664 © 1992 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 65, 664—667 (1992) [Vol. 65, No. 3

Radical Intermediates in the Thermal Decomposition of 1,1-Bis(*t*-butyldioxy)cyclohexane

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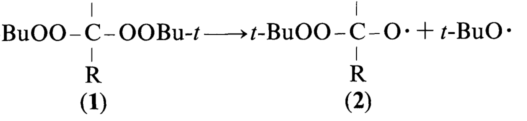
(Received September 24, 1991)

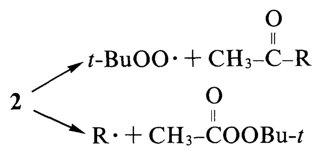
The thermolysis mechanism of 1,1-bis(*t*-butyldioxy)cyclohexane (**6**) has been studied in solutions. The activation parameters obtained in cumene are $\Delta H^{\ddagger}=139.5\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^{\ddagger}=44.8\ \mathrm{J\ K^{-1}\ mol^{-1}}$, and the volatile products are *t*-butyl alcohol, *t*-butyl peroxyhexanoate, and 2,3-dimethyl-2,3-diphenylbutane along with minor products of acetone, cyclohexanone, and *t*-butyl 1-methyl-1-phenylethyl peroxide. The thermolysis of **6** in benzene gave acetone and *t*-butyl alcohol as major volatile products. The polyester of 2-hydroxyhexanoic acid was obtained both in cumene and benzene as a non-volatile product, and the yield was as high as 76% in benzene. These facts indicate that [1-(*t*-butyldioxy)cyclohexyl]oxyl radical (**7**) undergoes a facile ring-opening reaction yielding 5-(*t*-butyldioxycarbonyl)pentyl radical (**8**). The resulting radicals abstract hydrogen atoms either intra- or intermolecularly. The former reaction is predominant in the absence of good hydrogen donors, affording 2-hexanolide and ultimately the corresponding polyesters.

gem-Bis(*t*-alkyldioxy)alkanes are important as free radical initiators for practical polymerizations, and their decomposition mechanism is quite interesting because of the presence of two dioxy bonds on the same carbon atom. Although a few earlier studies[1–3] were reported, the systematic and detailed investigations on their thermolysis had not been made until our recent studies[4–6] were started.

We have studied the decomposition mechanism of 2,2-bis(*t*-butyldioxy)alkanes (**1**) in solvents such as diphenylmethane,[4] cumene,[5] and styrene–benzene.[6] The results showed that **1** cleaved homolytically at one of the dioxyl bonds yielding 1-(*t*-butyldioxy)alkoxyl radical (**2**) (Eq. 1), which underwent β-scission to afford *t*-butyldioxyl radical (Eq. 2a) or alkyl radicals (Eq. 2b). Relative rates for the β-scission from **2** were found to be *i*-Pr:Et:*t*-BuOO:Me=133:33:7:1 in cumene at 100 °C.[5]

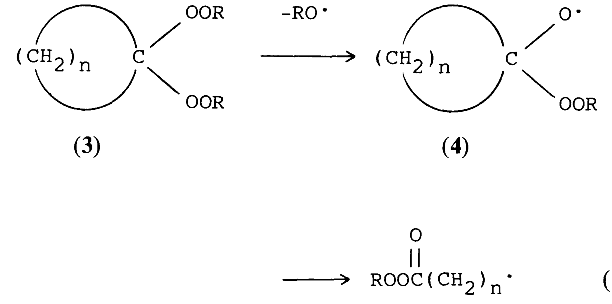


$$t\text{-BuOO}-\underset{\underset{\textstyle(\mathbf{1})}{\textstyle R}}{\overset{\textstyle CH_3}{C}}-\text{OOBu-}t \longrightarrow t\text{-BuOO}-\underset{\underset{\textstyle(\mathbf{2})}{\textstyle R}}{\overset{\textstyle CH_3}{C}}-O\cdot + t\text{-BuO}\cdot \tag{1}$$



