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Substituent Effects on the Decomposition of Bis(*tert*-butylperoxy)cycloalkanes

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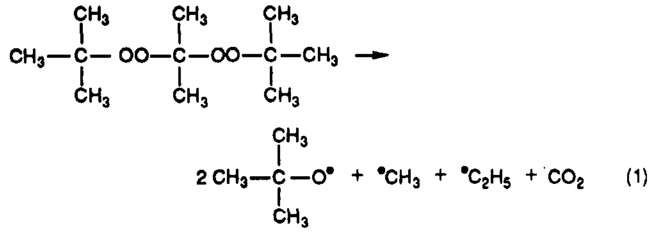
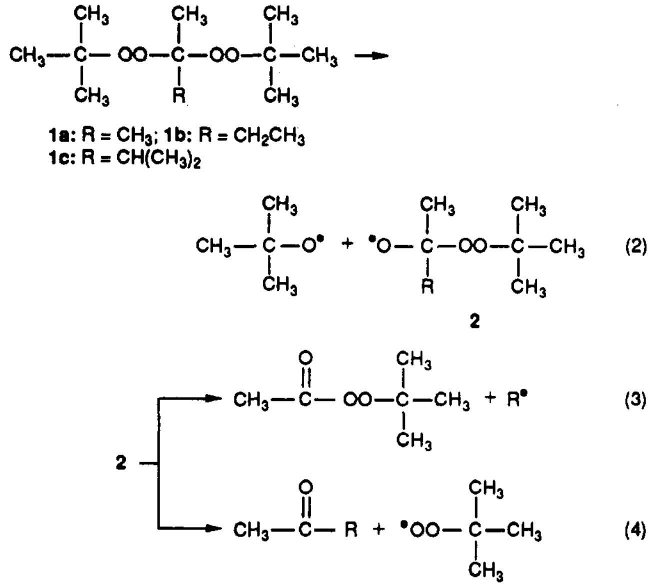
Decompositions of bis(*tert*-butylperoxy)cycloalkanes have been carried out in cumene and *n*-alkanes at temperatures of 80–120 °C and have been compared mainly with the decomposition of *tert*-alkyl *tert*-butyl peroxides in order to investigate substituent effects on the homolytic scission of one O–O bond in *gem*-diperoxides. The decomposition rates of bis(*tert*-butylperoxy)cycloalkanes are much faster than those of *tert*-alkyl *tert*-butyl peroxides; the decomposition rates of the cycloalkanes decrease in the following order: cyclopentane > 3,5,5-trimethylcyclohexane > cyclohexane > cyclooctane > cyclododecane. The effect of ring size on the decomposition and the isokinetic relationships between the activation parameters suggest that stabilization of the transition state by electron donation from the cycloalkyl substituents and repulsion between lone-pair electrons on different peroxy oxygen atoms in the ground state are important factors in the decomposition of *gem*-diperoxides.

Several researchers have investigated the decomposition of bis(*tert*-butylperoxy)alkanes,[1] but the substituent effects on the homolytic scission of the O–O bond in *gem*-diperoxides have not yet been clarified. One study concerning the decomposition of bis(*tert*-butylperoxy)cycloalkanes, which are important industrially as radical generators,[2] was not detailed. Luft and co-workers examined the decomposition of 2,2-bis(*tert*-butylperoxy)butane (later shown to be *gem*-diperoxide **1b**) in a flow reactor under high pressure at high temperatures of 135–215 °C. For these severe conditions, a concerted decomposition mechanism (eq 1) was proposed on the basis of the relatively high positive volume of activation ($\Delta V^{\ddagger}$ = 22.3 mL/mol at 200 °C).[1d] In contrast, Suyama and coworkers[1f] proposed the following stepwise mechanism for the decomposition at temperatures of 90–120 °C:



$$(CH_3)_3C-OO-C(CH_3)_2-OO-C(CH_3)_3 \rightarrow 2\,(CH_3)_3C-O^{\bullet} + {}^{\bullet}CH_3 + {}^{\bullet}C_2H_5 + CO_2 \quad (1)$$



1a: R = CH_3; **1b**: R = CH_2CH_3
1c: R = $CH(CH_3)_2$

$$(CH_3)_3C-OO-C(CH_3)(R)-OO-C(CH_3)_3 \rightarrow (CH_3)_3C-O^{\bullet} + {}^{\bullet}O-C(CH_3)(R)-OO-C(CH_3)_3 \quad (2)$$

2

$$\mathbf{2} \rightarrow CH_3-C(=O)-OO-C(CH_3)_3 + R^{\bullet} \quad (3)$$

$$\mathbf{2} \rightarrow CH_3-C(=O)-R + {}^{\bullet}OO-C(CH_3)_3 \quad (4)$$

The relative rates of β-scission from radicals **2** in cumene at 100 °C were shown to be 133:35:7:1 for R = $CH(CH_3)_2$/CH_2CH_3/$(CH_3)_3COO$/CH_3.

