Synthesis and Thermal Decomposition of Di-*t*-Butyl Peroxydicarbonate

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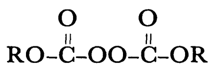
(Received February 25, 1985)

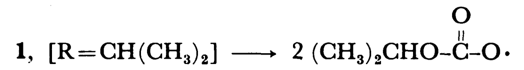
Di-*t*-butyl peroxydicarbonate(DBPD) has been synthesized in a novel route and thermally decomposed at 40—70 °C. The decomposition exhibits first-order kinetics and the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are 122 kJ mol^{-1} and 46 J K^{-1} mol^{-1}, respectively. 2-Methyl-2-propanol is obtained quantitatively as a decomposition product and the rates are a little dependant on the viscosities of solvents, normal alkanes. The mechanism that involves the initial scission of the O-O bond is discussed and the values of the rates and the activation parameters of DBPD are compared with those of diacetyl peroxide and dibenzoyl peroxide.

Dialkyl peroxydicarbonates (**1**) are useful low-temperature initiators of polymerization for vinyl chloride and other monomers.[1] The decomposition rate of di-isopropyl peroxydicarbonate in benzene containing styrene at 54 °C is equal to that of dibenzoyl peroxide in the same medium at 82 °C.[2] However, based on the overall activation energy for the decomposition, 118 kJ mol^{-1}, closer to the values (121 to 126 kJ mol^{-1}) reported for dibenzoyl peroxide, Strain and coworkers[3] proposed that the primary rate-determing step was the same for both peroxides, homolytic cleavage of the peroxide bond.

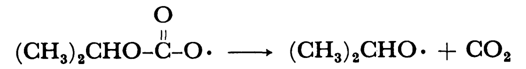


$$\mathrm{RO{-}\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}{-}OR}$$

(**1**)

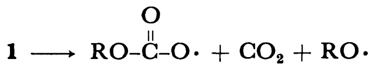


$$\mathbf{1},\ [\mathrm{R{=}CH(CH_3)_2}] \longrightarrow 2\,\mathrm{(CH_3)_2CHO{-}\overset{O}{\overset{\|}{C}}{-}O\cdot} \qquad (1)$$



$$\mathrm{(CH_3)_2CHO{-}\overset{O}{\overset{\|}{C}}{-}O\cdot} \longrightarrow \mathrm{(CH_3)_2CHO\cdot} + \mathrm{CO_2} \qquad (2)$$

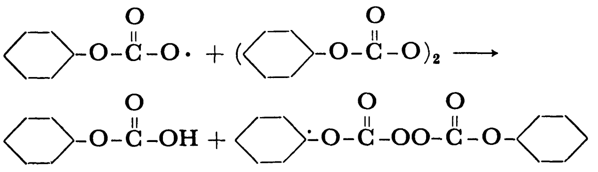
McBay and Tucker[4] examined the thermal decomposition products of peroxydicarbonates in several solvents at 140 °C, and proposed a different decomposition scheme.



$$\mathbf{1} \longrightarrow \mathrm{RO{-}\overset{O}{\overset{\|}{C}}{-}O\cdot} + \mathrm{CO_2} + \mathrm{RO\cdot} \qquad (3)$$

A more recent study[5] of dicyclohexyl peroxydicarbonate (**1**, R=C_6H_{11}) indicated that it was decomposed by the homolytic one-bond fission (Eq. 1) and the decarboxylation of the generated alkoxycarboxyl radical (Eq. 2) was negligible at 50 °C, compared to the reaction with solvent or bimolecular disproportionation.