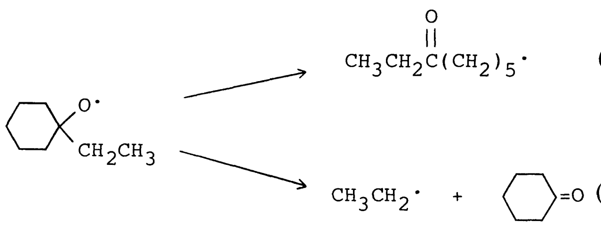
$$2 \nearrow t\text{-BuOO}\cdot + CH_3-\overset{O}{\overset{\|}{C}}-R \tag{2a}$$

$$2 \searrow R\cdot + CH_3-\overset{O}{\overset{\|}{C}}OOBu\text{-}t \tag{2b}$$



(3) (4) (5) (3)

Though the basic thermolysis mechanism of *gem*-diperoxides was established by the thermolysis of **1**, whether this mechanism applies to cyclic *gem*-diperoxides (**3**) or not is still an open question. If the thermolysis of **3** proceeds in the same manner, cycloalkoxyl radicals (**4**) will be formed as primary transient radicals. It is well-known that cycloalkoxyl radicals with five or six-membered ring decompose rapidly to ring-opened radicals.[7,8] For example, the ring-opening rate of 1-ethyl-1-cyclohexyloxyl radical (Eq. 4a) is about ten times as fast as that of scission of ethyl radical (Eq. 4b).[8] This suggests that the scission of [(1-alkyldioxy)cyclohexyl]oxyl radical (**4**) (n=5) leads to the formation of pentyl radical with terminal alkyldioxycarbonyl group (**5**) nearly quantitatively (Eq. 3). Intermediacy of radical **5** is quite interesting from a standpoint of designing of polymers since the addition of **5** to monomers leads to functionalized polymers with terminal dioxyl groups.



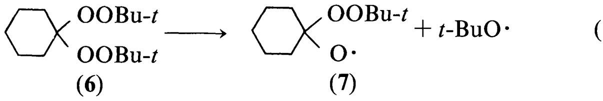
(4a) (4b)

In the present paper, we report on the products and mechanism of the thermal decomposition of 1,1-bis(*t*-butyldioxy)cyclohexane (**6**), focusing on the facile ring-opening of cycloalkoxyl radical (**7**) and the fate of resulting alkyl radical (**8**).

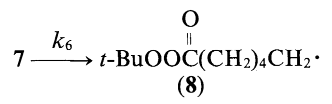
Results and Discussion

Thermolysis. The thermal decomposition of **6** was carried out in cumene under nitrogen. The thermolysis rates, as determined by measuring the disappearance of **6** by GLC analysis, satisfied the first-order kinetics over two half-lives reaction. The resulting rate constants and activation parameters are listed in Table 1. Though the initial concentrations of **6** were varied in the range of 0.02 M (1 M=1 mol dm^{-3}) to 0.20 M, the first-order rate constants remained constant within the experimental errors. This indicates the absence of induced decomposition of **6**. The activation parameters are close to those for di-*t*-butyl peroxide (i.e., $\Delta H^{\ddagger}=153.8$ kJ mol^{-1} and $\Delta S^{\ddagger}=48.1$ J K^{-1} mol^{-1}),[9] suggesting a non-concerted homolytic cleavage of one dioxyl bond in **6**.

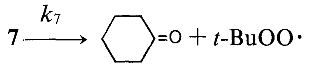
The decomposition products of **6** in cumene are listed in Table 2. The major volatile products were *t*-butyl alcohol, *t*-butyl peroxyhexanoate (**9**), and 2,3-dimethyl-2,3-diphenylbutane; acetone, cyclohexanone, and *t*-butyl 1-methyl-1-phenylethyl peroxide were obtained as minor products. A likely scheme leading to these products is shown in the following equations.