We previously investigated the substituent effects on the decomposition rates of *tert*-alkyl *tert*-butyl peroxides (alkyl-substituted in the β-position) and confirmed that the rate-retarding effect of electron-withdrawing polar substituents was very small.[3] However, bis(*tert*-butylperoxy)alkanes (i.e., *sec*-alkyl *tert*-butyl peroxides substituted in the α-position by *tert*-butylperoxy substituents) showed very fast decomposition rates, in spite of the fact that, as an electron-withdrawing polar substituent, the *tert*-butylperoxy group would be expected to retard the rate.[1a,3] Cafferata et al. found that cyclohexanone cyclic diperoxides (e.g., 7,8,15,16-tetroxadispiro[5.2.5.2]hexadecane (**5**)) had the slowest decomposition rates of all the aboved-mentioned peroxides.[4] Bis(*tert*-butylperoxy)cyclohexane decomposed preferentially by the scission of the C–C bond in a manner similar to that shown in eq 3.[5]

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[1] (a) Dickey, F. H.; Raley, J. H.; Rust, F. F.; Treseder, R. S.; Vaughan, W. E. *Ind. Eng. Chem.* **1949**, *41*, 1673. (b) Bukata, S. W.; Zabrocki, L. L.; McLaughlin, M. F.; Kolczynski, J. R.; Mageli, O. L. *I & EC Prod. Res. Dev.* **1964**, *3*, 261. (c) Komai, T.; Suyama, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3045. (d) Luft, G.; Lim, P.E.-C.; Pavlakis, S. *J. Macromol. Sci. Chem.* **1985**, *A22*, 1183. (e) Suyama, S.; Watanabe, Y.; Sawaki, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 716. (f) Watanabe, Y.; Ishigaki, H.; Okada, H.; Suyama, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1231.

[2] (a) Harpell, G. A. *Rubber Chem. Technol.* **1973**, *46*, 1007. (b) Sheppard, C. S., Mageli, O. L.; Kirk-Othmer *Encyclopedia of Chemical Technology*, 3rd ed. John Wiley & Sons: New York, 1982; Vol. 17 pp 27–90.

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[5] (a) Komai, T.; Matsuyama, K.; Kumura, H. 54th National Meeting of the Chemical Society of Japan, Tokyo, April 1987, Abstr. No. 3III 035. (b) Sugihara, Y.; Watanabe, Y.; Kumura, H.; Nakamura, T.; Suyama, S.; Sawaki, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 664.

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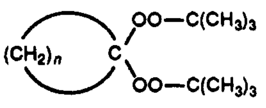
Table I. Rate Constants and Activation Parameters for Decomposition of Various Peroxides in Cumene[a]

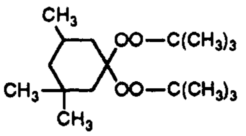
peroxide	temp (°C)	conc (mol/L)	rate const $10^5 \times k_d$ (s^{-1})	activation parameter $\Delta H^\ddagger$ (kcal/mol)	activation parameter $\Delta S^\ddagger$ (eu)
3a	80	0.0763	0.498 ± 0.015	33.3 ± 0.2	11.0 ± 1.0
	90	0.0763	1.80 ± 0.03		
	100	0.0200	6.67 ± 0.20		
	100	0.0763	6.73 ± 0.12		
	100	0.200	6.78 ± 0.12		
	110	0.0763	21.7 ± 0.4		
3b[b]	110	0.0501	16.2 ± 0.1	33.8 ± 0.1	12.0 ± 0.6
3c	90	0.0501	1.11 ± 0.01	33.8 ± 0.1	11.4 ± 0.4
	100	0.0198	4.15 ± 0.11		
	100	0.0501	3.95 ± 0.06		
	100	0.201	4.18 ± 0.06		
	110	0.0501	13.6 ± 0.1		
	120	0.0501	42.4 ± 0.6		
3d	90	0.0500	0.814 ± 0.010	34.6 ± 0.5	13.2 ± 2.7
	100	0.0500	3.22 ± 0.06		
	110	0.0200	9.93 ± 0.21		
	110	0.0500	10.5 ± 0.10		
	110	0.200	9.89 ± 0.43		
3e	80	0.0500	0.382 ± 0.009	33.5 ± 0.1	11.3 ± 0.5
	90	0.0500	1.5 ± 0.03		
	100	0.0201	5.34 ± 0.03		
	100	0.0500	5.31 ± 0.15		
	100	0.201	5.40 ± 0.03		
	110	0.0500	17.49 ± 0.44		
1a[c]	110	0.1	2.97 ± 0.02	34.9 ± 0.4	11.3 ± 2.1
1b[d]	110	–	3.89 ± 0.28	34.9 ± 0.0	11.7 ± 0.0
1c[e]	110	0.0981	13.8 ± 0.1	33.8 ± 0.5	11.6 ± 1.2
4a[f]	110	–	0.249	36.9 ± 0.1	11.5 ± 0.6
4b[f]	110	0.05	0.386 ± 0.004	36.8 ± 0.2	12.3 ± 1.0
4c[f]	110	0.05	0.707 ± 0.008	36.8 ± 0.0	12.3 ± 0.1
5[g]	110	–	0.059	40.0 ± 0.3	16.9 ± 0.8

