October, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 3045—3046 (1985)*

Thermal Decomposition of 2,2-Bis(*t*-butyldioxy)-3-methylbutane

Takeshi Komai* and Shuji Suyama
Chemicals and Explosives Research Laboratory, Nippon Oil & Fats Co., Taketoyo-cho, Chita-gun, Aichi 470-23

(Received April 1, 1985)

Synopsis. The activation parameters for decomposition of 2,2-bis(*t*-butyldioxy)-3-methylbutane (**2**) in diphenylmethane are $\Delta H^{*}=144.8$ kJ mol^{-1} and $\Delta S^{*}=49.4$ JK^{-1} mol^{-1}. The decomposition products of **2** are *t*-butyl alcohol, acetone, isopropyl methyl ketone and *t*-butyl peracetate. *t*-Butyl peracetate (**4**) is an intermediate which decomposes during reaction. This peroxide **2** decomposes with homolytic one-bond cleavage at one of the peroxide groups and the resulting 1-(*t*-butyldioxy)-1,2-dimethylpropoxyl radical (**3**) decomposes subsequently to *t*-butyldioxy or isopropyl groups with *β*-elimination.

A little report has been published on concerning the decomposition mechanism of peroxides with peroxyacetal structure. Dickey *et al.*[1] reported the thermal decomposition of 2,2-bis(*t*-butyldioxy)butane in cumene and dibutyl phthalate. Kinetic data indicate first order decomposition with an activation energy of 150.6 kJ mol^{-1}. They also obtained 92% of *t*-butyl alcohol per *t*-butoxyl radical as decomposition product. Mageli and co-workers[2] studied the thermal decomposition of butyl 4,4-bis(*t*-butyldioxy)valerate (**1**) in dodecane. As decomposition products they obtained acetone, *t*-butyl alcohol, butyl propionate and butyl levulinate. They proposed the decomposition mechanism of **1** based on some assumption. For example *t*-butyl peracetate (**4**) is proposed as one of the decomposition intermediates, but any amount of **4** was not detected in the decomposition products.

In the present paper, we have studied the thermal decomposition of 2,2-bis(*t*-butyldioxy)-3-methyl butane (**2**) in diphenylmethane.

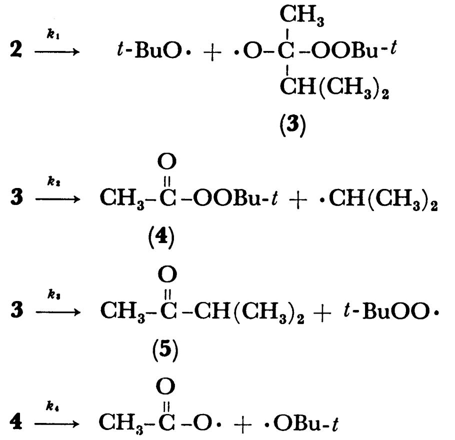
Results and Discussion

The rates of thermal decomposition of **2** were obtained by the disappearance of **2** by GLPC. The results gave good first-order rate constants over two half reaction. When the peroxide concentration was varied over ten to forty-fold range, the variation in the rates was within the experimental error as shown in Table 1. Addition of *t*-butyl catechol as a radical trapper also did not change the rate significantly. These results rule out radical-induced homolysis reactions under the experimental conditions.

The thermal decomposition products of **2** in diphenylmethane were analyzed by GLPC and GLPC-MS techniques, being identified by comparison with the corresponding authentic samples. The liquid products of the decomposition at 110 °C for 4 h are acetone, *t*-butyl alcohol, isopropyl methyl ketone, *t*-butyl peracetate and 1,1,2,2-tetraphenylethane. *t*-Butyl hydroperoxide was not detected. Decomposition products of 74 to 88 percent per the peroxide were obtained.

The dependence of these products on the reaction time is shown in Fig. 1. The decrease of **2** is compatible with the increase of the isopropyl methyl ketone (**5**) and **4**. However in the latter stage (after 12 h) the amount of consumed **2** does not agree with the sum of **4** and **5** because of consecutive decomposition of **4**.

