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Substituent Effects of Alkyl Groups on the Decomposition of *tert*-Alkyl Peroxides

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In order to clarify substituent effects of alkyl groups on the decomposition of various *tert*-alkyl peroxides ($RCMe_2OOR'$), the decomposition of 1-methoxy-1-(*tert*-alkylperoxy)cyclohexanes **3** and 1,1-bis(*tert*-alkylperoxy)cyclohexanes **4** has been studied by use of methods of kinetics and product analysis in cumene with the range of temperatures from 80−110 °C and compared with those of the corresponding peroxyesters (**1**; R′ = CO-*t*-Bu) and dialkyl peroxides (**2**; R′ = *t*-Bu). The decomposition rates for each peroxide series decrease in the following order: **1** ≫ **3** > **4** ≫ **2**. The decomposition rate for the series of peroxides **1** decreases in the following order: R = *t*-BuCH$_2$ ≫ *i*-Pr ≫ Et > Pr > Me. But, for the series of peroxides **2**, **3**, and **4**, R = *t*-BuCH$_2$ ≫ *i*-Pr ≫ Pr > Et ≫ Me. The decomposition rate is expressed by a modified Taft equation: $\log k_d = \varrho^*\Sigma\sigma_{CH_2R}^* + nh + C$, which contains both inductive and C−H hyperconjugation effects of alkyl groups. On the basis of the isokinetic relationship of the activation parameters, the Taft equation, and the decomposition products, the decomposion mechanism via an polar activation complex having a slightly stretched $C_\alpha - C_\beta$ bond neighboring to the peroxy oxygen atom is suggested and the abnormal behavior of neopentyl group is discussed.

Recently, a large number of investigators have been interested in substituent effects on the scission of C−C and O−O bonds as a primitive problem in chemistry and have studied unimolecular decompositions of various hydrocarbons and organic peroxides. Rüchardt and Beckhaus[1] studied the factors influencing homolytic dissociation energies of the C−C bond in the highly branched aliphatic hydrocarbons and indicated that free energies of activation were correlated with strain enthalpies at the ground states. The investigations concerning substituent effects on the homolytic scission of the O−O bond were mainly restricted to the change of the acyl moieties in the peroxides and usually gave negative values of Hammett ϱ and Taft ϱ^*,[2] except for the decompositions of *ortho*-substituted *tert*-butyl peroxybenzoates[3] and highly branched aliphatic *tert*-butyl peroxyesters,[4] which were accelerated significantly by sterically crowding alkyl groups and gave positively larger activation entropies.

We are interested in the substituent effects on the decomposition of *tert*-alkylperoxy moieties, which, until now, were studied mainly on the basis of heterolytic scission of the O−O bond and indicated that the C−H hyperconjugation of alkyl groups was relatively important even in the homolytic scission.[5] Concerning the homolytic scission, Richardson and co-workers[6] first correlated the decomposition rate constants of di-*tert*-alkyl peroxides with the sum of electron-withdrawing substituent constants, $\Sigma\sigma_{CH_2R}^*$, by using the Taft equation, $\log k_d = \varrho^*\Sigma\sigma_{CH_2R}^* + C$, where there was a very small change in the rate ($\varrho^* = -0.131$). On the other hand, the effects of electron-donating alkyl groups on the decomposition of *tert*-alkyl 2,2-dimethylperoxypropionates, $RCMe_2OOCO$-*t*-Bu (R = Me (**1a**), Et (**1b**), Pr (**1c**), and *i*-Pr (**1e**)) were correlated approximately with the inductive (σ_R^*) and C−H hyperconjugation parameters (Δn, the difference between the related peroxyester and peroxide **1a** for the number of the hydrogen atoms participating in the C−H hyperconjugation) and expressed by another modified Taft equation:[7a] $\log (k_d/k_{d0}) = \varrho^*\sigma_R^* + h(\Delta n)$, which gave the values of ϱ^* and h of 0.67 and 0.058 as reaction constants, respectively. However, this equation did not satisfy the rate data of the peroxyester of R = *t*-BuCH$_2$ without a hydrogen atom participating in the C−H hyperconjugation. The effects of electron-donating alkyl groups on the decomposition of *tert*-alkyl *tert*-butyl peroxides, $RCMe_2OO$-*t*-Bu (R = Me (**2a**), Et (**2b**), Pr (**2c**), *t*-BuCH$_2$ (**2d**), and *i*-Pr (**2e**)) were expressed by the Taft equation of Richardson, which gave the negatively larger ϱ^* values of −11.16 to −12.57.[8a]

There are some questionable aspects about the substituent effects on the decomposition of *tert*-alkyl peroxides ($RCMe_2OO$-R′) with the electron-donating alkyl groups. Firstly, the ϱ^* values were positively small for the peroxyester series but negatively large for the dialkyl peroxide series. Secondly, the neopentyl group does not contain a hydrogen atom participating in the C−H hyperconjugation but significantly accelerates the decomposition rate of the peroxyester derivatives. In this

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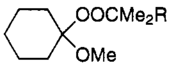
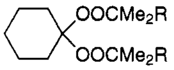
work, we have also carried out the decompositions of 1-methoxy-1-(*tert*-alkylperoxy)cyclohexanes (**3**) and 1,1-bis(*tert*-alkylperoxy)cyclohexanes (**4**), compared them



3 (**a** = Me; **b** = Et; **c** = Pr; **d** = *t*-BuCH$_2$)



4 (**a** = Me; **b** = Et; **c** = Pr; **d** = *t*-BuCH$_2$)

with those of the other *tert*-alkyl peroxides in order to clarify the substituent effects of alkyl groups on the homolytic scission of the O−O bond, and been able to obtain some important information.