[a] Rate constants and their standard deviations were calculated by a least-squares method. [b] See ref 5. [c] See ref 1c. [d] See ref 1a. [e] See ref 1f. [f] See ref 3. [g] Measured in toluene. See ref 4.

In this work, the effects of the ring size on the decomposition of various bis(*tert*-butylperoxy)cycloalkanes (**3**) have been investigated in order to clarify the effects of the α-(*tert*-butylperoxy)-substituted group on the O–O bond homolysis. These *gem*-diperoxides are suitable for kinetic study because they have a simple decomposition mechanism.



3a: $n = 4$; **3b**: $n = 5$; **3c**: $n = 7$; **3d**: $n = 11$



3e

Results and Discussion

Bis(*tert*-butylperoxy)cycloalkanes (**3**) were prepared by the reaction of *tert*-butyl hydroperoxide with the corresponding cyclic ketones in the presence of sulfuric acid. The rates and products of the decompositions of *gem*-diperoxides **3** in cumene or alkanes were determined by means of GC and HPLC. Good first-order rate constants were obtained at 10–80% conversion. The decomposition rate data for *gem*-diperoxides **3** are given in Table I together with calculated activation parameters. The data for **3** are compared with those for *gem*-diperoxides **1**,[1a,c,f] *tert*-alkyl *tert*-butyl peroxides **4a–c** (where the *tert*-alkyl groups are *tert*-butyl, *tert*-pentyl, and 1,1,2-trimethylpropyl, respectively)[3] and cyclic diperoxide **5**.[4] That the rate constants for *gem*-diperoxides **3** showed no appreciable change when the concentration was increased 10-fold seemed to rule out any induced decomposition. The decomposition rates for *gem*-diperoxides **3** were significantly faster than those for *gem*-diperoxides **1a** and **1b**, peroxides **4**, and cyclic diperoxide **5** and were comparable to the decomposition rate for *gem*-diperoxide **1c**. The activation enthalpies for *gem*-diperoxides **1** and **3** were lower than those for peroxides **4** and cyclic diperoxide **5**; however, the activation entropies were approximately equal in all cases except cyclic diperoxide **5**. The decomposition rate constants for cyclic diperoxide **5** were the slowest of all the rate constants, and the activation enthalpy and entropy were the largest (Table I).

Decomposition of Bis(*tert*-butylperoxy)cyclohexane (3b). The decomposition rates of *gem*-diperoxide **3b** in *n*-alkanes are given in Table II and are compared with those of peroxide **4a** and *tert*-butyl peroxypivalate (**6**) to clarify the kinetic effect of the solvent viscosity.[6a] The rate constants (k_d) for *gem*-diperoxide **3b** decreased with increasing solvent viscosity (η) and satisfied the following Pryor equation:[6a]

$$\frac{1}{k_d} = \frac{1}{k_1} + \frac{k^{-1}}{k_1 A_D}\left(\frac{\eta}{A_v}\right)^{0.5} \tag{5}$$

where k_1 and k_{-1} are the rate constants for bond homolysis and cage return, respectively; A_D and A_v are Arrhenius preexponential factors for solute diffusion and self-diffusive flow of solvent, respectively. The rate constants (k_1) for the bond homolysis of *gem*-diperoxide **3b** at 100 °C was calculated from the equation to be 4.30×10^{-5} s^{-1}. The fraction (f_r) of geminate radicals that combine to

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(6) (a) Pryor, W. A.; Morkved, E. H.; Bickley, H. T. *J. Org. Chem.* **1972**, *37*, 1999. (b) Decomposition of peroxides have been generally classified as nonconcerted (stepwise) or concerted. However, there is a borderline decomposition mechanism that cannot be distinguished from the others and probably changes continuously from the one to the other. See, for example, Koenig, T. In *Free Radicals*, ed by Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973, Vol. I, Chapt. 3.