(5)

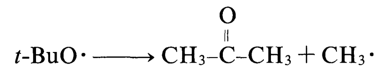


$$7 \xrightarrow{k_6} t\text{-BuOO}\overset{\text{O}}{\overset{\|}{\text{C}}}\underset{(\mathbf{8})}{(\text{CH}_2)_4\text{CH}_2\cdot} \qquad (6)$$

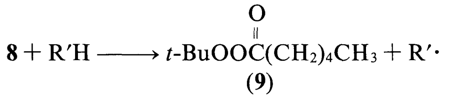


(7)

$$t\text{-BuO}\cdot + \text{R'H} \longrightarrow t\text{-BuOH} + \text{R'}\cdot \qquad (8)$$



$$t\text{-BuO}\cdot \longrightarrow \text{CH}_3\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-CH}_3 + \text{CH}_3\cdot \qquad (9)$$



$$\mathbf{8} + \text{R'H} \longrightarrow t\text{-BuOO}\overset{\text{O}}{\overset{\|}{\text{C}}}\underset{(\mathbf{9})}{(\text{CH}_2)_4\text{CH}_3} + \text{R'}\cdot \qquad (10)$$

$$t\text{-BuOO}\cdot + \text{R'}\cdot \longrightarrow t\text{-BuOOR'} \qquad (11)$$

$$\text{R'}\cdot + \text{R'}\cdot \longrightarrow \text{R'-R'} \qquad (12)$$

Here, R′H, R′-R′, and *t*-BuOOR′ denote cumene, 2,3-dimethyl-2,3-diphenylbutane, and *t*-butyl 1-methyl-1-phenylethyl peroxide, respectively. The O–O homolysis of **6** produces *t*-BuO· and [(1-(*t*-butyldioxyl)cyclohexyl]oxyl radical (**7**) (Eq. 5). It is well-known that *t*-BuO· reacts with cumene to afford *t*-butyl alcohol and R′·(Eq. 8), and/or decomposes to acetone and methyl radical (Eq. 9).

Table 1. Rate Constants and Activation Parameters for the Thermal Decomposition of 1,1-Bis(*t*-butyldioxy)cyclohexane (**6**) in Cumene[a)]

Temp	Concn	$k_1 \times 10^5$	Activation parameters	
°C	M	s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
80	0.05	0.347±0.003	139.5±1.4	44.8±3.7
90	0.05	1.45 ±0.02		
100	0.02	5.10 ±0.07		
100	0.05	5.06 ±0.06		
100	0.20	5.14 ±0.06		
110	0.05	16.2 ±0.1		

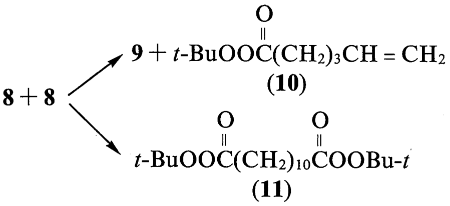
a) The decomposition of **6** was carried out up to about 70% conversion under nitrogen.

Table 2. Products from the Thermolysis of **6**[a)]

Products	Yield[b)]/%	
	in Cumene	in Benzene
Acetone	4	73
t-Butyl alcohol	135	72
t-Butyl peroxyhexanoate (**9**)	32	4
Cyclohexanone	3	2
t-Butyl 1-methyl-1-phenylethylperoxide (*t*-BuOOR′)	1	—
2,3-Dimethyl-2,3-diphenylbutane (R′-R′)	82	—
Polyester[c)] (**12**)	45[d)]	76[d)]

a) Decomposition of 0.1 M **6** at 100 °C for 5 h. Conversion was 55% in cumene and 60% in benzene. A different experiment was carried out for obtaining polyester (see Experimental section). b) % Yields of products: [(mols of products)/(mols of **6** consumed)]. c) Polyester of 2-hydroxyhexanoic acid. d) Yield of 2-hydroxyhexanoic acid after saponification of polyester.