Results and Discussion

Decomposition Rates and Products. Transetherification of cyclohexane dimethyl acetal with *tert*-alkyl hydroperoxides proceeded stepwise in dimethyl sulfoxide in the presence of *p*-toluenesulfonic acid (PTS). Peroxides **3a−d** were prepared with in 57−69% yield by the reaction for 3 h at 20 °C. Peroxides **4b−d** were prepared in 88−92% yield by the reaction in the presence of a large amount of PTS for 7 h at 20 °C. The yields of the latter reaction were higher than those of the former one. The reaction products were obtained 93−99% pure by distillation, recrystallization, and column chromatography. These transetherifications in the presence of PTS in dimethyl sulfoxide are a good method for the preparation of peroxides **3d** and **4d**, where the *tert*-alkyl hydroperoxide used as a raw material is susceptible to ionic decomposition in the presence of acid catalyst.[9]

Table 1. Rate Constants and Activation Parameters for Decomposition of Peroxides 3 and 4 in Cumene[a]

				activation parameter	
peroxide	temp (°C)	concn (mol/L)	rate const $10^5 \times k_d$ (s^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)
3a	80	0.05	0.479 ± 0.005	33.4 ± 0.2	11.2 ± 1.1
	90	0.05	1.898 ± 0.007		
	100	0.02	6.57 ± 0.31		
	100	0.05	6.79 ± 0.05		
	100	0.20	6.70 ± 0.05		
	110	0.05	21.39 ± 0.09		
3b	80	0.05	0.782 ± 0.003	33.1 ± 0.1	11.6 ± 0.7
	90	0.05	3.07 ± 0.07		
	100	0.05	10.58 ± 0.07		
	110	0.05	34.50 ± 0.46		
3c	80	0.05	0.834 ± 0.011	33.2 ± 0.1	11.8 ± 0.2
	90	0.05	3.17 ± 0.06		
	100	0.05	11.20 ± 0.08		
	110	0.05	36.53 ± 0.08		
3d	70	0.05	0.59 ± 0.11	32.0 ± 0.1	10.9 ± 0.3
	80	0.05	2.30 ± 0.03		
	90	0.05	8.18 ± 0.03		
	100	0.05	28.40 ± 0.36		
	110[c]		90.51		
4a[b]	110	0.050	16.2 ± 0.1	33.8 ± 0.1	12.0 ± 0.6
4b	80	0.05	0.534 ± 0.03	33.6 ± 0.1	12.0 ± 0.3
	90	0.05	2.02 ± 0.01		
	100	0.05	7.32 ± 0.07		
	110	0.05	24.4 ± 0.1		
4c	80	0.05	0.538 ± 0.002	33.6	12.2 ± 0.2
	90	0.05	2.06 ± 0.01		
	100	0.05	7.48 ± 0.01		
	110	0.05	24.8 ± 0.1		
4d	80	0.05	1.513 ± 0.011	32.7 ± 0.1	11.7 ± 0.5
	90	0.05	5.62 ± 0.04		
	100	0.05	19.83 ± 0.11		
	110	0.05	62.6 ± 0.3		

[a] Rate constants and their standard deviations were calculated by the method of least squares. [b] From the data of ref 13 and 14. [c] The rate constant was extraporated by using an Arrhenius equation.

Table 2. Decomposition Products of 1-Methoxy-1-(*tert*-alkylperoxy)cyclohexanes (Peroxides 3) and 1,1-Bis(*tert*-Alkylperoxy)cyclohexanes (Peroxides 4) in Cumene at 110 °C

		dec products[a] (mol mol^{-1})				
peroxide	dec time (min)	acetone	alcohol[b]	ester[c]	alkoxy ester[d]	[PhCMe$_2$]$_2$[e]
3a	345	0.10	0.47	0.59	0.19	0.50
3b	240	0.71	0.14	0.64	0.10	0.49
3c	280	0.60	0.31	0.65	0.20	0.53
3d	75	0.79	0.01	0.62	0.18	0.50
4a[f]	300	0.04	1.35			0.83
4b	300	0.73	0.26			0.63
4c	300	0.83	0.65			0.75
4d	140	0.41	0.24			0.82

[a] The amount of decomposition products formed per the decomposed peroxide. [b] The corresponding *tert*-alkanol. [c] Methyl hexanoate. [d] Methyl (*tert*-alkoxy)hexanoate. [e] 2,3-Dimethyl-2,3-diphenylbutane. [f] From the data of ref 13.

