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The Decomposition of *t*-Butyl Heptafluoroperoxybutyrate in Aromatic and Aliphatic Solvents

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Kinetical studies and products analyses of the thermal decomposition of *t*-butyl heptafluoroperoxybutyrate (TBH) in benzene, octane, nitrobenzene, pyridine, and methoxybenzene have been carried out. In benzene and octane, the decomposition appears to be entirely a radical process. In nitrobenzene and pyridine, the reactions are found to give ionic decomposition products exclusively. On the other hand, the decomposition of TBH in methoxybenzene is characteristic of mixed ionic and radical cleavages.

Although the mechanisms for the thermolysis of a series of peroxy esters have been extensively investigated,[1] studies on fluorinated peroxy esters are very limited. Fluorinated peroxy esters are expected to show a different decomposition behavior from corresponding aliphatic peroxy esters due to the strong electron-withdrawing properties of fluoroalkyl groups. Strong electron-withdrawing groups in peroxide weaken the O–O bond and lower the energy level of an antibonding (σ^*) O–O bond.[2] Bartlett and Traylor reported that the *t*-butyl peroxy esters derived from a strong organic acid might well undergo an ionic cleavage with a Criegee rearrangement.[3] Recently, we also reported that *t*-butyl heptafluoroperoxybutyrate (TBH) decomposes in methanol to give methyl heptafluorobutyrate and *t*-butyl hydroperoxide in good yields according to the following transesterification.[4]

$$C_3F_7CO_2OC(CH_3)_3 \xrightarrow[CH_3OH]{} C_3F_7CO_2CH_3 + (CH_3)_3COOH$$

However, we found that the thermal decomposition of TBH suffered extreme solvent effects. In this paper, we wish to report on studies regarding the reaction mechanism for the thermal decomposition of TBH in benzene, octane, nitrobenzene, pyridine, and methoxybenzene.

Results and Discussion

The thermal decomposition of TBH in benzene was monitored by iodometry at various temperatures from 60.0 to 80.0 °C; the rate of decomposition deviated upwards remarkably from a first-order rate plot after about 30% of the reaction. However, the rate of decomposition of TBH was found to follow very well a first-order equation when pyridine was added in order to suppress the autocatalyzed decomposition by produced heptafluorobutyric acid. The anomalous behavior regarding the thermal decomposition of highly acid-sensitive peroxy esters is well-known and in order to prevent autocatalysis, pyridine has usually been used.[5,6] The decomposition of 0.02 M†† TBH in benzene was carried out at 75.0 °C in the presence of various (0.005—0.025 M) amounts of pyridine. It was found that as the amount of pyridine was increased, the decomposition rates of TBH decreased and the apparent rate constants leveled off at about 0.015 M pyridine as shown in Fig. 1. Products attributable to a reaction between TBH and pyridine were not obtained except for pyridinium heptafluorobutyrate. In the

Table 1. Rate constants and activation parameters for the thermal decomposition of TBH in benzene

Temp/℃	Initial Conc. M[a]	k_d(s^{-1})×10^5	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/JK^{-1} mol^{-1}
65.0	0.02[b]	1.56±0.01	112.6	−4.2
70.0		3.09±0.02		
75.0		5.27±0.04		
80.0		9.08±0.10		
60.0	0.10[c]	0.95±0.02	108.8	−15.5
65.0		1.61±0.02		
70.0		2.70±0.03		
75.0		5.23±0.07		
80.0		9.18±0.10		
60.0	0.10[d]	0.96±0.03	118.4	13.4
65.0		1.93±0.06		
70.0		3.57±0.08		
75.0		6.35±0.07		

a) M=mol dm^{-3}. b) 0.02 M pyridine was added. c) 0.10 M pyridine was added. d) 0.10 M 2,6-lutidine was added.

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†† 1M=1 mol dm^{-3}.

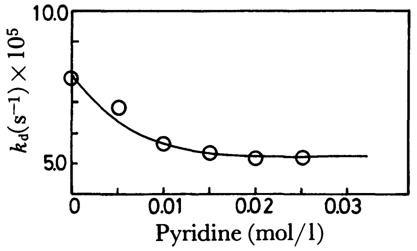


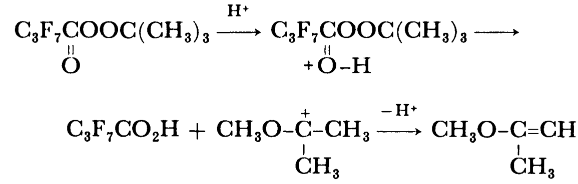
Fig. 1. Effect of added pyridine on the apparent rate constants for the thermal decomposition of 0.02 mol/l TBH in benzene at 75.0 ℃.