Alkoxyl radical **7** undergoes two scission reactions, that is, a ring-opening reaction yielding alkyl radical with *t*-butyldioxycarbonyl group (**8** in Eq. 6) or alternative scission of *t*-BuOO· to afford cyclohexanone (Eq. 7). Alkyl radical **8** abstracts a hydrogen atom from cumene leading to *t*-butyl peroxyhexanoate (**9**) (Eq. 10). The two stable radicals, R′· and *t*-BuOO·, undergo coupling reactions to give *t*-BuOOR′ (Eq. 11) and R′–R′ (Eq. 12). The relative low yields of cyclohexanone and *t*-BuOOR′ show that the scission reaction of Eq. 7 is a minor path. Therefore, if alkoxyl radical **7** undergoes only two reactions (i.e., Eq. 6 or 7), products from alkyl radical **8** must be yielded in higher yields. However, we could detect no product other than **9** by GLC analysis. We attempted and failed to detect olefin **10** or bis(peroxycarboxylate) **11** which were expected to be formed by disproportionation (Eq. 13) or combination of **8** (Eq. 14).

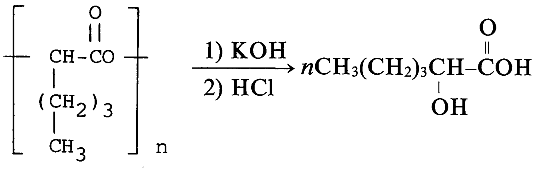


$$\mathbf{8}+\mathbf{8} \nearrow \mathbf{9} + t\text{-BuOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}(\mathrm{CH_2})_3\mathrm{CH=CH_2} \quad \mathbf{(10)} \qquad (13)$$

$$\mathbf{8}+\mathbf{8} \searrow t\text{-BuOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}(\mathrm{CH_2})_{10}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OOBu}\text{-}t \quad \mathbf{(11)} \qquad (14)$$

As listed in Table 2, the thermolysis products in benzene were somewhat different from those in cumene. The major volatile products were acetone and *t*-butyl alcohol, and peroxyester **9** became a minor product. The increased formation of acetone is easily understood since the β-scission of *t*-butyloxyl radical (Eq. 9) becomes a major reaction in the absence of good hydrogen atom donors such as cumene. The low yield (i.e., only 4 %) formation of peroxyester **9** is rationalized similarly in the absence of good hydrogen atom donors. The recovery of pentyl moiety in the volatile products was quite low, and hence the non-volatile products were analyzed as described in the following section.

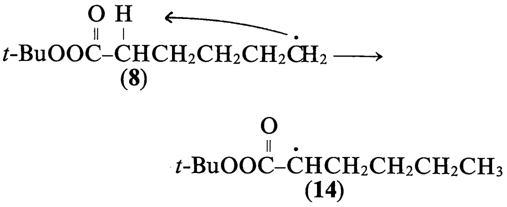
Analysis of High Boiling Residues. The recovery of pentyl moiety in volatile products was quite low, that is, 35% in cumene and 6% in benzene. The low recovery is considered to be due to the conversion of 8 to high boiling residues that were not detected by GLC analysis. In order to analyze high boiling residues, 2.6 g (0.01 mol) of **6** was allowed to decompose completely both in cumene and benzene, and the volatile materials were removed in vacuo. The remaining viscous liquid was an oligomer having the number-average molecular weight of about 900 as determined by GPC, exhibiting a strong IR absorption at 1760 cm^{-1}. This oligomer was saponified with 0.2 M KOH to yield a white slurry. The slurry was acidified with HCl and recrystallized from toluene. A white crystalline having a melting point of 59.5 °C was obtained. Its IR spectrum shows strong absorptions at 1720, 3400—3600, and 1130 cm^{-1}, indicating the existence of carboxylic acid. The ^{1}H NMR spectrum (CDCl$_3$) was as follows: δ=0.92 (t, 3, J=7.0 Hz), 1.35—1.43 (m, 4), 1.64—1.95 (m, 2), and 4.29 (dd, 1, J=4.05, 7.56 Hz). From the mass spectrum after esterification with methanol, it was shown that the molecular weight of parent acid was 132. These analyses data agreed well with those of an authentic sample of 2-hydroxyhexanoic acid (**13**) (Aldrich Chemical Co., mp 60—62 °C). Thus, it is concluded that the oligomer produced by the decomposition of **6** is polyester (**12**) (Eq. 15). From the amounts of **13** (0.59 g, 0.0045 mol in cumene and 1.0 g, 0.0076 mol in benzene), the yields of polyester can be estimated to be 45% in cumene and 76% in benzene (Table 2.)



