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The Thermal Decompositions of Dialkyl Peroxides

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With the purpose of obtaining information needed for hazard prevention, pure liquid dialkyl peroxides (di-*t*-butyl peroxide (**1**), bis(1-methyl-1-phenylethyl) peroxide (**2**), *t*-butyl 1-methyl-1-phenylethyl peroxide (**3**), 2,5-bis(*t*-butyldioxy)-2,5-dimethylhexane (**4**)) were subjected to thermal-decomposition experiments, in which thermal analyses were conducted by the use of a thermogravimetry (TG)-differential scanning calorimetry (DSC) apparatus equipped with a pinholed pan with a minute pinhole. From the DSC curves recorded, we obtained the decomposition temperature of Samples **2**, **3**, and **4**, as a constant value for each sample, and the maximum exothermic peaks at the optimum pinhole diameters (0.07—0.2 mm). The heats of decomposition obtained could be considered appropriate, as they roughly agreed with the estimated value, on the other hand, **1** shows no exothermic peak under these condition. Plotting by the Coats-Redfern method based on the TG-curve data (**2**, **3**, and **4**) gave reaction orders of more than unity, activation energies of 33—37 kcal_{th}/mol, and frequency factors of 10^{16}—10^{18} s^{-1}. It is conceivable that these results could be derived by virtue of the TG–DSC curves that were suitable in obtaining thermochemical parameters. In other words, the analysis method introduced in this paper was found to be an efficient one for liquid peroxides that are difficult to analyze by a conventional TG–DSC method.

Organic peroxides are used as polymerization initiators, curing agents, and crosslinking agents in polymer industries,[1] but they are so unstable that they readily decompose or explode when affected by heat or impact.[2] From the viewpoint of hazard prevention, it is important to have knowledge about the thermal instability of organic peroxides,[3] and one of the means to achieve this is the measurement of the activation energy[4,5] as well as the heat of decomposition.[6] However, almost all reported examples have been measurements of activation energies and frequency factors through a determination of the thermal decomposition rates either in a gas phase or in a low-concentration solution diluted in a solvent.[4,5] Furthermore, there have been hardly studies of measuring heats of decomposition.[6]

Recently, thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have come to be commonly used in measuring the thermal decomposition of organic peroxides.[7] Uetake *et al.* determined the activation energy and heat of decomposition of benzoyl peroxide through thermal decomposition by means of a TG–DSC apparatus.[8] Although a TG–DSC for solid materials like this is generally satisfactory, an analysis of liquid materials is extremely difficult because of the influense of the vaporization of the sample.[9,10] The difficulties in performing an acurate measurememt come from the following facts: a TG curve is a result of the overlapping of the weight change pertaining to the reaction and the weight loss caused by the vaporization of the sample, while a DSC curve is the outcome of the overlapping of the exotherm, along with its apparent decrease caused by the sample loss, and the latent heat of vaporization. As a matter of fact, most organic peroxides are in a liquid state around their decomposition temperatures; hence, examinations of either the procedure or the apparatus used for measurement are necessary in order to obtain an appropriate TG curve or DSC curve by the use of a TG–DSC apparatus. A sealed cell reportedly gives an apparently lower heat of decomposition[11] and, furthermore, cannot provide a TG curve, so that it is not suitable for our present purpose, a comprehensive evaluation. The use of a pinholed pan can, though, be proposed as a solution to this problem.[12]

This study of such organic peroxides deals with experiments using an apparatus with a pinholed pan, and intends to establish the procedure for obtaining an appropriate TG–DSC curve and derive the basic data to provide useful knowledge for hazard prevention. From an analysis of the pyrolysis experiments, an evaluation of the values of the heat of decomposition obtained is also attempted.

Experimental

Materials. Selected dialkyl peroxides are: di-*t*-butyl peroxide (**1**), bis(1-methyl-1-phenylethyl) peroxide (**2**), *t*-butyl 1-methyl-1-phenylethyl peroxide (**3**), and 2,5-bis(*t*-butyldioxy)-2,5-dimethylhexane (**4**). The commercial product (Nippon Oil and Fats Co., Ltd.) for each was used after purification. Peroxide **2** was recrystallized from ethanol.[13] Peroxide **3** was recrystallized twice at −70 °C, and the product was distilled *in vacuo* at room temperature.[14] Both **1**[15] and **4**[16] were distilled *in vacuo* at room temperature. All the samples were at least 99.0% pure.