The following scheme for the thermal decomposition of **2** explains the observed experimental data. The initial step is a homolytic one-bond cleavage to give a primary radical (**3**) rather than simultaneous fission of both peroxyl bonds as discussed below.



$$\mathbf{2} \xrightarrow{k_1} t\text{-BuO}\cdot + \cdot\text{O-}\overset{\text{CH}_3}{\underset{\text{CH(CH}_3)_2}{\text{C}}}\text{-OOBu-}t \qquad (1)$$

(**3**)

$$\mathbf{3} \xrightarrow{k_2} \underset{(\mathbf{4})}{\text{CH}_3\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OOBu-}t} + \cdot\text{CH(CH}_3)_2 \qquad (2)$$

$$\mathbf{3} \xrightarrow{k_3} \underset{(\mathbf{5})}{\text{CH}_3\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-CH(CH}_3)_2} + t\text{-BuOO}\cdot \qquad (3)$$

$$\mathbf{4} \xrightarrow{k_4} \text{CH}_3\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O}\cdot + \cdot\text{OBu-}t \qquad (4)$$

Table 1. Rate constants and activation parameters for the decomposition of 2,2-bis(*t*-butyldioxy)-3-methylbutane in Ph_2CH_2

Temp	Initial Concd	$k_d \times 10^4$	Activation Parameters	
°C	M	s^{-1}	ΔH^{*} kJ mol^{-1}	ΔS^{*} JK^{-1} mol^{-1}
90	0.0952	0.108±0.006	141.6±2.0	48.6±5.2
100	0.0952	0.375±1.006		
110	0.0116	1.29±0.06		
110	0.0981	1.38±0.01		
110	0.100[a]	1.36±0.01		
110	0.196	1.33±0.01		
110	0.448	1.37±0.01		
120	0.0952	4.11±0.03		

a) 0.025 M of *t*-butyl catechol is present.

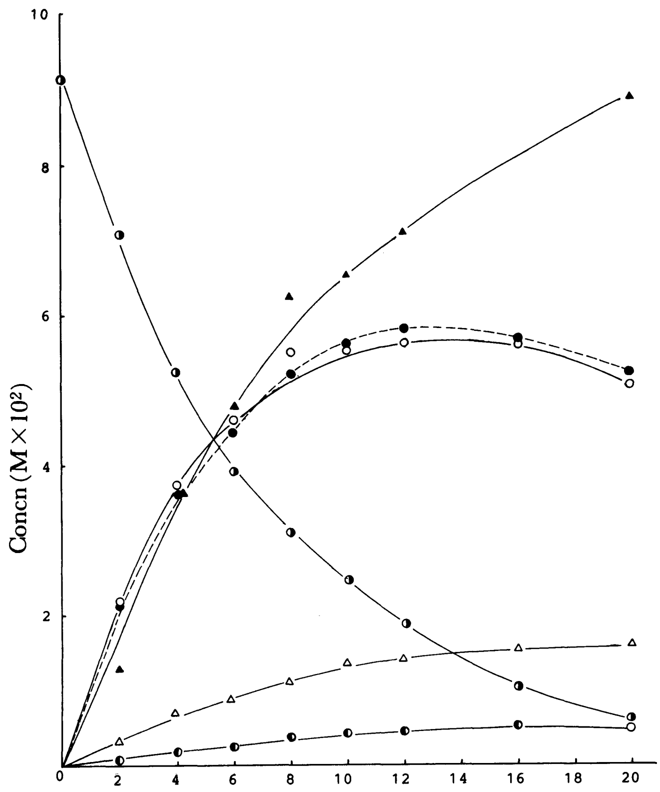


Fig. 1. Decomposition of **2** in Ph_2CH_2 at 100 °C. ▲: *t*-BuOH, △: CH_3COCH_3, ◑: **2**, ◐: **5**, ○: **4**, Observed data. ●: **4**, Theoretical data calculated by Eq. 6 using $[\mathbf{2}]_0=0.0915$ M, $k_1=3.75\times10^{-5}\,s^{-1}$ and $k_4=1.23\times10^{-5}\,s^{-1}$.

The first reason is that the activation parameters for the decomposition of **2** are similar to those of di-*t*-butyl peroxide[3] ($\Delta H^{\neq}=153.8$ kJ mol^{-1}, $\Delta S^{\neq}=48.1$ JK^{-1} mol^{-1}), which shows homolytic cleavage of the peroxyl bond. The second reason is that *t*-butyl peracetate (**4**) is formed in the initial stage of the reaction. From Table 1 and Fig. 1, *t*-butyl peracetate is assumed to be more stable than the peroxyacetal (**2**). In fact, we obtained $1.23\times10^{-5}\,s^{-1}$ at 100 °C and $4.19\times10^{-5}\,s^{-1}$ at 110 °C as the first order rate constants for **4** in diphenylmethane. These values are 30 to 40 percent lower than those of **2**.