Decomposition rate constants and products in cumene were determined by means of GC for peroxides **3** and **4** and are given in Tables 1 and 2 together with the calculated activation parameters and also by means of iodometric titration and GC for peroxides **1**[7] and **2**,[8] presented in Table 3. Good first-order rate constants were obtained in 10−80% conversion. The rate constants for peroxides **3** and **4** seem to rule out any induced decomposition, because there was no appreciable change when the concentration was 10-fold.[10,11] The decomposition rates of the peroxides with the same alkyl groups in each peroxide series decreased in the following order (Tables 1 and 3): **1** ≫ **3** > **4** ≫ **2**. The decomposition rate for the series of peroxides **1** at 60 °C decreased in the following order (the value of the relative ratio for the corresponding alkyl derivatives against the Me derivative is shown in parentheses): R = *t*-BuCH$_2$ (2.09) ≫ *i*-Pr (1.74) ≫ Et (1.19) > Pr (1.14) > Me (1.00). For the series of peroxides **2−4** at 110 °C the order is as follows: R = *t*-BuCH$_2$ (3.87−4.31) ≫ *i*-Pr (2.81) ≫ Pr (1.53−1.74) > Et (1.51−1.61) ≫ Me (1.00). The former order of alkyl groups except for R = *t*-BuCH$_2$ is related to the number of hydrogen atoms participating in the C−H hyperconjugation,[5] but the latter order is roughly related to the sum of the inductive substituent constants.[6,12] Table 2 shows the decomposition products of peroxides **3** and **4** (0.05 mol/L) in cumene at the conversion of about 80%. The amounts of acetone (β-scission product) and *tert*-alkanols (hydrogen abstraction products) formed from the *tert*-alkoxy moieties in peroxides **3** were influenced significantly by the type of the alkyl groups, but those of the other products were hardly changed. A coupling product within a solvent cage, methyl ω-(*tert*-alkoxy)hexanoate, was first detected in the decomposition of

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Table 3. Rate Constants, Activation Parameters, and Decomposition Products for Decomposition of Peroxides 1 and 2 in Cumene

	rate const		activation parameter[a]		decomposition products[b] (mol mol^{-1})				
peroxide	temp (°C)	$10^5 \times k_d$ (s^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)	temp (°C)	Me_2CO	*t*-BuOH	$RCMe_2OH$	$(PhCMe_2)_2$
1a[c]	60	2.96	28.2 ± 0.2	5.5 ± 2.4	60	0	0.88	0	0.68
1b[c]	60	3.51	27.5 ± 0.3	3.3 ± 1.7	60	0.28	0	0.66	
1c[c]	60	3.37	27.8 ± 0.2	4.3 ± 1.2	60	0.17	0	0.76	
1d[c]	60	6.18	26.9 ± 0.3	2.9 ± 1.9	60	0.43	0	0.59	
1e[c]	60	5.14	27.3 ± 0.4	3.6 ± 2.2	60	0.54	0	0.38	
2a[d]	110	0.252	36.9 ± 0.2	11.6 ± 0.6	130	0.39	1.57		0.99
2b[d]	110	0.386	36.8 ± 0.2	12.3 ± 1.0	130	0.95	0.78	0.13	0.91
2c[d]	110	0.438	36.5	11.8 ± 0.2	130	0.86	0.83	0.29	0.96
2d[d]	110	1.085	35.3 ± 0.1	10.3 ± 0.4	130	1.02	0.77	0.12	0.94
2e[d]	110	0.707	35.8	10.8 ± 0.1	130	1.16	0.84	0	0.89

[a] Activation parameters and their standard deviations were calculated by the method of least squares. [b] The amount of decomposition products formed per the decomposed peroxide. [c] From the data of ref 7. [d] From the data of ref 8.

peroxides **3**. The decomposition products of peroxides **4** were complicated by further reaction of the ω-(*tert*-alkylperoxycarbonyl)pentyl radical which gave 1-(*tert*-alkylperoxycarbonyl)pentyl radical by intramolecular hydrogen atom abstraction and the formed polyester by ring-opening polymerization via an intermediate α-lactone formation by a cyclization–elimination reaction.[14] The ratios of acetone against the *tert*-alkoxy group-containing compounds (the sum of *tert*-alkanol and methyl ω-(*tert*-alkoxy)hexanoate) formed from *tert*-alkoxy moieties for peroxides **3** and **4** are compared with those of peroxides **1** and **2**[7,8] and *tert*-alkyl hypochlorites.[15] The ratios of the acetone formation for each series of peroxides **1** at 60 °C,[7] peroxides **2** at 130 °C,[8] and peroxides **3** at 100 °C were decreased in the following order (the relative rates of the corresponding alkyl derivatives against the Et ones are shown in parentheses): R = *i*-Pr (3.8 to infinity) > *t*-BuCH$_2$ (1.18–1.74) > Et (1.00) > Pr (0.40–0.69) ≫ Me (0–0.10). For peroxides **4** at 100 °C the order is as follows: R = Et (1.00) > *t*-BuCH$_2$ (0.61) > Pr (0.46) ≫ Me (0.01). For the hypochlorites[15] the order is as follows: R = *i*-Pr (27.1) ≫ Et (1.00) > Pr (0.78) > *t*-BuCH$_2$ (0.44) ≫ Me (0.01). It is surprising that the ratios of the acetone formation for the peroxide derivatives of R = *t*-BuCH$_2$ were significantly larger than that for the hypochlorite of R = *t*-BuCH$_2$. Probably, this fact suggests that the acetone from *tert*-alkyl peroxides may be formed in a significant amount by direct β-scission from an activation complex at the transition state.