One of the complexities of the decomposition mechanisms of peroxydicarbonates is that the homolytic decomposition is accompanied with the induced decomposition. For instance, the α-hydrogen atom of dicyclohexyl peroxydicarbonate is abstracted easily by the alkoxycarboxyl radical.[5]

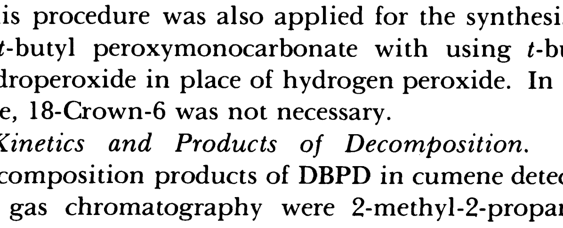


(4)

The amounts of homolytic (Eq. 1) and induced decompositions (Eq. 4) are nearly equal at 0.1 M† in benzene solution.[5] Hence, we have supposed that di-*t*-alkyl peroxydicarbonate (**I**, R=*t*-alkyl) which lacks the α-hydrogen atom in the alkyl group is more suitable for clarifying the homolytic decomposition mechanisms than primary or secondary analogues. For this purpose, we have synthesized di-*t*-butyl peroxydicarbonate (**I**, R=*t*-C_4H_9, DBPD) and measured the decomposition rates and products at 40—70 °C.

Results and Discussion

Synthesis. Di-primary and secondary alkyl peroxydicarbonates have been synthesized by conventional reactions between alkyl chloroformates and hydrogen peroxide in aqueous alkali solution.[6] However, in the case of the synthesis of DBPD the yield is low because *t*-butyl chloroformate is unstable under the reaction conditions.[7] We synthesized DBPD in a novel route from 2-(*t*-butoxycarbonyloxyimino)-2-phenylacetonitrile (Boc ON) (**2**) and hydrogen peroxide in the presence of dicyclohexyl 18-crown-6 (18-Crown-6) equivalent to potassium hydroxide at 2 °C (See Experimental).



$$2\,t\text{-}\mathrm{BuO\overset{O}{\overset{\|}{C}}ON{=}\underset{\underset{CN}{|}}{C}{-}Ph} + \mathrm{H_2O_2} \xrightarrow[\text{in THF}]{\text{18-Crown-6, KOH}} t\text{-}\mathrm{BuO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}OBu}\text{-}t \qquad (5)$$

(**2**) DBPD

This procedure was also applied for the synthesis of di-*t*-butyl peroxymonocarbonate with using *t*-butyl hydroperoxide in place of hydrogen peroxide. In this case, 18-Crown-6 was not necessary.

Kinetics and Products of Decomposition. Decomposition products of DBPD in cumene detected by gas chromatography were 2-methyl-2-propanol, 1,1,2,2-tetramethyl-1,2-diphenyl-ethane and a small amount of *t*-butyl α,α-dimethylbenzyl carbonate. In dodecane and chlorobenzene containing 0.1 M cyclo-

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† 1 M=1 mol dm^{-3}.

Table 1. Decomposition products of dbpd

Temp	Solvent	Initial concd	Products/M		
°C		of DBPD/M	t-BuOH	t-BuOCO$_2$CMe$_2$Ph	(PhCMe$_2$)$_2$
50	PhCHMe$_2$	0.0203	0.0400	ca. 0.0006	0.0104
50	PhCHMe$_2$	0.201	0.436	ca. 0.014	0.105
50	n-C$_{10}$H$_{22}$	0.0200	0.0442	—	—
40	PhCl (0.1 M c-C$_6$H$_{12}$)	0.0212	0.0443	—	—

Table 2. Rate constants for thermal decomposition of dbpd

Solvent	Viscosity[a] cP	Initial concd of DBPD/M	Temp °C	10^5k_{obsd}[b] s^{-1}
Cumene	0.613	0.0203	40	0.722±0.012
Cumene	0.560	0.0203	50	3.12±0.07
Cumene	0.560	0.201	50	3.78±0.12
Cumene	0.490	0.0203	60	11.6±0.3
Cumene	0.440	0.0203	70	49.0±0.4
Hexane	0.235	0.0229	50	3.29±0.03
Decane	0.623	0.0215	50	3.23±0.03
Octadecane	2.29	0.0209	50	3.10±0.07

a) Viscosity of cumene was obtained from *Beilstein III*, **5**, p. 879 and those of n-alkanes from Ref. 12. b) Rate constants and their standard deviations were calculated by the method of least squares.

hexane, 2-methyl-2-propanol and unidentified products were obtained. Table 1 summarizes the products data on DBPD decomposition. Thermal decomposition rates were measured by following the disappearance of DBPD by the iodometric titration. The data exhibit first-order kinetics over the temperature range employed (40—70 °C).