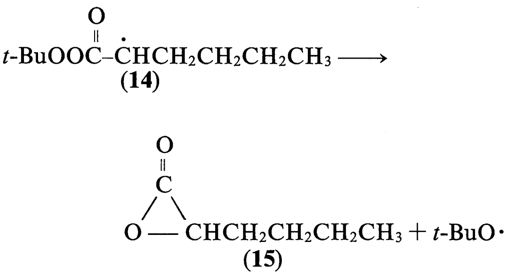
$$\left[\mathrm{CH}(\mathrm{(CH_2)_3CH_3})\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\right]_n \xrightarrow[\text{2) HCl}]{\text{1) KOH}} n\mathrm{CH_3(CH_2)_3}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \qquad (15)$$

(12) **(13)**

Formation of Polyester via 2-Alkanolide Intermediate. Now it is apparent that the major reaction of **6** is the polyester formation. A likely mechanism for the formation of polyester is proposed as follows:



$$t\text{-BuOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2CH_2CH_2\dot{C}H_2} \;\mathbf{(8)} \longrightarrow t\text{-BuOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\dot{\mathrm{C}}\mathrm{HCH_2CH_2CH_2CH_3} \;\mathbf{(14)} \qquad (16)$$



$$t\text{-BuOO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\dot{\mathrm{C}}\mathrm{HCH_2CH_2CH_2CH_3} \;\mathbf{(14)} \longrightarrow \mathbf{(15)} + t\text{-BuO}\cdot \qquad (17)$$

$$n\ \mathbf{15} \longrightarrow \mathbf{12} \qquad (18)$$

Alkyl radical **8** formed by the ring-opening reaction of **7** undergoes an intramolecular hydrogen abstraction from the α-position of carbonyl group, i.e., 1,5-hydrogen shift (Eq. 16). The resulting 1-(*t*-butyldioxycarbonyl)pentyl radical (**14**) attacks the dioxyl bond intramolecularly to afford 2-hexanolide (**15**) (Eq. 17).

It is known that 2-alkanolides are thermally unstable and polymerize spontaneously yielding polyesters, and that such alkanolides are formed from 1-(*t*-butyldioxycarbonyl)alkyl radicals.[10] Thus, 2-hexanolide **15**, if formed, will readily polymerize to yield polyesters.

The key reaction here is the efficient intramolecular hydrogen abstraction (Eq. 16). The high selectivity is obviously based on the quasi-six-membered transition state in the intramolecular S_H2 reaction.[11] An alternative intramolecular S_H2 reaction of **8** is the attack on the peroxidic oxygen via a seven-membered ring transition state.[12] However, no detection of ε-caprolactone or 6-hydroxyhexanoic acid after saponification of polyesters excluded clearly such a reaction. Thus, when in the absence of good hydrogen donors (i.e., in benzene solution), the predominant reaction of **8** is the intramolecular hydrogen atom abstraction to yield 2-hexanolide and ultimately polyester. While in cumene, the intermolecular hydrogen abstraction by **8** from cumene occurs in competition with the intramolecular reaction.