Isokinetic Relationship. The decomposition rates of peroxides are determined by the difference between the free energies at the transition and ground states.[6,10,16] That is, the decomposition rates of α-oxygen atom-containing peroxides are accelerated by repulsions between lone-pair orbitals on the oxygen atoms of an O–O bond and between those of the peroxy oxygen atom and the oxygen atom next to the peroxy bond at the ground state and by stabilization of an activated complex at the transition state. An isokinetic relationship rule may be applied to the substituent effects of alkyl groups when the differences among the decomposition rates takes place with a single interaction mechanism of the substituents at the transition state. However, when the repulsion at the ground state is significantly increased, the decomposition does not give the isokinetic relationship in the peroxide series to make the activation entropy increase.[3,4,10]

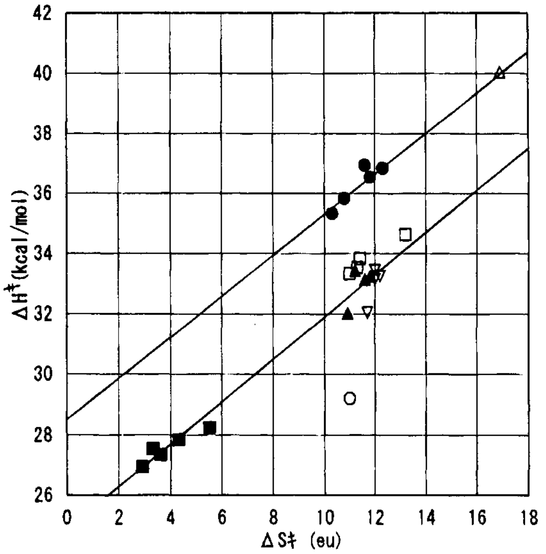

Figure 1. Isokinetic relationships in the decomposition of various organic peroxides: ■, peroxides **1**; ●, peroxides **2**; ▲, peroxides **3**; ▽, peroxides **4**; □, bis(*tert*-butylperoxy)cycloalkanes; ○, di-*tert*-butylperoxy dicarbonate; △, cyclohexanone cyclic peroxide.

The relationships between the activation enthalpies and entropies for the decompositions of peroxides **3** and **4** in cumene are shown in Figure 1 and compared with those of the other peroxides such as peroxides **1** and peroxides **2**, bis(*tert*-butylperoxy)cycloalkanes,[10] cyclohexanone cyclic diperoxide,[17] and di-*tert*-butyl peroxydicarbonate.[18] Two isokinetic relationships were obtained for the series of peroxides **1** and alicyclic ketone peroxyketals containing peroxides **3**, peroxides **4**, and bis(*tert*-butylperoxy)cycloalkanes and for the series of peroxides **2** and cyclohexanone cyclic peroxide, respectively. The data for di-*tert*-butyl peroxydicarbaonate deviated from both of the linear lines. The difference between peroxides **2** and the alicyclic ketone peroxyketals is very remarkable. The linear line for the series of peroxides **1** may be extrapolated nearly to the data for the alicyclic ketone peroxyketals. The alicyclic ketone peroxyketals and peroxides **1** have the bond structures of $-O_\alpha O_{\alpha'} C_{\beta'}(O_{\gamma'})$-

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Table 4. Reaction Constants ϱ^* and h, Intecept C, and Correlation Coefficient of the Modified Taft Equation for Various Peroxides, $RCMe_2OOR'$[a]

params for the Taft eqn	peroxides **1** (60 °C)	peroxides **3** (110 °C)	peroxides **4** (110 °C)	peroxides **2** (110 °C)
Correlation except for Peroxides R = *t*-$BuCH_2$				
ϱ^* value	−0.20	−4.70	−3.29	−5.79
h value	0.039	0.046	0.043	0.036
C	−4.67	−6.49	−5.76	−9.08
correlation coefficient	0.9782	1.0000	1.0000	0.9997
estimated *n* value of R = *t*-$BuCH_2$	8.4	9.2	10.3	10.6
Correlation Calculated by Using $n = 9$ for Peroxides of R = *t*-$BuCH_2$				
ϱ^* value	−0.50	−4.66	−3.00	−5.01
h value	0.036	0.047	0.051	0.045
C	−4.85	−6.47	−5.60	−8.61
correlation coefficient	0.9897	1.0000	0.9994	0.9982

[a] The values of the substituent constants in the modified Taft equation were as follows (substituent, R: $\Sigma\sigma_{CH_2R}^*$ and n): Me, −0.600 and 0; Et, −0.613 and 3; Pr, −0.630 and 2; *t*-$BuCH_2$, −0.644 and 0 or 9; *i*-Pr, −0.640 and 6.

$C_{\gamma'}-$ and $-O_\alpha O_{\alpha'}C_{\beta'}(=O_{\gamma'})C_{\gamma'}-$, respectively, and contain γ'-oxygen atoms next to the O−O bond. The lone-pair orbitals on the γ'-oxygen atom repel with those on the α-peroxy oxygen atom at the ground state and make the activation entropy increased.[10] The activation parameters for the decomposition of di-*tert*-butyl peroxydicarbonate were $\Delta H^{\ddagger} = 31.1$ kcal/mol and $\Delta S^{\ddagger} = 11$ eu[18] and gave the larger activation entropy compared with the activation enthalpy, probably because of the presence of four γ'-oxygen atoms next to the O−O bond in a molecule. However, a plot of the largest activation parameters ($\Delta H^{\ddagger} = 40.0$ kcal/mol and $\Delta S^{\ddagger} = 16.9$ eu)[17] for cyclohexanone cyclic diperoxide having two pairs of neighboring γ'-oxygen atoms participating in the repulsion is on the linear line for the series of peroxides **2**. Probably the rigid conformation of staggered and skew types in the ring avoid the steric interaction between the lone-pair orbitals on the oxygen atoms.[10]