Table 2 summarizes the rate constants for the decomposition in cumene and other solvents. When the decomposition is carried out over a ten fold variation in the initial concentration, the rate constant of the reaction increases approximately 20%. This indicates that the data of Table 2 are not pure unimolecular first-order but involving some induced decomposition.

Using the method of Nozaki and Bartlett[8] an attempt was made to separate the induced decomposition (k_i) and the unimolecular decomposition (k_d) by the following equation.

$$-\frac{\mathrm{d[DBPD]}}{\mathrm{d}t} = k_d\mathrm{[DBPD]} + k_i\mathrm{[DBPD]}^{3/2} \qquad (6)$$

The values of $k_d=2.77\times10^{-5}\,\mathrm{s}^{-1}$ and $k_i=3.47\times10^{-5}\,\mathrm{M}^{-1/2}\,\mathrm{s}^{-1}$ are obtained. In the decomposition of dicyclohexyl peroxydicarbonate (**I**, R=C$_6$H$_{11}$) in benzene at the same temperaure (50 °C), the values of $k_d=3.9\times10^{-5}\,\mathrm{s}^{-1}$ and $k_i=1.39\times10^{-4}\,\mathrm{M}^{-1/2}\,\mathrm{s}^{-1}$ were reported.[5] For the decomposition of dibenzoyl peroxide the values of $k_d=3.3\times10^{-5}\,\mathrm{s}^{-1}$ and $k_i=4.3\times10^{-5}\,\mathrm{M}^{-1/2}\,\mathrm{s}^{-1}$ were reported in both benzene and toluene at 80 °C.[8] From these results it can be understood that the ratio of the induced decomposition of DBPD to the unimolecular one is similar to that of dibenzoyl peroxide, but its value is 1/3-fold of that of dicyclohexyl peroxydicarbonate.

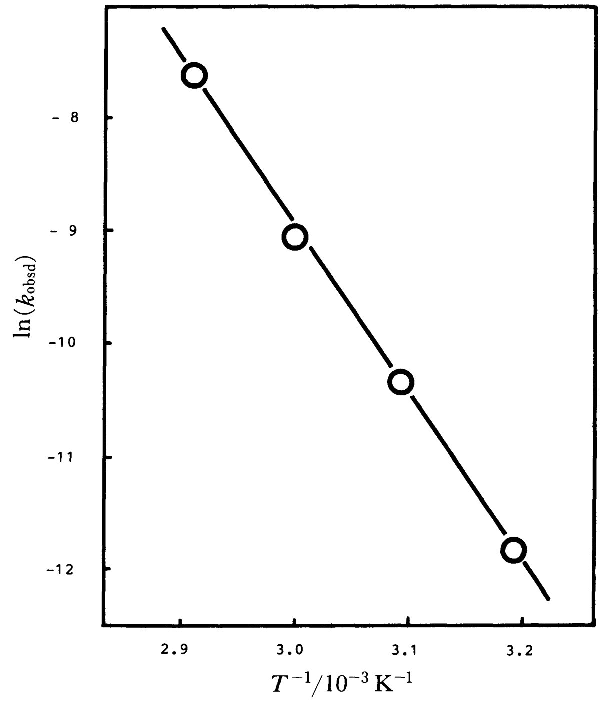


Fig. 1. Arrhenius plot for decomposition of 0.0203 M DBPD in cumene.