Measurement. An aluminum sealed-type cell, with an outer diameter of 4.6 mm, 2 mm deep, and 0.1 mm thick, was utilized as a sample cell for measurement. After placing a sample in it, it was covered with an aluminum cover pinholed beforehand and was sealed by hermetical pressing by the use of a sample sealer. Hereafter, this type of sample cell will be called "a pinholed pan." After sealing, the dimensions of the pinholed pan came to be 4.6 mm in outer diameter, 2.8 mm thick, and 46.5 mm^2 in capacity. The weighing of the sample taken in was quickly carried out just after the sealing. The pinhole was bored by a needle at the center of the cover, and its diameter was measured by a microscopic scale.

The behavior on the heating of the sample in a pinholed pan was followed by a standard-type TG–DSC apparatus made by Rigaku Denki. The conditions of measurement

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were: sample weight, 1.2—2.0 mg; heating rate, 2.5 °C/min; air atmosphere. For comparison, experiments with an open cell with no cover and those with a sealed cell with no pinhole in the cover were also conducted.

The relationships between the pinhole diameter of the pinholed pan and the TG curve as well as the DSC curve were examined, and the activation energy, the frequency factor, and the reaction order were derived from the appropriate TG curve by the use of the Coats-Redfern method.[17] The decomposition temperature and the heat of decomposition were also derived from the DSC curve.

The pyrolysis gas-chromatograph apparatus employed has been described previously.[8] The procedures used for the pyrolysis of the sample and the analysis of the pyrolysis products are essentially the same as those reported in a previous paper.[18] About 1 milligram of **4** was used for pyrolysis.[19] Samples were then pyrolyzed rapidly at 330 °C. The analytical conditions were as follows; column, Porapak Q (100—120 mesh), 3 m, 70 °C (in the case of acetone, 150 °C); detector, FID, 220 °C; N_2-flow rate, 20 ml/min; injection temperature, 150 °C.

Results and Discussion

Before proceeding to a detailed evaluation of the thermal decomposition of dialkyl peroxides by the use of the TG–DSC apparatus with a pinholed pan, let us mention that a study was made of the effects of the sample weight and the heating rate, which could conceivably have influenced the results. In the sample-weight (1—4 mg)-dependence determinations, all the runs were made at a heating rate of 2.5 °C/min, while in the heating-rate (1.25—20 °C/min)-dependence determinations, the sample weight in each case was 1.0—2.0 mg.

Consequently, it was found in the present study that the exothermic peak areas decreased with an increase in either the heating rate or the sample weight. However, there were no detectable differences in the peak areas obtained under the conditions of a sample weight of 1.0—2.0 mg, and a heating rate of 2.5 °C/min. The standard procedure described above can, therefore, be employed and is, as a matter of fact, more desirable.

Pinhole-diameter Dependence of the Thermal Properties. Figure 1 shows the relationship between the TG–DSC curve and the pinhole diameter of the pinholed pan for **2**, **3**, and **4**. The TG curves for all three samples shift to the high-temperature side, and their slopes become gentle, with a decrease in the pinhloe diameters. In the case of **2**, no change was observed in the initial decomposition temperature for the pinhole diameter range of 0.05—0.08 mm, while with an open cell the initial decomposition temperature gave rise to a small shift to the low-temperature side. Similar tendencies were observed for **3** and **4**, while, with an open cell, the plateaus of the curves were scarcely observed at all because of the drastic vaporization loss.

As for the DSC curves, all three samples showed a somewhat different pattern in relation to the decrease in the pinhole diameter. In the case of **2** with a pinhole diameter of less than 0.15 mm, we observed an endotherm trough behind the exotherm peak. As an explanation for this, we can postulate that, with a decrease in the pinhole diameters, the high-boiling decomposition products come to remain in the cell for a longer period of time, giving rise to the appearance of an endotherm trough caused by their vaporization, accompanied by a tendency for the trough to deepen gradually. The run with a closed cell gives a reduced area of the exotherm peak. In the case with an open cell, the starting of the decomposition is obscure and the exotherm peak is small, making the analysis very difficult.