Table II. Solvent Viscosity Dependence of the Decomposition Rate Constants of *gem*-Diperoxide 3b, Peroxide 4a, and Peroxyester 6[a]

peroxide	solvent	viscosity (cp)	temperature (°C)	rate constant $10^5 \times k_d$ (s^{-1})	cage return, f_r
3b	*n*-hexane	0.168	100	3.82 ± 0.07	0.11
	n-nonane	0.305	100	3.62 ± 0.07	0.16
	n-dodecane	0.520	100	3.51 ± 0.06	0.18
	n-hexadecane	0.900	100	3.15 ± 0.10	0.27
4a[b]	*n*-nonane	0.305	100	0.0373	0.33
6[b]	*n*-octane	0.257	80	23.4	0

[a] Rate constants and their standard deviations were calculated by a least-squares method. [b] See ref 6a.

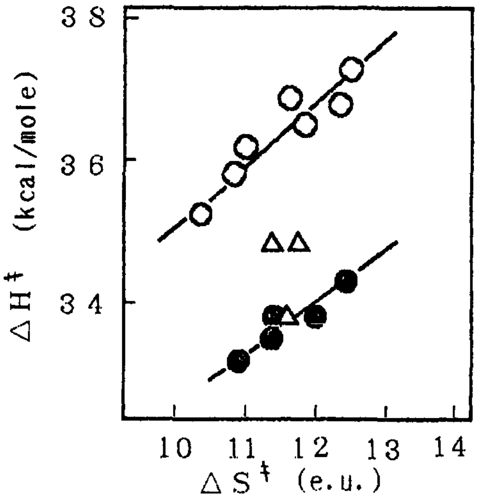

Figure 1. Isokinetic relationships in the decomposition of *tert*-alkyl *tert*-butyl peroxides and *gem*-diperoxides: (○) *tert*-alkyl *tert*-butyl peroxides; (△) *gem*-diperoxides from acyclic ketones; (●) *gem*-diperoxides from cyclic ketones.

reform the parent peroxide was estimated from the equation $f_r = 1 - k_d/k_1$ to be 0.11–0.27 (Table II). The values for peroxide **4a** ($f_r = 0.33$) and peroxyester **6** ($f_r = 0$) were typical of one-bond homolytic and two-bond concerted scissions, respectively.[6a] When compared in a solvent of the same viscosity, values of f_r for *gem*-diperoxide **3** were larger than 0.1, as expected for the peroxides[6a] that decompose with one-bond scission, but were much smaller than the value for peroxide **4a**. The equilibrium of the bond homolysis for *gem*-diperoxides **3** lies very far to the right.[6b]

We examined the decomposition products of *gem*-diperoxide **3b** and detected *n*-pentane (2%), *tert*-butyl alcohol (139%), acetone (8%), *tert*-butyl peroxyhexanoate (42%), and 2,3-dimethyl-2,3-diphenylbutane (71%) by GC analysis, but did not detect cyclohexanone and ε-caprolactone, a starting material and an intramolecular-induced decomposition product, respectively.[5a] The data collected for **3b** show that the decomposition of **3b** proceeds by one-bond homolysis followed preferentially by the scission of the C–C bond of the resulting α-(*tert*-butylperoxy)cyclohexoxy radical. The scission of the C–O bond seems to be retarded by the strain energy of the formed cyclohexanone which is larger than the strain energy of the formed acyclic ketone.[7]

Isokinetic Relationship. Figure 1 shows the relationship between the activation enthalpies and entropies in the decomposition of *gem*-diperoxides **1** and **3** and peroxides **4** in cumene; Figure 1 also shows the data from our previous work.[3] Different isokinetic relationships were obtained for *gem*-diperoxides **3** and peroxides **4**. The activation parameters for *gem*-diperoxides **1a** and **1b** were scattered between the lines, and the activation parameters for *gem*-diperoxide **1c** were on the line for *gem*-diperoxides **3**. The linearity of the free-energy relationships suggests that, within each series, the substituted *gem*-diperoxides decompose by a single interaction mechanism.[3,8] *gem*-Diperoxides **3** and peroxides **4** can be considered to decompose by different interaction mechanisms. The ground state steric interactions are not important for comparison of the substituent effects within each isokinetic peroxide series, but do become important for comparisons between the isokinetic series. However, the important difference between those two series seems to be in the entropies, and the difference suggests that there are important interactions (repulsions) between lone-pair electrons on the four peroxy oxygen atoms in the ground state for *gem*-diperoxides.