TABLE 2. PRODUCTS FROM THE THERMAL DECOMPOSITION OF 0.10 M TBH AND 0.10 M PYRIDINE IN BENZENE AT 80 °C FOR 11 h AND IN OCTANE AT 100°C FOR 10 h

Benzene Product	mol/mol	Octane Product	mol/mol
$(CH_3)_2C{=}CH_2$	Trace	$(CH_3)_2C{=}CH_2$	0.01
$(CH_3)_2CO$	0.02 (0.20)[a]	C_3F_7H	—[b]
$C_3F_7CO_2C(CH_3)_3$	0.02	$(CH_3)_2CO$	Trace
$PhCH_3$	0.03	$C_3F_7CO_2CH_3$	0.30
$C_6H_3(CH_3)_3$	0.01	$C_3F_7CO_2C(CH_3)_3$	0.03
Ph-Ph	0.01	$CH_3COCH{=}C(CH_3)_2$	Trace
$C_3F_7CO_2H$	0.63[c]	$C_3F_7CO_2H$	0.02
$CH_3COCH{=}C(CH_3)_2$	0.01		
$(CH_3)_3COC(CH_3)_3$	0.04		

a) 1.0 M pyridine was used. b) Heptafluoropropane could be detected by GC-MS, however, the exact yield could not be determined. c) Isolated yield of pyridinium heptafluorobutyrate recrystallized from toluene.

absence of pyridine, the decomposition of TBH gave a considerable amount of 2-methoxy-1-propene (**1**: $CH_3OC(CH_3){=}CH_2$, 0.15 mol/mol peroxide) in addition to the products listed in Table 2. The production of propene shows the acid-catalyzed decomposition of TBH.



$$C_3F_7\underset{\underset{O}{\|}}{C}OOC(CH_3)_3 \xrightarrow{H^+} C_3F_7\underset{\underset{+O\text{-}H}{\|}}{C}OOC(CH_3)_3 \longrightarrow$$

$$C_3F_7CO_2H + CH_3O\text{-}\overset{+}{\underset{CH_3}{C}}\text{-}CH_3 \xrightarrow{-H^+} CH_3O\text{-}\underset{CH_3}{C}{=}CH_2$$

(**1**)

The rates of decomposition of TBH in benzene in the presence of an equimolar amount of 2,6-lutidine, which is known to play the role of a proton acceptor and not a nucleophile, gave similar values as those for TBH, using pyridine as a suppresser. These results indicate that pyridine or lutidine played the role of the suppresser of the heptafluorobutyric acid-catalyzed decomposition.

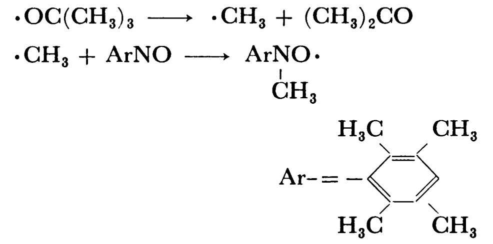
The rate constants and activation parameters for the thermal decomposition of TBH in several solvents are summarized in Table 3. The decomposition was extremely solvent-dependent as shown in Table 3, while the thermal decomposition of nonfluorinated peroxy esters, for example, *t*-butyl peroxyacetate in aliphatic and aromatic solvents showed a weak solvent dependence.[7]

As shown in Tables 1 and 3, the activation parameters for the thermal decomposition of TBH in benzene and octane have similar values as those for the homolytic decomposition of non-fluorinated peroxy esters; *t*-butyl peroxybenzoate in chlorobenzene, $\Delta H^{\neq}=140.2$ KJ mol^{-1}, $\Delta S^{\neq}=32.6$ JK^{-1} mol^{-1};[5] *t*-butyl phenylperoxyacetate in chlorobenzene, $\Delta H^{\neq}=116.7$ kJmol^{-1}, $\Delta S^{\neq}=8.4$ JK^{-1} mol^{-1}.[8] The products obtained from the thermal decomposition of TBH in benzene and in octane are shown in Table 2. The decomposition of TBH in benzene gave no ionic Criegee rearrangement products such as 2-methoxy-1-propene, but heptafluorobutyric acid, toluene, biphenyl, *t*-butyl heptafluorobutyrate, acetone, and condensation products of acetone such as mesityl oxide and 1,3,5-trimethylbenzene. The production of toluene, biphenyl, *t*-butyl heptafluorobutyrate, acetone, and acetone derivatives indicates that TBH decomposes homolytically in benzene. The generation of the radical species was also confirmed by ESR studies. In studies on the decomposition of TBH using nitrosodurene as a spin-trapping reagent, the ESR signal of some nitroxide radicals were observed: one signal was assigned to the adduct of methyl radical to nitrosodurene from the following h.f.s.c.; $a_N=14.0$ G, $a_{\beta\text{-}H}=12.2$ G, $g=2.0068$, (lit, $a_N=13.70$ G, $a_{\beta\text{-}H}=12.17$ G, $g=2.0060$).[9] Formation