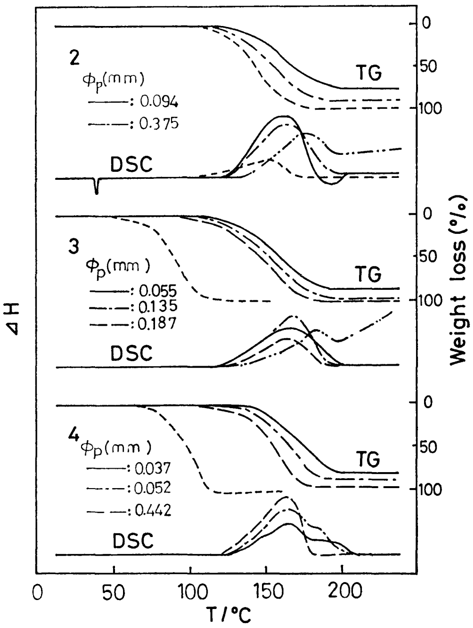

Fig. 1. Variations of TG and DSC curves for each of **2**, **3**, and **4** with various pinhole diameter (ϕ_p). ----: Open cell, ——; — — —; ——: pinholed pan —··—: closed cell.

Peroxide **3** behaved very much like **2**, but it did not display a decomposition exotherm peak for the open cell. Peroxide **4** showed a similar tendency in the range down to the pinhole diameter of about 0.1 mm, but at a more reduced diameter (as low as 0.05 mm or below) a shoulder peak appeared behind the main exotherm peak; furthermore, at a diameter of 0.037 mm or below, another shoulder peak appeared before the main peak. These small peaks seem to be the outcome of the clear detection of such minute thermal changes that were not detectable with an open cell, but came to be apparent with a pinholed pan with a minute pinhole. Peroxide **1** gave neither a TG curve nor a DSC curve that could afford analysis, even with a pinholed pan with a minute pinhole (0.037 mm or below), because of its too rapid vaporization.

Figure 2, showing the DSC curve for **2**, presents the relationships of the starting of the exotherm peaks, the peak temperatures, and the end temperatures *versus* the pinhole diameters. These decomposition-related temperatures exhibit little change and are nearly constant with a decrease in the pinhole diameters. Peroxides **3** and **4** give nearly content values in a similar manner, except that the end temperature for **4** shifts almost linearly to the high-temperature side. This is understandably related to the phenomena pertaining

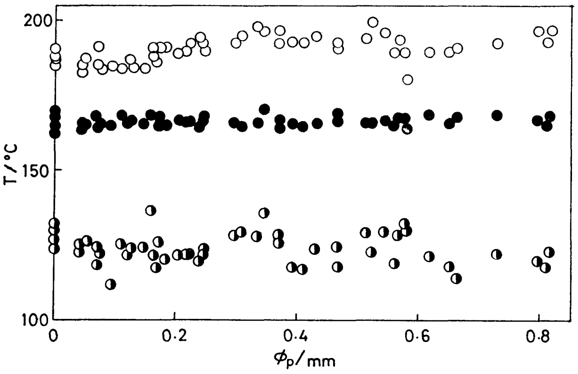

Fig. 2. The relationships of starting of exotherm peaks (◑), peak temperatures (●), and end temperatures (○) *vs.* pinhole diameters as related with the DSC curves for **2**.

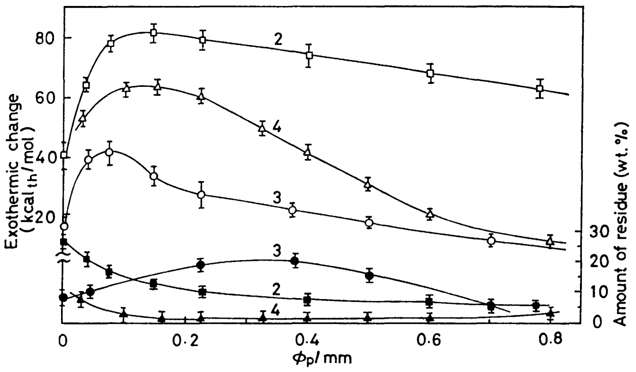

Fig. 3. Plots of exothermic change (□, ○, △) and amount of residues after decomposition (■, ●, ▲) *vs.* change in pinhole diameters for each of **2**, **3**, and **4**.

to the complicated decomposition reaction of **4** (see Fig. 1). The results of the decomposition-temperature measurements for these three samples are summarized in Table 1. The end temperature of **4** is shown for the run with a pinhole diameter of 0.1 mm (the value in the parentheses is for 0.6 mm).