Taft Equation. It was strange that the substituent effects of electron-donating alkyl groups were expressed by two different Taft equations for the decompositions of peroxides **1** and **2**, respectively. Therefore, we again examined the correlation of the decomposition rates with the alkyl substituent parameters for various *tert*-alkyl peroxides such as peroxides **1**−**4**, and found that two different Taft equations were concentrated to the following modified Taft equation

$$\log k_d = \varrho^*\Sigma\sigma_{CH_2R}^* + hn + C \qquad (1)$$

where k_d is the rate constant for the decomposition of the related peroxide, $\Sigma\sigma_{CH_2R}^*$ the sum of the substituent constant by Taft,[6,12] ϱ^* the reaction constant, n the number of hydrogen atoms participating in the C−H hyperconjugation, h the emperical constant, and C the intercept, respectively. Kreevoy and Taft[19] previously proposed an equation similar to eq (1) as providing an approximately quantitative evaluation of the C−H hyperconjugation effect on the rate in an aliphatic reaction series and showed that reactivity was correlated in an approximately quantitative manner based on the assumption that the inductive and hyperconjugation effects of substituent on the rate were independent and separable variables. The values of ϱ^*, h, and C for the decomposition of peroxides **1**−**4** except for the peroxides of R = *t*-$BuCH_2$ were estimated by the method of multiple regression analysis and showed good multiple correlation coefficients as depicted in Table 4. With the use of these parameters, the values of 8.40−10.58 were calculated tentatively as the number of the hydrogen atoms participating in the C−H hyperconjugation-like interaction for the peroxy derivatives of R = *t*-$BuCH_2$ and approximately equal to total number of the hydrogen atoms on γ-carbon atoms, **9**. With the use of a tentative value of **9** as the number of the hydrogen atoms participating in long range interaction corresponding to the C−H hyperconjugation, the values of the reaction parameters were obtained with better multiple correlation coefficients (Table 4). The h values indicate that the stabilization effect by the C−H hyperconjugation of one hydrogen atom was unchanged in each series of the *tert*-alkyl peroxides despite the change of the peroxide series. The ϱ^* values were correlated mainly with the magnitude for the positive charge of *tert*-alkoxy moiety formed partially at the transition state and influenced by the character of the partner moiety in the peroxide. The smallest ϱ^* value for peroxides **1** may be considered because the magnitude for the positive charge of the *tert*-alkoxy moiety becomes the smallest value by the resonance

$$[RCMe_2O^{+-}OCOCMe_3 \leftrightarrow RCMe_2O^{-}CO_2{}^{+}CMe_3] \qquad (2)$$

which partially forms a structure of the decarboxydation at the transition state.[7] Similarly, the contribution of $RCMe_2O^{-+}OR'$ to the transition peroxides **3** or **4** may be increased by the formation of ester or peroxyester bonds at the transition state, respectively.[10]

In order to examine the possible use of other parameters, these rate data were applied to another Taft equation,[12] $\log k_d = \varrho^*\Sigma\sigma_{CH_2R}^* + \delta\Sigma E_s{}^c + C$, which contained both inductive and steric[20] parameters of a type similar to eq 1. The calculated results gave a poorer correlation compared with those of eq 1, particularly in the series of peroxides **1**, and unreasonable reaction constants.[21]

Decomposition Mechanism. It is well known that polar solvent effects accelerate the homolytic O−O bond scission of organic peroxides and may be explained by

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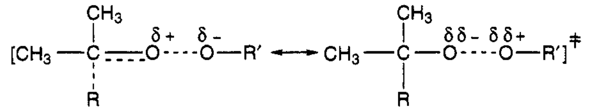
(19) Kreevoy, M. M.; Taft, R. W., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 5590.

(20) Instead of the Taft steric constants E_s, we used the Hancock corrected steric constants, E_{s^c}, which were separated from the hyperconjugation effect from the "true steric effect" and calculated by the equation $E_{s^c}\ (CR^1R^2R^3) = -2.104 + 3.429E_{s^c}(1) + 1.978D_{s^c}(2) + 0.649E_{s^c}(3)$ in the reference; see: Fugita, T.; Takayama, C.; Nakajima, M. *J. Org. Chem.* **1973**, *38*, 1623. *tert*-Alkyl substituent, calculated E_{s^c} value: CMe_3, −2.10; CMe_2Et, −2.35; CMe_2Pr, −2.54; CMe_2CH_2-*t*-Bu, −3.43; CMe_2-*i*-Pr, −2.80.