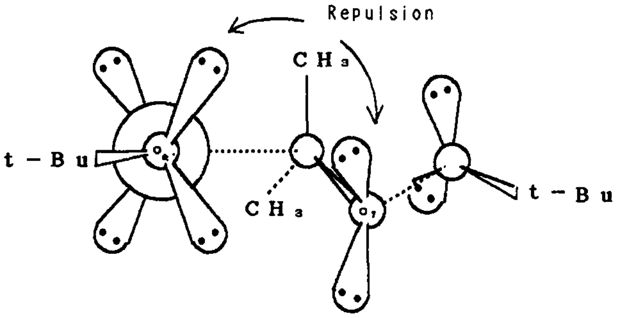

Figure 2. A MINDO/3-RHF optimized conformational picture of **1a** including lone-pair orbitals.

The structures of *gem*-diperoxide **1a** and peroxide **4a** were optimized energetically by means of the MINDO/3-RHF method with the MOPAC program to give atomic charges and bond lengths. Figure 2 shows the optimized picture including the lone-pair orbitals for *gem*-diperoxide **1a**.[9] Symbols α′, α, β, and γ indicate the positions of the oxygen and carbon atoms in the *gem*-diperoxides ($O_{\alpha'}$-O_α-C_β(-O_γ-)-C_γ). The atomic charges ($Q_{\alpha'} = -0.2440$ and $Q_\alpha = -0.2629$) on the two peroxy oxygen atoms in *gem*-diperoxide **1a** were approximately equal to those in peroxide **4a** ($Q_{\alpha'} = -0.2529$ and $Q_\alpha = -0.2528$), and the length ($r_{\alpha'\alpha}$) of the O–O bonds was the same for both peroxides (1.410 Å). Accordingly, the electrostatic repulsion energies between the peroxy oxygen atoms in *gem*-

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[7] The strain energies for the parent ketones of *gem*-diperoxides **3a** and **3b** are 6.0 and 3.4 kcal/mol, respectively, and are larger than those of the corresponding acyclic ketones (see Benson, S. W. et al. *Chem. Rev.* **1969**, *69*, 279.

[8] No isokinetic relationship was found in the decomposition of more crowded peroxy esters and di-*tert*-butyl peroxydicarbonate. See Ernst, J. A.; Thankachan, C.; Tidwell, T. T. *J. Org. Chem.* **1974**, *39*, and Komai, T.; Matsuyama, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2207.

[9] The optimized picture was similar to the results of an ab initio theoretical calculation for dimethyl peroxide by Bair et al., which showed a conformation with a skew relationship between the four lone-pair orbitals on the oxygen atoms and a staggered relationship between the methyl groups. See Bair, R. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 2719.

Table III. A Comparison of the Relative Decomposition Rates of Various *gem*-Diperoxides at 110 °C, the Relative Rates for Solvolysis of *p*-Cycloalkyl-*tert*-cumyl Chlorides, and Various Parameters of Cycloalkanes

substituent	relative rate		parameters of cycloalkanes	
	decomposition[a]	solvolysis[b]	strain (kcal/mol)[c]	J_{C-H} (cps)[d]
cyclopentane	7.31	1.26	6.0	131
cyclohexane	5.45	1.04	0	127
cyclooctane	4.58	–	9.7	127
cyclododecane	3.54	–	5.1	123
3,5,5-trimethylcyclohexane	5.89	–	–	–
isopropyl	1.00[e]	1.00[f]	–	119[g]

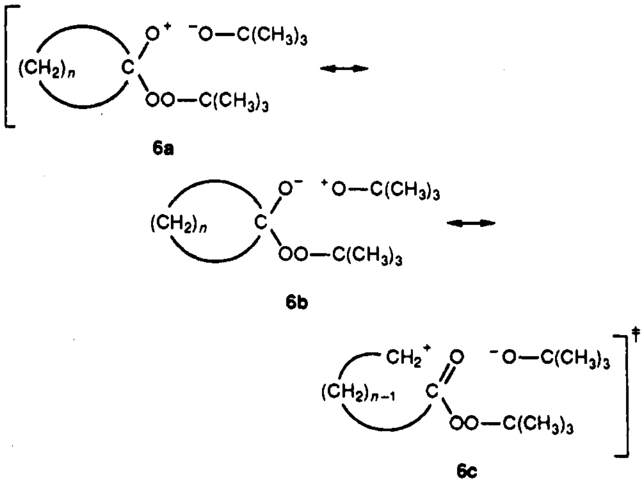
[a] The decomposition rates of various bis(*tert*-butylperoxy)cycloalkanes 3 relative to *gem*-diperoxide 1a at 110 °C. [b] The rates of solvolysis of some *p*-cycloalkyl-*tert*-cumyl chlorides relative to *p*-isopropyl-*tert*-cumyl chloride in 90% aqueous acetone. See ref 12. [c] See ref 13. [d] See ref 14. [e] *gem*-diperoxide 1a. [f] *p*-Isopropyl-*tert*-cumyl chloride [g] Methylene hydrogen in propane.