Figure 3 shows the relationships of the heats of decomposition and the amounts of the residue after decomposition *versus* the change in the pinhole diameters. In the case of **2**, the heat of decomposition increases linearly with a decrease in the pinhole diameter and reaches the peak of 80.0 kcal$_{th}$/mol*** at the diameter of 0.2—0.1 mm. With a further reduction of pinhole diameter, the calorific value sharply decreases, giving the minimum value of 40.0 kcal$_{th}$/mol for the case with a closed cell. The amount of residue after the reaction increases slightly with a decrease in the pinhole diameter, while the rate of increase is enhanced by decreasing the diameter to 0.15 mm or below.

In contrast with **2**, **3**, and **4** exhibit somewhat different tendencies in both the heat of decomposition and the amount of residue after the reaction, but are similar to **2** in their maximum values of heat of decomposition: 41.5 kcal$_{th}$/mol at the pinhole diameter of 0.08 mm for **3** and 62.5 kcal$_{th}$/mol at the pinhole diameter of 0.13 mm for **4**.

TABLE 1. VALUES OF THE DECOMPOSITION TEMPERATURES FOR THESE THREE SAMPLES

Compound	Starting of exothermic peak (°C)	Peak temperature (°C)	End temperature (°C)
2	123±3.8	165±3.5	186±4.0
3	126±4.0	167±3.0	196±5.0
4	123±4.0	163±3.2	200±4.0 (174±5.4)

From the above findings, it can be postulated that the increase in the apparent heat of decomposition with an early decrease in the pinhole diameter is caused by some suppression of the sample vaporization of the spreading of heat,[12] and that the decrease in the apparent heat of decomposition with a further decrease in the pinhole diameter, nearing the closed state, is the outcome of the suppression of the decomposition itself effected by the enhanced partial pressure of the produced gas.[20,21] In addition, the increased amount of tarry residue after the reaction at the smaller pinhole diameter suggests the occurrence of endothermic reactions associated with the conversion of products into high-boilers and the deposition of carbon.

Thermochemical Parameters. The results and discussion of the above experiments suggest that the TG curve best fitted for obtaining thermochemical parameters is the one obtained from a measurement using a pinholed pan with a pinhole diameter suitable for minimizing the overall effect of the sample vaporization and the partial pressure of the produced gas. From such a TG curve, the reaction order (n), activation energy (E_a), and frequency factor (A) were obtained by the Coats-Redfern method:

$$\log\left[\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{\phi E_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \tag{1}$$

where x is the fraction of the sample decomposed at a certain time, t, and where ϕ is the heating rate. T is the absolute temperature, and R is the gas constant. This equation holds for an n-order reaction when n is not unity, and the left-hand side of the equation should be replaced by $\log[-\log(1-x)/2.3T^2]$ for a first-order reaction. Since the first term on the right-hand side of the equation can be considered nearly constant, the calculating of the left-hand side for an assumed n, followed by a plotting of this result against $1/T$, may give a straight line whose slope will give E_a and whose intercept will make possible the rough estimation of the A factor.

The results of analysis are listed in Table 2. The calculated values of the activation entropies (ΔS^*)[22] are also listed in this table. There are found in the literature some more data: for **2** in the solvent cumene,[23] A factor $10^{14.6}\,s^{-1}$ and E_a 34.8 kcal$_{th}$/mol; and for **3** in the solvent dodecane,[23] A factor $10^{14.4}\,s^{-1}$ and E_a 33.5 kcal$_{th}$/mol. The data for the two compounds under no-solvent conditions are not available. For **4**, neither data for a solution nor those for no-solvent conditions have been found in the literature. As for the reported data on various dialkyl peroxides other

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*** Throughout this paper, cal$_{th}$=4.184 J.