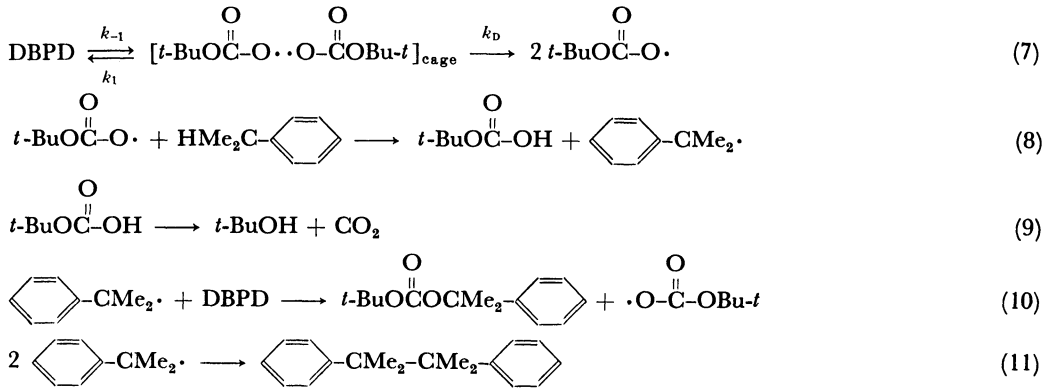
Figure 1 shows an Arrhenius plot for the decomposition of DBPD of 0.0203 M in cumene in the range of 40—70 °C. Table 3 indicates the relative rate at 50 °C and the activation parameters of the DBPD together with those of dibenzoyl peroxide and diacetyl peroxide.

The formation of above-mentioned products and the observed kinetic data can be understood in terms of the reactions in Scheme 1.

Table 3. Relative rates and activation parameters with decomposition of DBPD, diacetyl and dibenzoyl peroxide

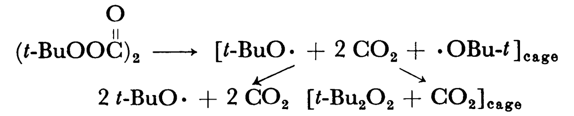
Peroxide	Solvent	Relative rate at 50 °C	Activation parameter	
			$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/JK^{-1} mol^{-1}
DBPD	Cumene	43	122	46
Diacetyl[a]	Toluene	1.8	130	44
Dibenzoyl[b]	Acetophenone	1.0	126	19

a) See Ref. 9. b) See Ref. 10.



Scheme 1.

Niki and Kamiya decomposed di-*t*-butyl diperoxyoxalate in a cumene–benzene mixture at 45 °C and obtained 5.8% of di-*t*-butyl peroxide as the cage product, 4.4% of acetone and 90.8% of 2-methyl-2-propanol.[11]



$$(t\text{-BuOO}\overset{\text{O}}{\overset{\|}{\text{C}}})_2 \longrightarrow [t\text{-BuO}\cdot + 2\,\text{CO}_2 + \cdot\text{OBu-}t]_{\text{cage}} \swarrow 2\,t\text{-BuO}\cdot + 2\,\text{CO}_2 \quad \searrow [t\text{-Bu}_2\text{O}_2 + \text{CO}_2]_{\text{cage}} \qquad (12)$$

$$t\text{-BuO}\cdot \xrightarrow{\text{RH}} t\text{-BuOH} \qquad (13)$$

$$t\text{-BuO}\cdot \longrightarrow \text{Me}_2\text{CO} + \text{Me}\cdot \qquad (14)$$

In the case of DBPD decomposition 2-methyl-2-propanol was nearly quantitaively obtained, but acetone, *β*-scission product of *t*-butoxyl radical (Eq. 14) was not detected (Table 1). Furthermore, di-*t*-butyl peroxide, as the cage product of two *t*-butoxyl radicals (Eq. 12) and di-*t*-butyl peroxymonocarbonate, that of *t*-butoxyl and *t*-butoxycarboxyl radicals, also were not detected. These results show that *t*-butoxyl radical is not present under the experimental conditions. Accordingly DBPD decomposes with one-bond homolysis, and the decarboxylation of the resulting *t*-butoxycarboxyl radical does not compete with hydrogen abstraction from cumene. This agrees with Van Sickle's results.[5]