TABLE 3. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF 0.10 M TBH & 0.10 M PYRIDINE IN VARIOUS SOLVENTS

Solvent	Temp/℃	$k_d(s^{-1})\times10^5$	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/JK^{-1} mol^{-1}
Octane	85.0	0.51±0.01	136.8	34.7
	90.0	0.95±0.01		
	95.0	1.75±0.04		
	100.0	3.41±0.06		
$PhNO_2$	40.0	3.26±0.04	85.8	−56.9
	45.0	6.36±0.03		
	50.0	9.31±0.23		
Pyridine	30.0	2.74±0.03	75.3	−82.8
	40.0	7.66±0.11		
	50.0	18.68±0.18		
$PhOCH_3$	55.0	5.01±0.05	95.4	−37.2
	60.2	8.56±0.11		
	65.0	13.78±0.22		
	70.0	24.44±0.45		

of this nitroxide is explained by the decomposition of a cage-escaped *t*-butoxyl radical to acetone and methyl radical.

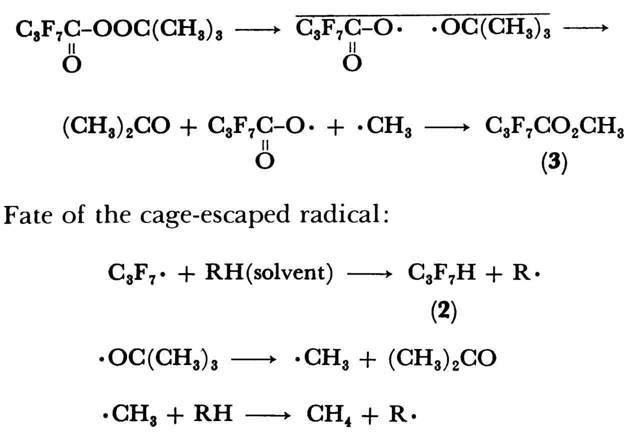


$$\cdot\mathrm{OC(CH_3)_3} \longrightarrow \cdot\mathrm{CH_3} + \mathrm{(CH_3)_2CO}$$

$$\cdot\mathrm{CH_3} + \mathrm{ArNO} \longrightarrow \mathrm{Ar\underset{\substack{|\\ CH_3}}{N}O\cdot}$$

No adduct radical due to $\mathrm{C_3F_7\cdot}$ and nitrosodurene was observed.[10]

In the decomposition of TBH in octane, the heptafluoropropane (**2**), and methyl heptafluorobutyrate (**3**) were produced, and their production can be attributed to homolytic cleavages of TBH. Thus, the decomposition of TBH in octane may also be proceeded by a homolytic cleavage, according to Scheme 1. The homolysis of TBH in octane was further confirmed by ESR studies using nitrosodurene as a spin-trapping reagent. When TBH was decomposed in the presence of nitrosodurene, ESR signals of more than three nitroxide radicals were observed; the main signal was a triplet of doublet with coupling to nitrogen and hydrogen. This signal is probably due to the adduct radical of the secondary alkyl radicals to nitrosodurene. Also, the adduct radical of $\mathrm{C_3F_7\cdot}$ to nitrosodurene could not be observed in this case. The radicals generated by the homolysis of TBH did not attack nitrosodurene but abstracted a hydrogen atom from solvent octane to give a mixture of secondary alkyl radicals ($\mathrm{C_8H_{17}\cdot}$) which could be trapped by nitrosodurene. In order to confirm this, an ESR study of TBH in cyclohexane was also carried out. In this case, the spin adduct of the produced single radical (cyclohexyl radical) to nitrosodurene was observed; $a_\mathrm{N}=13.4\,\mathrm{G}$, $a_\mathrm{H}=6.7\,\mathrm{G}$, $g=2.0059$, (lit, $a_\mathrm{N}=13.57\,\mathrm{G}$, $a_\mathrm{H}=6.93\,\mathrm{G}$, $g=2.0060$).[9]



$$\mathrm{C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}OOC(CH_3)_3} \longrightarrow \overline{\mathrm{C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}O\cdot\quad \cdot OC(CH_3)_3}} \longrightarrow$$

$$\mathrm{(CH_3)_2CO} + \mathrm{C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}O\cdot} + \cdot\mathrm{CH_3} \longrightarrow \underset{(\mathbf{3})}{\mathrm{C_3F_7CO_2CH_3}}$$