TABLE 2. REACTION ORDERS, ACTIVATION ENERGIES, FREQUENCY FACTORS, AND ACTIVATION ENTROPIES *vs.* PINHOLE DIAMETER(ϕ_p) FOR SEVERAL PEROXIDES

Compound	ϕ_p / mm	n	E_a / kcal$_{th}$ mol^{-1}	log A / s^{-1}	ΔS^* / cal deg^{-1} mol^{-1}
2	0.090—0.150	1.55±0.25	34.8±0.3	16.6±0.8	17.5
3	0.070—0.100	1.55±0.25	33.5±0.2	16.1±0.5	15.2
4	0.130—0.200	1.20±0.10	36.5±1.7	18.5±0.6	26.2

TABLE 3. HEATS OF DECOMPOSITION(ΔH_d) FOR SEVERAL PEROXIDES

Compound	ΔH_d / kcal$_{th}$ mol^{-1}	
	Obsd	Calcd
2	81.0±4.5	89.8
3	41.5±5.5	45.3
4	64.2±4.6	67.3

than these three peroxides, the A factors are in the range of $10^{14.0}$—$10^{16.8}$ s^{-1}, and E_a, in the range of 31—39 kcal$_{th}$/mol.[24–28] According to Benson,[29] the unimolecular fission of a large polyatomic molecule generally gives a large A factor ($10^{16\pm1.5}$ s^{-1}) when the mother molecule splits into two polyatomic fragments. He suggests also that the A factor will become very large when reaction order becomes large, and when the rate of decomposition decreases with a rise in the pressure in a reaction, under pressure, with positive value of the activation volume and the ΔS^*.[30,31] Huyser and Van Scoy[32] have reported that ΔS^* becomes large when the apparent rate of decomposition decreases with a reaction in a solvent.[33] It has also been reported that a thermal decomposition accompanied by an increase in the number of moles would give positive values of the activation volume and the ΔS^*.[30]

The large A factors obtained in the above experiments on the thermal decomposition without a solvent seem to be understandable when one considers, along with above arguments, the following fators: the orders of reaction $n>1$; the reactions accompanied with an increase in the number of moles; the effect of the partial pressure change in the homolysis products in the pinholed pans with a minute pinhole, and the influence of the solvent behavior of the decomposition products.

Listed in Table 3 are the values for three samples estimated by means of Eqs. 2—4; we assume an ideal thermal decomposition, based on the heats of decomposition in pinholed pans at the optimum pinhole diameters and on the data of the pyrolysis (Table 4).[18]

$$\mathbf{2} \rightarrow 1.8CH_4 + 1.8C_6H_5COCH_3 + 0.2C_6H_5C(CH_3)_2OH \quad (2)$$

$$\mathbf{3} \rightarrow C_2H_6 + (CH_3)_2CO + C_6H_5COCH_3 \quad (3)$$

$$\mathbf{4} \rightarrow 0.3CH_4 + 0.8C_2H_4 + C_2H_6 + 4(CH_3)_2CO \quad (4)$$

If available, observed values were used as the heats of formation; if they were not available, the values obtained by the method of Benson and others,[34] which applies the group-additivity rule to organic peroxides,

TABLE 4. AMOUNTS OF THE PRODUCTS OBTAINED BY PYROLYSIS OF SEVERAL PEROXIDES (Molar fraction)

Product	Compound		
	2[a)]	**3**[b)]	**4**
CH_4	0.36	trace	0.03
C_2H_4			0.09
C_2H_6	trace	0.41	0.19
$(CH_3)_2CO$	trace	0.29	0.69
$C_6H_5COCH_3$	0.57	0.30	
$C_6H_5(CH_3)_2COH$	0.06	trace	
$C_6H_5(CH_3)_2COOH$	0.01		

a) Pyrolysis temperature, 230 °C. b) Pyrolysis temperature 280 °C.

were used. These observed values were in approximate agreement with the estimated ones, although the former values were somewhat lower. The difference in ΔH_d may be due to the decomposition temperatures[35] and other factors. In order to make this clear, however, further work is necessary.

In conclusion, it can be proposed that the use of the pinholed pans are efficient for the thermal analysis of liquid organic peroxides by means of TG–DSC.

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