The solvent viscosity dependence of the observed rate is one of the methods of separating the concerted and stepwise mechanisms for the peroxide decomposition. The relationship[12] between the observed rate constant (k_{obsd}) and the solvent viscosity (η) is written as

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 A_{\text{D}}}\left(\frac{\eta}{A_{\text{v}}}\right)^{\alpha} \qquad (15)$$

Table 4. Cage return of peroxides

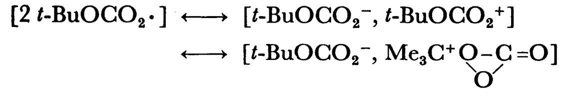
Peroxide	Temperature °C	f_{r}
DBPD[a]	50	0.04
Diacetyl[b]	80	0.28
Dibenzoyl[c]	80	0.02

a) In decane. b) In octane (See Ref. 13). c) In 2,2,4-trimethylpentane (See Ref. 13).

where k_1 is the rate constant for bond homolysis; k_{-1} is the rate constant for cage return; A_{D} and A_{v} are Arrhenius preexponential factors for solute diffusion and self-diffusive flow of solvent, respectively, and α is a proportionality constant between the activation energies for the above-mentioned diffusion and flow ($E_{\text{D}}=\alpha E_{\text{v}}$), set equal to 0.5 for the calculation. The fraction (f_{r}) of geminate radicals which combine to reform the parent peroxydicarbonate is defined as

$$f_{\text{r}} = \frac{k_{-1}}{k_{-1}+k_{\text{D}}} = 1 - \frac{k_{\text{obsd}}}{k_1} \qquad (16)$$

The value of the rate constant for bond homolysis (k_1) of DBPD is estimated to be $3.37\times10^{-5}\,\text{s}^{-1}$ from the intercept of a plot of $1/k_{\text{obsd}}$ *vs.* $(\eta/A_{\text{v}})^{0.5}$ using the values in Table 2 and Ref. 12. The value of f_{r} in decane can be calculated from Eq. 16. The obtained data are presented in Table 4 with those of dibenzoyl and diacetyl peroxides.[13] The values of $f_{\text{r}}>0.1$ have been expected for the peroxides which decompose with one-bond fission. The value of $f_{\text{r}}=0.04$ for DBPD may suggest its two-bond concerted fission. However, dibenzoyl peroxide which decomposes with one-bond fission also has very low f_{r} value (Table 4). Pryor[13] proposed that a larger activation barrier exists for the combination of benzoyloxyl radicals than for acetoxyl radicals. In the case of DBPD, the resonance structures can be written for geminate pair.



$$[2\ t\text{-BuOCO}_2\cdot] \longleftrightarrow [t\text{-BuOCO}_2^-, t\text{-BuOCO}_2^+] \longleftrightarrow [t\text{-BuOCO}_2^-, \text{Me}_3\text{C}^+\text{O}\!-\!\text{C}\!=\!\text{O}]$$

We believe that the solvent viscosity effect test is not a sure method for distinguishing between one-bond and concerted two-bond fission.