The formation of **5** is possible by several paths. One possibility is that **3** abstracts hydrogen atom from solvent and resulting half peroxyacetal decomposes to **5** and *t*-butyl hydroperoxide. However, this route is ruled out with following reason. Table 2 shows yields of **4** and **5** in several solvents at 90 °C. From these results, it is seen that amounts of **5** per consumed **2** and ratio of **4**/**5** are not changed by the solvents, indicating that the hydrogen abstraction is unimportant. Another possibility, the elimination of *t*-butyl peroxyl radical, is reasonable. (Eq. 3). This type of reaction has been already proposed for the decomposition of α,α-bis(*t*-butyldioxy)toluene.[6]

$$\mathrm{Ph{-}C(H)(OOBu\text{-}}t\mathrm{){-}O\cdot \longrightarrow PhC(=O)H + }t\mathrm{\text{-}BuOO\cdot} \qquad (5)$$

Table 2. Yields of isopropyl methyl ketone and *t*-butyl peracetate for the decomposition of **2** in several solvents at 90 °C

Solvent	Consumed **2**	Product M mole		**4**/**5**
	M moles	**4**	**5**	
Ph_2CH_2	0.34	0.28	0.05	5.6
$CFCl_2$–$CFCl_2$	—[a)]	0.17	0.03	5.7
t-BuOH	0.33	0.26	0.04	6.5
$PhC(CH_3)_3$	0.31	0.18	0.03	6.0

a) Not determined.

The methyl radical elimination from the radical **3** is unimportant, since the rate of the elimination of isopropyl radical is thousand order larger than that of methyl radical.[8]

Using equations (1),(2), and (3) and the steady-state assumption, the concentration of **4** is given by Eq. 5.

$$\mathrm{d}[\mathbf{4}]/\mathrm{d}t = \alpha k_1[\mathbf{2}] - k_4[\mathbf{4}] \qquad (5)$$

$$\text{where } \alpha = k_2/(k_2 + k_3),$$

Integration of Eq. 5 gives Eq. 6.

$$[\mathbf{4}] = k_1[\mathbf{2}]_0(\mathrm{e}^{-k_4 t} - \mathrm{e}^{-\alpha k_1 t})/(\alpha k_1 - k_4) \qquad (6)$$

Using $k_1=3.75\times10^{-5}\,s^{-1}$, $k_4=1.23\times10^{-5}\,s^{-1}$, and $[\mathbf{2}]_0=0.0915$ M (1 M=1 mol dm^{-3}), the α value of 0.88 is obtained with simulation. The obtained curve is shown by the dotted line in Fig. 1. The elimination rate of *t*-butyldioxy radical from *t*-alkoxyl radical is about one-seventh of isopropyl radical.

Experimental

Materials. 2,2-Bis(*t*-butyldioxy)-3-methylbutane was prepared by the reaction of isopropyl methyl ketone with *t*-butyl hydroperoxide in the presence of 65% surfuric acid. The purity of this compound was determined by GLPC method was 98.9%: MS (70 eV) *m/z* (rel intensity) 159(2), 73(100), 59(28), and 43(44). IR(CCl_4) 2980, 2930, 2880, 1480, 1390, 1370, 1250, 1200, 1150, 1100, 1030 and 880 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.94 (6H, d, $CH(CH_3)_2$) δ=1.20 (21H, m, *t*-CH_3), δ=2.22 (1H, q, CH).

Analysis of Decomposition Products. Products were analyzed in comparison with an authentic sample by GLPC and GLPC–MS. GLPC analysis was performed on a Shimadzu GC-6A gas chromatograph with column of Silicone SE-30 on Shimalite W, 2m using undecane as an internal standard. The GLPC–MS analysis of the products was carried out with a JEOL JMS D300 mass spectrometer.

References

1) F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Treseder, and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1947).

2) S. W. Bukata, L. L. Zabrocki, M. F. Mclaughlin, J. R. Kolczynsky, and O. L. Mageli, *Ind. Eng. Chem., Prod. Res. Dev.*, **3**, 261 (1964).

3) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

4) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

5) C. Walling and R. T. Clark, *J. Am. Chem. Soc.*, **96**, 4530 (1974).

6) Y-L. Fan and R. G. Shaw, *J. Chem. Soc.*, **1973**, 1803.

7) A. V. Tobolsky and R. B. Mescrobian, "Organic Peroxides," Interscience, New York, (1954), pp. 91—92.

8) D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, **1964**, 2552.