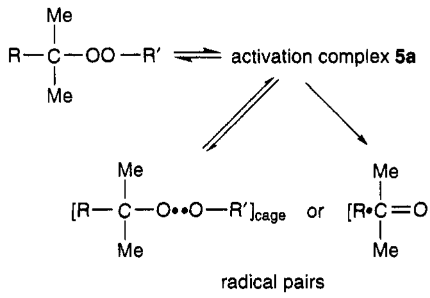
the dipolar character of the C−O bond at the transition state based on the difference of electronegativity between carbon and oxygen atoms. Huyser and Van Scoy[22] indicated the isokinetic relationship concerning the decomposition of peroxide **2a** in various solvents, and Engstrom and DuBose[23] reported the correlation of the rate constants with the parameters of solvent polarities and polar substituents in the decomposition of *para*-substituted *tert*-butylperoxy α-phenylisobutyrates. Accordingly, the O−O bond may be polarized when stretched at the transition state in the decomposition of unsymmetric *tert*-alkyl peroxides. An activation complex may be written as a resonance hybrid of the following formulas



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

5a **5b**

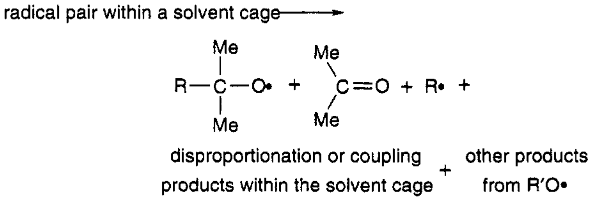
which are stabilized by the electron-donating alkyl and electron-withdrawing polar substituents of the R group, respectively. The substituent effects by electron-donating alkyl groups of formulas **5a** and **5b** are expected to be $\varrho^* < 0$ and $\varrho^* > 0$, respectively, but the absolute value of ϱ^* for the former seems to be much larger than that for the latter, by considering the fact that the R′O moieties such as *tert*-butoxy, 1-methoxycyclohexoxy, 1-(*tert*-alkylperoxy)cyclohexoxy, and 2,2-dimethylpropionoyloxy groups are not very able to stabilize the positive charge of **5b**. On the basis of the decomposition data for each series of the *tert*-alkyl peroxides, it may be suggested that the decomposition reaction proceeds via the polar activation complex, of which the $C_\alpha-C_\beta$ bond neighboring to the peroxy oxygen atom may be slightly stretched, as follows:



$$R-\overset{Me}{\underset{Me}{C}}-OO-R' \rightleftharpoons \text{activation complex } \mathbf{5a} \qquad (3)$$

$$[R-\overset{Me}{\underset{Me}{C}}-O\bullet\bullet O-R']_{cage} \text{ or } [R\bullet\overset{Me}{\underset{Me}{C}}=O\bullet O-R']_{cage} \qquad (4)$$

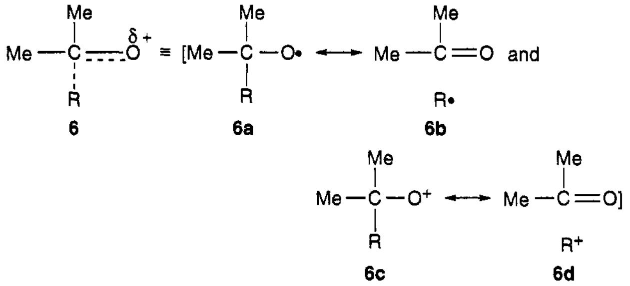
Here, OR′ is *tert*-butoxy, 1-methoxycyclohexoxy, 1-(*tert*-alkylperoxy)cyclohexoxy, and (2,2-dimethylpropionyl)oxy. Various decomposition products may be formed from the radical pair within a solvent cage as follows:



$$\text{radical pair within a solvent cage} \longrightarrow R-\overset{Me}{\underset{Me}{C}}-O\bullet + \underset{Me}{\overset{Me}{\diagdown}}C=O + R\bullet + \text{disproportionation or coupling products within the solvent cage} + \text{other products from R'O}\bullet \qquad (5)$$

Here, the disproportionation or coupling products within the solvent cage were isobutylene and 2-methyl-2-propanol from peroxide **1a**[7a,24] and methyl ω-*tert*-alkoxyhexanoate from peroxides **3** in this work, respectively. On the other hand, these products were not formed from peroxides **2**[8a] and not detected from peroxides **4** in this work. The β-scission of the *tert*-alkoxy radical out of the solvent cage competes with the hydrogen abstraction from cumene. The various radicals produced in such ways abstract easily the α-hydrogen atom of cumene to form the 1-methyl-1-phenylethyl radical which couples mainly in each other to give 2,3-dimethyl-2,3-diphenylbutane.

A positively charged partner (**6**) of activation complex **5a** may be written as a resonance hybrid of the following formulas



$$Me-\overset{Me}{\underset{R}{C}}\overset{\delta+}{\cdots}O \equiv [Me-\overset{Me}{\underset{R}{C}}-O\bullet \longleftrightarrow Me-\overset{Me}{C}=O \;\; R\bullet \text{ and } Me-\overset{Me}{\underset{R}{C}}-O^+ \longleftrightarrow Me-\overset{Me}{C}=O] \;\; R^+$$

6 **6a** **6b** **6c** **6d**

where formulas **6c** and **6d** correspond to those of the transition state for the migration to electron-deficient oxygen (the heterolytic scission of the O−O bond).[5a] These formulas can easily explain the substituent effects on the decomposition rates and products of the *tert*-alkyl peroxides. The contribution of formula **6c** to the activation complex gives the negative ϱ^* value in the Taft equation, and the contribution of formula **6d** can explain the C−H hyperconjugation effect by an R group such as Me, Et, Pr, and *i*-Pr. Similarly, the contribution of formulas **6b** and **6d** can accelerate the β-scission of the *tert*-alkoxy moiety.