The decomposition rate of DBPD is 43 and 24 fold faster than those of dibenzoyl and diacetyl peroxides at 50 °C, respectively (Table 3). However, the activation enthalpies of these three peroxides are almost the same values (*ca.* 125 kJ mol^{-1}), which support the above-mentioned one-bond fission of DBPD (Eq. 7). Hammett's σ_p values of alkoxycarbony,[14] benzoyl and acetyl groups are 0.310, 0.459, and 0.509, respectively. Those of methoxyl, phenyl and methyl groups are −0.37, −0.01, and −0.170, respectively.[15] The alkoxycarbonyl or methoxyl group is the most electron-donating substituent, respectively, in the above-mentioned two sequences, but the difference of electron-donating ability among the substituents in each sequence is small. We suppose that the faster decomposition rate of DBPD than those of diacetyl and dibenzoyl peroxides arises not only from the simply electrostatic repulsion between the peroxyl oxygen atoms, but also from the structural factor of *t*-butoxycarboxyl group.[16]

t-Butyl α,α-dimethylbenzyl carbonate is produced by radical induced decomposition of DBPD (Eq. 10). It is clear from the effects of initial peroxide concentration on the rate and product (Table 1 and 2). But its amount is small. On the other hand, the yield of a radical coupling product, 1,1,2,2-tetramethyl-1,2-di-phenylethane (Eq. 11) is *ca.* 50%. Thus, di-primary or secondary alkyl peroxydicarbonates accept two types of induced decompositions, one is the attack to the peroxyl bond and the other is the abstraction of the α-hydrogen atom on the alkoxyl group.

Experimental

IR and NMR spectra were recorded on a JASCO A-3 and a JEOL JNM-MH-100 spectrometer, respectively. GC analysis was carried out by a Shimadzu GC-6A gas chromatograph using two columns: PEG 20 M, 5% on Shimalite AW-DMCS, 2 m; Silicon GE SE-30, 5% on Shimalite W, 0.5 m. GC-MS spectra were recorded on a JEOL JMS-D300 mass spectrometer.

Materials. 2-(*t*-Butoxycarbonyloxyimino)-2-phenylacetonitrile (Boc-ON) was obtained from Protein Research Foundation. Potassium hydroxide, THF, acetone, 2-methyl-2-propanol, cyclohexane, petroleum ether and dicyclohexyl-18-crown-6 (18-Crown-6) were the products of Wako Pure Chemical Ind. Co. Di-*t*-butyl peroxide was the product of Nippon Oil & Fats Co., Ltd. Cumene, chlorobenzene, cyclohexane, hexane, decane and octadecane, pure grade, obtained commercially, were stirred for several hours with concentrated sulfuric acid, washed with 10% sodium hydrogencarbonate and distilled water, dried with drying agents and distilled through a 24-in Vigreux column. The sample of 1,1,2,2-tetramethyl-1,2-diphenylethane was prepared by the literature method.[17] Purities of these materials were checked by melting point, IR, NMR, and/or GC analysis.

Di-t-Butyl Peroxydicarbonate. To a solution of dicyclohexyl-18-crown-6 (18-Crown-6)(81.9 g, 0.22 mol) in THF (200 cm^3) was added the fine powder of potassium hydroxide (14.5 g, 0.22 mol). After being stirred at room temperature till the powder was dispersed completely, 50% hydrogen peroxide (27.2 g, 0.40 mol) in THF (200 cm^3) was added dropwise to the mixture at 5 °C. Then the mixture was added dropwise at 2 °C for 15 min to Boc-ON (50.8 g, 0.20 mol) in THF (200 cm^3) and the reaction mixture was stirred again at 20 °C for 5 h. After petroleum ether (400 cm^3) was added to the reaction mixture the precipitate formed was filtered. The filtrate was washed four times with water (100 cm^3) and dried over anhydrous Na_2SO_4, and then the solvent was evaporated. The oily residue was crystallized twice from ether by cooling in Dry Ice-acetone to give di-*t*-butyl peroxydicarbonate (DBPD) as white crystals in 8.4% yield. On titration for active oxygen, the purity of the product was shown to be 98.4%. mp 32—34 °C (lit,[7] mp 28—30 °C); IR (CCl_4): 1820 (C=O) and 1795 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ=1.58 (1H, s, *t*-CH_3). Found: C, 50.57; H, 7.98% Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75%.

