_2-CH_2-$], 1.20 [9H, m, $-OO-C(CH_3)_3$], and 1.3—1.5 [4H, m, $-(CH_2)_2-CH_3$]; MS(m/z) 174 [M$^+$].

***t*-Butyl 1,1,3,3-Tetramethylbutyl Peroxide ($\mathbf{1}_d$).** To an aqueous solution of 80% H_2SO_4 (14.8 g, 0.12 mol) there was added dropwise 2-methyl-2-propanol (22.2 g, 0.30 mol) below 10 °C. Then, the solution was kept at 0 °C for 20 min, added dropwise for 10 min by 1,1,3,3-tetramethylbutyl hydroperoxide (15.0 g, 0.10 mol), stirred for 2 h at 25 °C to complete the reaction. The oil layer was separated from the reaction mixture, added with hexane and H_2O, washed with 10% NaOH and H_2O, dried with anhydrous $MgSO_4$, and distilled at reduced pressure (57—58 °C/6 mmHg) to give $\mathbf{1}_d$ of 17.8 g (purity 95.7%, yield 60.5%). IR $\nu_{O\text{-}O}$ 880 cm^{-1}; ^{1}H NMR δ=1.02 [9H, s, $-CH_2-C(CH_3)_3$], 1.22 [6H, s, $-OO-C(CH_3)_3$], 1.28 [6H, s, $-OO-C(CH_3)_2-CH_2-$] and 1.54 [2H, s, $-CH_2-$]; MS (m/z) 202 [M$^+$].

***t*-Butyl 1,1,2-Trimethylpropyl Peroxide ($\mathbf{1}_e$).** To an aqueous solution of 80% H_2SO_4 (33.7 g, 0.275 mol) there was added dropwise 2,3-dimethyl-2-butanol (25.5 g, 0.25 mol) below 10 °C. Then, the solution was kept at 0 °C for 10 min, added dropwise for 15 min by 70% *t*-butyl hydroperoxide (36.3 g, 0.25 mol), and stirred for 2 h at 20 °C to complete the reaction. The oil layer was separated from the reaction mixture, washed with 10% NaOH and H_2O, dried with anhydrous $MgSO_4$ and distilled at reduced pressure (73—75 °C/47 mmHg) to give $\mathbf{1}_e$ of 10.6 g (purity 95.6%, yield 23.2%). IR $\nu_{O\text{-}O}$ 865 cm^{-1}; ^{1}H NMR δ=0.89 ppm [6H, d, $-CH(CH_3)_3$], 1.12 [6H, s, $-OO-C(CH_3)_2-$], 1.21 [9H, s, $-OO-C(CH_3)_3$], and 1.91 [1H, m, $-CH(CH_3)_2$]; MS (m/z) 174 [M$^+$].

***t*-Butyl 1,1-Dimethyl-2-phenylethyl Peroxide ($\mathbf{1}_f$).** To an aqueous solution of 80% H_2SO_4 (4.54 g, 37 mmol) there was added dropwise 2-methyl-2-propanol (7.41 g, 100 mmol) below 10 °C. Then, the solution was kept at 0 °C for 20 min, added dropwise for 5 min by a solution of diethyl ether (3 cm^3) and 1,1-dimethyl-2-phenylethyl hydroperoxide (4.73 g, 28.5 mmol) which was prepared by reaction of the corresponding alcohol with 50% H_2O_2 in the presence of 72% H_2SO_4 at 40 °C in THF,[5] and stirred for 2 h at 20 °C to complete the reaction. The oil layer was separated from the reaction mixture, washed with 10% NaOH and H_2O, and dried with anhydrous $MgSO_4$. The crude product (5.2 g) after evaporation of solvent was purified by flash chromatography to give $\mathbf{1}_f$ of 3.68 g (purity 99.5%, yield 57.8%). IR $\nu_{O\text{-}O}$ 880 cm^{-1}; ^{1}H NMR δ=1.15 [6H, s, $-C(CH_3)_2-CH_2-$], 1.22 [9H, s, $-OO-C(CH_3)_3$], 1.28 [6H, s, $-CH_2-Ph$] and 1.54 [2H, s, $-Ph$]; MS (m/z) 222 [M$^+$].

***t*-Butyl 2-Chloro-1,1-dimethylethyl Peroxide ($\mathbf{1}_g$)** was prepared by the method of Richardson et al.[2] and purified to

95.2% by distillation (54—55 °C/20 mmHg) of the crude reaction product.

Kinetic Procedure. A dilute solution of dialkyl peroxide in cumene was placed in sealed tubes (content of 7.5 cm^3) under vacuum and heated in a constant-temperature bath (±0.2 °C). The remaining amount of dialkyl peroxide was determined by GC with a column of SE-30 (5%) using unternal standards. The reaction was followed up to 70—80% decomposition and exhibited first-order kinetics.

Decomposition Products. Di-*t*-alkyl peroxide at the concentration of 0.05 $\mathrm{mol\ dm^{-3}}$ in cumene was decomposed completely at 130 °C and the solution was analyzed by GC using internal standards. The yields of acetone and 2-methyl-2-propanol were determined with columns of PEG-20M (25%), and the others, SE-30 (5%).

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