diperoxide **1a** and peroxide **4a** could be estimated by the equation[10] $Q_{\alpha'}{\cdot}Q_\alpha/r_{\alpha'\alpha}$ to be 0.655 eV [i.e., $(-0.2440)e \times (-0.2629)e/(1.410 \times 10^{-8}\ \text{cm}) = 4.549 \times 10^6\ e^2/\text{cm} = 1.049 \times 10^{-12}$ erg] and 0.653 eV, respectively. The atomic charge on the γ-oxygen atom and the distance between the α'- and γ-oxygen atoms in *gem*-diperoxide **1a** were $Q_\gamma = -0.2440$ and $r_{\alpha'\gamma} = 2.92$ Å, respectively. These values gave an electrostatic repulsion energy of 0.342 eV. The lone-pair orbital on the α'-oxygen atom is comparatively near to the lone-pair orbital of the γ-oxygen atom in **1a** (Figure 2), and the repulsion between these lone-pair orbitals in *gem*-diperoxide **1a** is significantly larger than the repulsion in peroxide **4a**. Thus, the ground state of **1a** is much more unstable.

In contrast, cyclic diperoxide **5** in the crystal state exists in a chair conformation, stabilized strongly by rotational angles that minimize the repulsion between the lone-pairs.[11] The oxygen lone-pair orbitals in cyclic diperoxide **5** have staggered or skew conformations to avoid steric interactions with alkyl groups or electron–electron repulsions of lone-pair electrons. An electron–electron repulsion between lone-pair electrons of α'- and γ-oxygen atoms is small because the two lone-pair orbitals in the same direction on the peroxide ring are in an axial and an equatorial position, respectively. The deviations of *gem*-diperoxides **1a** and **1b** from the isokinetic relationship of *gem*-diperoxides **1c** and **3** seem to arise from a different decomposition mechanism, which involves scission of the C–O bond as shown in eq 4. The stretching of the C–O bond accompanied by the scission of the O–O bond would decrease the repulsion between the lone-pair orbitals on the α'- and γ-oxygen atoms. In the case of *gem*-diperoxides **1c** and **3**, the C_β–C_γ bond may be more stretched at the transition state that it is in the transition state for **4**, as shown by the smaller values of f_r for **3b** compared with that for **4**.[6b]

Effects of Ring Size on the Decomposition of *gem*-Diperoxides 3. The rates of decomposition of *gem*-diperoxides **3** at 110 °C relative to the rate for *gem*-diperoxide **1a** are shown in Table III and are compared with the relative rates of solvolysis of *p*-cycloalkyl-*tert*-cumyl chlorides in 90% aqueous acetone.[12] The strain energies[13] and coupling constants $J(^{13}\text{C-H})$[14] of some cycloalkanes are also shown in Table III. The rates of decomposition decreased in the following order: **3a** > **3e** > **3b** > **3c** > **3d** ≫ **1a**. The larger the ring size becomes, the slower the decomposition rate is. The *gem*-diperoxides from cyclic ketones decomposed faster than the peroxide from the acyclic ketone. The decomposition rates do not correlate with the strain energies, but do approximately correlate with the relative rates of the solvolysis and the coupling constants $J(^{13}\text{C–H})$, which may be measures of the electronegativity or sp^2 character of the substituent. *p*-Cycloalkyl substituents produce more than a 10-fold increase in the rate of solvolysis of cycloalkyl-*tert*-cumyl chlorides compared with meta substituents. This acceleration is based not only on an inductive effect but also on a conjugative effect of the cycloalkyl ring transmitted through the aromatic system.[14] The electron-donating ability of the cycloalkyl substituent may be related to the value of the coupling constant $J(^{13}\text{C–H})$ as a measure of sp^2 character in accelerating the decomposition of *gem*-diperoxides **3**.