Abnormal Behavior of the Neopentyl Group. 1,1,3,3-Tetramethylbutyl peroxides showed the same behavior as the peroxides, having a tentative value of **9** as the number of hydrogen atoms participating in the C−H hyperconjugation. Abnormal behavior like this was sometimes seen in the stability and the reaction rate of neopentyl-like structures. Ando and co-workers[25] reported the abnormal rate enhancement and positive carbon-14 and deuterium kinetic isotope effects on the solvolysis of neopentyl nosylate and considered that these were based on a small interaction between α- and γ-carbon atoms in the neopenyl cation. *gem*-Dimethyl-substituted cyclopropane was more stable than *gem*-dimethyl-substituted propane because the outside bond angle was broadened out when bond angles became shrunken in small ring compound.[26] Accordingly, there is one possibility that the neopentyl cation may be stabilized by the resonance of the following formulas:

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[21] The calculated values of ϱ^* and δ were 0.38 to −1.92 and −0.21 to −0.43, with poorer multiple correlation coefficients of 0.951 to 0.990, respectively. The ϱ^* value for the series of peroxides **4** gave a positive value being different from those for the other peroxides. The order of the calculated rates from the Taft equation with the use of the Hancock corrected steric constants for peroxides **1b** and **1c** was reversed against that of the observed ones.

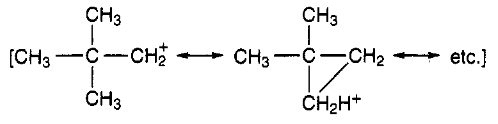
[22] Huyser, E. S.; Van Scoy, R. M. *J. Org. Chem.* **1968**, *33*, 3524.

[23] Engstrom, J. P.; DuBose, J. C. *J. Org. Chem.* **1973**, *38*, 3817.

[24] Lorand, J. P.; Chodroff, S. D.; Wallance, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 526.

[25] Ando, T.; Yamataka, H.; Morisaki, H.; Yamawaki, J.; Kuramochi, J.; Yukawa, Y. *J. Am. Chem. Soc.* **1981**, *103*, 430.

[26] (a) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill Book Co., Inc.: New York, 1962. (b) Beesley, R. M.; Ingold, C. K. *J. Chem. Soc.* **1915**, *107*, 1080. (c) Ingold, C. K. *Ibid.* **1921**, *119*, 305.



7a **7b**

On the other hand, the investigation concerning the stability of 1,3,5-trineopentylbenzene adopted a more favored conformation with its three *tert*-butyl groups on the same face of the aromatic ring and showed that a weak hydrogen-bond-like interaction, which was named the CH/π interaction, was important in understanding the conformational behaviors of organic molecule.[27] These facts suggest that the neopentyl moiety next to cationic or π-electron centers has a weak long range interaction.

The substituent effects of alkyl groups on the decomposition of *tert*-alkyl peroxide are significantly different from those of highly branched aliphatic hydrocarbons and play an important role in the transition state. This is based on the dipolar character in the C−O bond and very smaller repulsion of *tert*-alkyl/peroxy bond compared with that of *tert*-alkyl/*tert*-alkyl. Consequently, the decomposition reaction proceeds via the polar activation complex which is stabilized by the electron-donating alkyl substituents and slightly stretches the $C_\alpha-C_\beta$ bond next to the peroxy oxygen atom.

Experimental Section

IR, NMR, GC, and iodometric analyses were carried out according to the previously described methods.[10] The purities of peroxides **3** and **4** were determined by GC analysis and checked by iodometric titration.

Materials. *tert*-Alkyl hydroperoxides were prepared or purified by the previously described methods.[7] 2,3-Dimethyl-2,3-diphenylbutane was purified by recrystallization of Nofmer BC (product of NOF Corp.). Cyclohexanone dimethyl acetal, dimethyl sulfoxide, acetone, *n*-alkanes, and *p*-toluenesulfonic acid monohydrate were the reagent grade products of Wako Pure Chemical Inc., Co.

Preparation of 1-Methoxy-1-(*tert*-alkylperoxy)cyclohexanes. Peroxide **3a** was prepared as follows. To a solution of dimethyl sulfoxide (16.4 g, 0.21 mol) containing *p*-toluenesulfonic acid monohydrate (1.2 g, 0.0063 mol) was added a mixture of cyclohexanone dimethyl acetal (2.9 g, 0.20 mol) and 96% *tert*-butyl hydroperoxide (1.5 g, 0.20 mol) at 20 °C, and then the solution was stirred for 3 h to complete the reaction. The reaction solution was added with petroleum ether (20 mL), washed once with H_2O (10 mL) and 5% NaOH aqueous solution (50 mL), respectively, and twice with H_2O (20 mL), dried with anhydrous Na_2SO_4, and distilled under reduced pressure to give the crude peroxide of 26.1 g. The crude peroxide was purified by distillation in vacuum to give peroxide **3a**. Peroxides **3b−d** were prepared and purified by a method similar to that for peroxide **3a**. These peroxides were identified by ^{1}H NMR and ^{13}C NMR spectra, refractive index, and elemental analysis, and the results of the preparation are shown in Table 5.