β-Scission of Alkoxy Radicals. The low yield of cyclohexanone and higher recovery of products from alkyl radical **8** suggest that the ring-opening scission of alkoxyl radical **7** is much faster than the scission of *t*-BuOO·. We have previously reported that relative rates of β-scission of radicals from alkoxyl radicals **2** are *i*-Pr:Et:*t*-BuOO:Me=133:33:7:1 at 100 °C. The β-scission ratio, k_6/k_7, can be calculated to be 32 from the yield of cyclohexanone in cumene. The relative ratio indicates that the ring-opening reaction is about 200 times as fast as the scission of methyl radical.

Experimental

IR and NMR spectra were recorded on a JASCO A-3 and a JEOL JNM-GSX270 spectrometers, respectively. GLC analyses were performed with a Shimadzu GC-14A gas chromatograph with a flame ionization detector by using a 15 m flexible fused silica capillary column (0.53 mm in diameter) coated with silicone OV-1. A Shimadzu Chromatopac C-R4A integrator was used for quantitative analyses. Mass spectra were obtained on a JEOL JMS-DX300 mass spectrometer at 70 eV under electron impact conditions. GPC analysis was accomplished on a Shimadzu CTO-6A equipped with a Shimadzu RID-6A using THF as the eluent. Two columns, a Shodex KF-80M (60 cm) and a Shimadzu HSG-10S (60 cm), were connected in series. The calibration curve was made using standard samples of polystyrene.

Materials. 1,1-Bis(*t*-butyldioxy)cyclohexane (**6**) was prepared in the following procedure. To a solution of cyclohexanone (39.3 g, 0.4 mol) and 70% *t*-butyl hydroperoxide (128.7 g, 1.0 mol), cooled to 10 °C, was added dropwise a solution of 65% sulfuric acid (60.3 g, 0.4 mol). After stirring for 2 h at 15 °C, ice water was added, and the organic layer was separated, washed with 5% aqueous KOH and water, and dried over anhydrous magnesium sulfate. The yield of colorless liquid obtained was 89.0%, and the purity by iodometric titration[1] 99.3%. ^{1}H NMR ($CDCl_3$) δ=1.36—1.38 (10H, m, CH_2) and 1.23 (s, 18H, *t*-CH_3).

Cumene was purified by distillation after washing with concentrated sulfuric acid. Reagent grade benzene was used as received.

Typical Procedure for the Thermolysis. A 2 ml solution of **6** (0.05 M) was placed in a glass ampoule. The ampoule was purged with nitrogen, sealed, and immersed in a constant-temperature bath regulated at 100±0.1 °C. For kinetic study, the remaining peroxide was determined by GLC analysis. The decomposition products were analyzed by GLC and/or GC-MS in comparison with authentic samples.

Analysis of High Boiling Residues. The complete decomposition of **6** (2.6 g, 0.1 M) was carried out in benzene for 8 and 10 h at 100 and 120 °C, respectively. After removing benzene and low boiling materials, 1.55 g of viscous liquid was obtained. The viscous liquid was analyzed by IR and GPC. Then 100 g of ethyl alcohol solution of KOH (0.2 M) was added to the viscous liquid, heated under reflux for an hour, and neutralized with 2 M aqueous HCl. After evaporating ethyl alcohol, ether was added to the residue and the ethereal layer was removed. The remaining aqueous layer was acidified to pH=3 with 2 M aqueous HCl and extracted with ether. After drying over anhydrous magnesium sulfate, the solvent was evaporated under reduced pressure. A 1.02 g white crystalline was obtained and analyzed by IR and NMR. After the BF_3-catalyzed esterification with methyl alcohol, the resulting ester was analyzed by GC-MS.

A similar procedure was carried out in cumene and a 0.59 g of white crystalline was obtained.

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