The O–O bond of *gem*-diperoxides **3** or peroxides **4** may be polarized when stretched at the transition state of the decomposition.[3] An activation complex may be described as a resonance hybrid of the following limiting formulas:



Formula **6a** may be stabilized by the conjugative and electron-donating cycloalkyl substituents; formula **6b**, by the electron-withdrawing *tert*-butylperoxy substituent; and formula **6c**, by the inductive effect of the methyl groups on the cyclohexyl ring in *gem*-diperoxide **3e** or by the hyperconjugative alkyl groups CH_3, CH_2CH_3, and $CH(CH_3)_2$ in *gem*-diperoxides **1a**, **1b**, and **1c**, respectively (Table I). Formula **6c** may also be stabilized by the formation of a peroxyester group.[15]

Experimental Section

IR and NMR spectra were recorded on JASCO A-3 and JEOL JNM-MH-100 spectrometers, respectively. GC analyses were carried out on Shimazu GC-6A and GC-2D gas chromatographs,

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(10) Klopman, G.; Tsuda, K.; Louis, J. B.; Davis, R. E. *Tetrahedron*, **1970**, *26*, 4549.

(11) Silbert, L. S. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. II, p 660.

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(13) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; p 215.

(14) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870.

and LC analyses were performed on a LC-6A high performance liquid chromatograph. GC-MS spectra were recorded on a JEOL JMS-D300 mass spectrometer. The purities of *gem*-diperoxides were checked by iodometric titration. The procedure was carried out in 2-propyl alcohol containing a small amount of acetic acid and sodium iodide; a small amount of concd hydrochloric acid was added after the solution was boiled in a reflux condenser for a few minutes.[1a]

Materials. *tert*-Butyl peroxyhexanoate was prepared by a Schotten–Baumann reaction of hexanoyl chloride with *tert*-butyl hydroperoxide. To a mixture of 10% aq NaOH (116.4 g, 0.32 mol) and 70% *t*-butyl hydroperoxide (38.6 g, 0.3 mol) at 10 °C was added the acid chloride (36.4 g, 0.27 mol) dropwise over a period of 20 min; the mixture was then heated gradually from 15 to 40 °C over a period of 80 min to complete the reaction. After the reaction was complete, the mixture was washed twice with water for 5 min at room temperature and dried with anhydrous $MgSO_4$, and peroxy ester (42.0 g, yield 79.9%) of purity of 86.8% was obtained: IR (CCl_4) 1780 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.90 (3 H, m, CH_3), 1.34–1.80 (15 H, m, *t*-CH_3 and $(CH_2)_3$), 2.28 (2 H, t, $COCH_2$); n_D^{20} = 1.4224 (lit.[16] 1.4294). *tert*-Butyl hydroperoxide, 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (**3e**), and 1,1-bis(*tert*-butylperoxy)cyclododecane (**3d**) were obtained from Perbutyl H (70% purity), Perhexa 3M (90% purity), and Perhexa CD (99% purity) (products of NOF Corp.), respectively. Cumene, *n*-hexane, *n*-nonane, *n*-tridecane, and *n*-hexadecane were stirred for several hours with concd H_2SO_4, washed with 10% aq NaOH in distilled H_2O, dried with drying agents, and distilled through a 24-in. Vigreaux column.

1,1-Bis(*tert*-butylperoxy)cyclopentane (3a). To a solution of cyclopentanone (15.9 g, 0.18 mol) and cumene (35 g) at 0 °C was added 65% H_2SO_4 (21.7 g, 0.14 mol) dropwise over a period of 10 min. To the solution was added 70% *tert*-butyl hydroperoxide (46.4 g, 0.36 mol) dropwise over a period of 30 min while the reaction was maintained at 0–10 °C. Then, the reaction mixture was stirred for 45 min at 10 °C to complete the reaction. The oil layer was separated from the reaction mixture, washed twice with 5% aq NaOH for 3 min at 10 °C and three times with water for 5 min at 30 °C, and dried with anhydrous $MgSO_4$ to give *gem*-diperoxide **3a** (40.0 g of a solution 39.5% purity in cumene, yield 36%): IR (CCl_4) 870 cm^{-1} (O–O); ^{1}H NMR ($CDCl_3$) δ 1.23 (9 H, s, *t*-CH_3), 1.70 (2 H, d, $(CH_2)_2$), and 1.97 (2 H, d, $C(CH_2)_2$).