Preparation of 1,1-Bis(*tert*-alkylperoxy)cyclohexanes. Peroxide **4b** was prepared as follows. To a solution of dimethyl sulfoxide (12.4 g, 0.16 mol) containing *p*-toluenesulfonic acid monohydrate (6.7 g, 0.035 mol) was added a mixture of cyclohexanone dimethyl acetal (21.7 g, 0.15 mol) and 95% *tert*-pentyl hydroperoxide (49.7%, 0.45 mol) at 20 °C, and the solution was stirred for 7 h under a reduced pressure of 15−20 mmHg to complete the reaction. The reaction solution was added with petroleum ether (50 mL), washed once with H_2O (50 mL) and 5% NaOH aqueous solution (50 mL), respectively, and twice with H_2O (50 mL), dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude peroxide (42.0 g). Moreover, the peroxide was recrystallized with a mixture of methanol and diethyl ether to give peroxide **4b**. Peroxides **4c** and **4d** were prepared and purified by the method similar to that for peroxide **4b**. These peroxides were identified by ^{1}H NMR and ^{13}C NMR spectra, refractive index, and elemental analysis, and the results of the preparation are shown in Table 5.

Table 5. Purities and Yields of Crude and Purified 1-Methoxy-1-(*tert*-alkylperoxy)cyclohexanes (Peroxides 3) and 1,1-Bis(*tert*-alkylperoxy)cyclohexanes (Peroxides 4)

	crude peroxide			purity[c] (%)	
peroxide	purity (%)	yield[a] (%)	purification[b]	based on GC	based on ACT
3a	88.1	57.2	dist (40−42 °C/1 mmHg)	98.7	99.6
3b	85.9	67.1	dist (43 °C/0.1 mmHg)	98.5	97.6
3c	81.0	68.6	dist (47−50 °C/0.1 mmHg)	99.3	97.0
3d	79.4	72.7	column (silica/hexane)	97.2	90.3
4b	95.9	92.8	recryst (MeOH/Et_2O)	97.4	97.3
4c	93.3	90.9	recryst (MeOH/Et_2O)	98.6	97.2
4d	91.4	88.3	column (silica/hexane)	92.7	92.0

[a] Based on cyclohexanone dimethyl ether. [b] The abbreviations used are as follows: dist, vacuum distillation (bp/pressure); column, column chromatography (support/solvent); recryst, recrystallization (mixed solvent). [c] The abbreviations used are as follows: GC, gas chromatography; ACT, active oxygen amount measured by iodometric titration.

Kinetic Procedure. Dilute solutions of peroxides **3** and **4** in cumene were placed in sealed glass tubes (10 mL) under vacuum and heated in a constant-temperature bath. Then, the concentration of the peroxides in the solution was determined by GC using 3 mm i.d. × 0.5 m columns with the following conditions (peroxide: analytical conditions). Peroxide **3a**: column of OV-1 (methylsilicone; 1%) with n-$C_{13}H_{28}$ as an internal standard. Peroxides **3b** and **3d**: column of OV-1 (1%) with n-$C_{14}H_{30}$ as an internal standard. Peroxides **3c** and **4b**: column of OV-1 (1%) with n-$C_{15}H_{32}$ as an internal standard. Peroxide **4c**: column of OV-17 (a mixture of methylsilicones; 1%) with n-$C_{18}H_{38}$ as an internal standard. Peroxide **4d**: column of OV-1 (1%) with n-$C_{18}H_{38}$ as an internal standard.

Decomposition Products. Peroxides **3** and **4** (0.05 mol/L) in cumene were decomposed at 110 °C for the desired time which could achieve a conversion of about 80%. The solution was analyzed by GC with a 0.25 mm i.d. × 50 m capillary column of Shimazu HR-1701 (methylsilicone). The relative concentrations of the decomposition products were determined by using cumene solvent as internal standard.

Methyl ω-(*tert*-butoxy)hexanoate was isolated from the decomposed solution and identified as follows: 1-methoxy-1-(*tert*-butylperoxy)cyclohexane of 1.82 g was dissolved with 138 g (0.056 g mol/L) of cumene in a flask equipped with a reflux condenser and decomposed for 6 h at 110 °C under nitrogen gas. The residual peroxide was analyzed by iodometric titration and found to be at 96% conversion. At first, volatile components were evaporated a the range of temperatures from 40 to 120 °C under vacuum, and then the distillate of 0.5 g with the highest boiling point was fractionated. Residual cumene in the distillate was carefully excluded by the bubbling of nitrogen gas to give methyl ω-(*tert*-butoxy)hexanoate (0.2 g) with a purity of 95%. IR (neat): $\nu_{C=O}$ 1738 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20 (9H, s, *t*-BuO), 1.30−1.80 (6H, m, methylene chain), 2.30 (2H, t, $-CH_2CO$), 3.33 (2H, t, $-OCH_2-$), 3.68 (3H, s, $-OCH_3$). The other methyl ω-(*tert*-alkoxy)hexanoates in the decomposed solution were judged by the retention time of GC and the relative molecular weight.

Supporting Information Available: Tabulated data of ^{1}H NMR and ^{13}C NMR spectra, refraction index and elemental analysis for peroxides **3a−d** and **4b−d** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[27] (a) Carter, R. E.; Stilbs, P. *J. Am. Chem. Soc.* **1976**, *98*, 7515. (b) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201.