Di-t-Butyl Peroxymonocarbonate. To a suspension of the fine powder of potasium hydroxide (13.2 g, 0.20 mol) in THF (120 cm^3) there was added 80.5% *t*-butyl hydroperoxide (44.8 g, 0.40 mol), and stirred at room temperature till the powder was dispersed completely. Then to the mixture there was added dropwise Boc-ON (24.6 g, 0.10 mol) in THF (100 cm^3) at 30 °C for 1 h and stirred at 35 °C for 6 h. After petroleum ether (200 cm^3) was added to the reaction mixture, the precipitate formed was filtered. The filtrate was washed with 5% NaOH (50 cm^3) and water (50 cm^3), respectively twice, and dried over anhydrous Na_2SO_4, and the solvent was evaporated. The crude product was distilled through a short Vigreux column at 48—50 °C under decreased pressure of 0.9 mmHg (1 mmHg=133.322 Pa) (lit,[18] bp 46—47 °C at 0.47 mmHg) to give di-*t*-butyl peroxymonocarbonate (DBPM); IR (Neat): 1785 (C=O) and 1760 cm^{-1} (C=O); ^{1}H NMR (CCl_4): δ=1.46 (1H, s, *t*-CH_3) and (1H, s, Peroxyl *t*-CH_3). Found: C, 62.59; H, 6.93% Calcd for $C_9H_{18}O_4$: C, 62.84; H, 6.71%.

Kinetic Procedure. A weighed sample of DBPD was dissolved in a known volume of the solvent. Samples (generally 4 cm^3) of solution were pipetted into test tubes. The solutions were exhaustively evacuated, and the tubes were sealed in an atmosphere of nitrogen. The evacuation procedure consisted of cooling in a Dry Ice-acetone bath, evacuation on an oil pump and warming to 10 °C. This was repeated three times before sealing. The tubes were completely immersed in an oil thermostat regulated to ±0.05 °C. At successive time intervals, tubes were removed from the constant temperature bath and immersed in a Dry Ice-acetone bath. Then the concetration of DBPD in the solution was measured by iodometry titration. The reaction were followed up to 75—80% decomposition and exhibited first-order kinetics. The titration procedure involved the use of a mixture (20:2) of isopropyl alcohol and acetic acid as the solvent, and saturated potassium iodide as the source of iodine. After boiling of 3 min for liberation of iodine, the iodine was titrated to a starch end point with 0.01 N thiosulfate for the dilute solution and 0.1 N thiosulfate for the concentrated solution. The values for the observed first-order rate constants and their standard deviations were calculated from the first-order rate equation using the method of least squares. The values for the activation parameters and their standard deviations were calculated from absolute rate equation of Eyring using the method of least squares.

Decomposition Products. DBPD in solutions was decomposed completely at 40 °C for 130 h and at 50 °C for 40 h and the solutions were analyzed by gas chromatography and mass spectrometer. Effluent peaks were identified by comparing retension times with those of authentic samples and by GC–MS spectra; product, *m/z* (rel. intensity); 2-methyl-2-propanol, 49 (100), 41 (17), and 31 (25); *t*-butyl α,α-dimethylbenzyl carbonate, 236 (M^+, 10), 180 (57), 162 (20), 119 (100) and 57 (65); 1,1,2,2-tetramethyl-1,2-diphenylethane, 238 (M^+, 4), 119 (100) and 91 (22). Cyclohexane and decane were added as internal standards, and the response factors were determined for the identified products with the column of PEG 20 M. The factor of *t*-butyl α,α-dimethylbenzyl carbonate was estimated by comparing its peak with that of 1,1,2,2-tetramethyl-1,2-diphenylethane taking into account the difference of the molecular weight. Di-*t*-butyl peroxide and DBPM were not detected from the gas chromatograph using the columns of PEG 20 M (DBPM was decomposed through the measurement.) and Silicone GE-SE-30 (DBPM was not decomposed through the measurement.) in comparision with the authentic samples.

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