1,1-Bis(*tert*-butylperoxy)cyclohexane (3b). To a solution of cyclohexanone (17.7 g, 0.18 mol) and cumene (35 g) at 0 °C was added 65% H_2SO_4 (21.7 g, 0.14 mol) dropwise over a period of 10 min. To the solution was added 70% *tert*-butyl hydroperoxide (46.4 g, 0.36 mol) dropwise over a period of 20 min while the reaction temperature was maintained at 0–10 °C. Then, the reaction mixture was stirred for 30 min at 10 °C to complete the reaction. The oil layer was separated from the reaction mixture, washed once with 5% aq NaOH for 3 min at 10 °C and three times with water for 5 min at 20 °C and dried with anhydrous $MgSO_4$. The crude product was purified by recrystallization from methanol to give *gem*-diperoxide **3b** (purity 96.7%, yield 43%): IR (CCl_4) 885 cm^{-1} (O–O); ^{1}H NMR ($CDCl_3$) δ 1.24 (9 H, s, *t*-CH_3), 1.50 (3 H, d, $(CH_2)_2$), 1.80 (2 H, d, $C(CH_2)_2$); n_D^{20} 1.4402.

1,1-Bis(*tert*-butylperoxy)cyclooctane (3c). To a mixture of petroleum ether (33.3 g), cyclooctanone (12.9 g, 0.10 mole), and 70% *tert*-butyl hydroperoxide (32.2 g, 0.25 mol) was added 70% H_2SO_4 (24.0 g, 0.19 mol) dropwise over a period of 40 min while the reaction temperature was maintained below −5 °C. Then the mixture was kept near a temperature of −10 °C and stirred for 90 min to complete the reaction. The oil layer was separated from the reaction mixture, washed once with 3% aq NaOH for 5 min below 10 °C and then three times with brine for 5 min, and dried with anhydrous $MgSO_4$. After evaporation of solvent, the crude product (13.0 g) was purified by recrystallization from methanol to give *gem*-diperoxide **3c** (4.7 g, purity 97.4%, yield 17%): IR (CCl_4) 880 cm^{-1} (O–O); ^{1}H NMR ($CDCl_3$) δ 1.21 (9 H, s, *t*-CH_3), 1.58 (5 H, s, (CH_2)), and 1.90 (2 H, s, $C(CH_2)_2$). Anal. Calcd for $C_{16}H_{32}O_4$: C, 66.63; H, 11.18. Found: C, 66.57; H, 11.12.

1,1-Bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (3e). The commercial product (purity 90%, NOF Corp.) was purified by distillation (86 °C/1 mmHg) to give *gem*-diperoxide **3e** (purity 99.0%): IR (CCl_4) 885 cm^{-1} (O–O); ^{1}H NMR ($CDCl_3$) δ 0.6–1.14 (9 H, m, CH_3), 1.14–1.52 (18 H, m, *t*-CH_3), 1.52–2.44 (7 H, s, cyclohexyl ring).

Kinetic Procedure. Dilute solutions of *gem*-diperoxide in cumene or *n*-alkane were placed in sealed tubes (content of 7.5 cm^3) under vacuum and heated in a constant-temperature bath (±0.2 °C). The amount of *gem*-diperoxide remaining was determined by GC or LC with the following conditions (*gem*-diperoxide in solvent: analytical conditions): *gem*-diperoxide **3a** in cumene, *gem*-diperoxide **3b** in *n*-alkanes: GC analysis by Silicon GE SE-30 (5%) on Shimalite W with *n*-$C_{14}H_{30}$ as an internal standard; *gem*-diperoxides **3b** and **3e** in cumene: GC analysis by Silicon GE SE-30 (5%) on Uniport HP and *n*-$C_{13}H_{28}$ as an internal standard; *gem*-diperoxide **3c** in cumene: GC analysis by Silicon GE SE-30 (5%) on Shimalite W with *n*-$C_{17}H_{36}$ as an internal standard; *gem*-diperoxide **3d** in cumene: LC analysis by Shimpack CLC ODS with CH_3OH/H_2O = 95:5 as the eluent.

Decomposition Products. *gem*-Diperoxide **3b** (0.05 M in cumene) was decomposed for 40 h at 80 °C, and the solution was analyzed by GC and GC-MS and compared with authentic samples. The yields of *t*-butyl alcohol and acetone were determined with columns of PEG-20M (25%), and the yield of theother products were determined with columns of SE-30 (5%).

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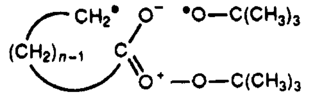
(15) The *tert*-butylperoxy substituent can similarly stabilize activation complex 6 by a limiting formula as follows:



(16) Trachtman, M.; Miller, J. G. *J. Am. Chem. Soc.* 1962, 84, 4828.