Fate of the cage-escaped radical:

$$\mathrm{C_3F_7\cdot} + \mathrm{RH(solvent)} \longrightarrow \underset{(\mathbf{2})}{\mathrm{C_3F_7H}} + \mathrm{R\cdot}$$

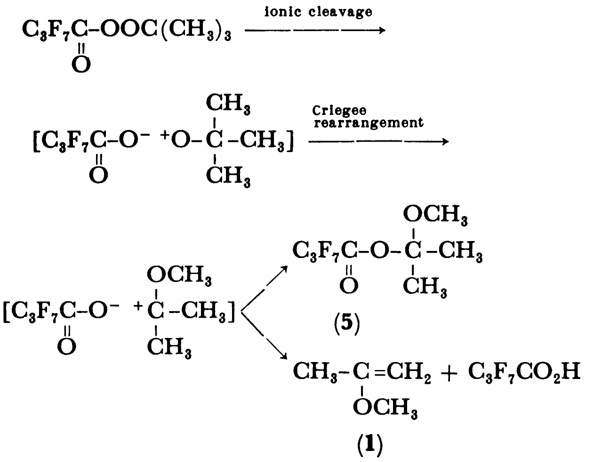
$$\cdot\mathrm{OC(CH_3)_3} \longrightarrow \cdot\mathrm{CH_3} + \mathrm{(CH_3)_2CO}$$

$$\cdot\mathrm{CH_3} + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{R\cdot}$$

Scheme 1.

As mentioned before, it was considered that TBH decomposes homolytically in octane and in benzene. However, the activation parameters for the thermal decomposition of TBH in benzene have smaller values compared with those in octane, and heptafluorobutyric acid was obtained in much higher (63%) yield than that in octane. These results suggest that the induced decomposition of TBH by the cyclohexadienyl radicals, which were formed by the attack of radicals to benzene, may occur, in part, in benzene.

On the other hand, the activation parameters for the thermal decomposition of TBH in nitrobenzene and pyridine have similar values as those for the ionic decomposition of other *t*-butyl peroxy esters accompanied by a Criegee rearrangement; for instance, *t*-butyl peroxytosylate in methanol, $\Delta H^{\ne}=90.0\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ne}=3.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$.[3] It was also found that TBH decomposed in nitrobenzene and pyridine to give one molar equivalent of heptafluorobutyric acid and several Criegee rearrangement products such as 2-methoxy-1-propene (**1**), 2,2-dimethoxypropene (**4**), and 1-methoxy-1-methylethyl heptafluorobutyrate (**5**) as shown in Table 4. 2,2-Dimethoxypropane is probably produced by the reaction of a 1-methoxy-1-methylethylium ion with water (giving acetone and methanol) followed by a reaction involving the evolved methanol with another 1-methoxy-1-methylethylium ion. These results indicate that the decomposition of TBH in nitrobenzene and pyridine is principally an ionic decomposition accompanied by a Criegee rearrangement, according to the following scheme. However, nonfluorinated *t*-butyl peroxy esters are reported to decompose homolytically even in a polar solvent such as nitrobenzene.[11]



$$\mathrm{C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}OOC(CH_3)_3} \xrightarrow{\text{ionic cleavage}}$$

$$\mathrm{[C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}O^- \ {}^+O\text{-}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}\text{-}CH_3]} \xrightarrow{\text{Criegee rearrangement}}$$

$$\mathrm{[C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}O^- \ {}^+\underset{\substack{|\\ CH_3}}{\overset{\substack{OCH_3\\ |}}{C}}\text{-}CH_3]} \begin{cases} \nearrow\ \underset{(\mathbf{5})}{\mathrm{C_3F_7\underset{\substack{\|\\ O}}{C}\text{-}O\text{-}\underset{\substack{|\\ CH_3}}{\overset{\substack{OCH_3\\ |}}{C}}\text{-}CH_3}} \\ \searrow\ \underset{(\mathbf{1})}{\mathrm{CH_3\text{-}\underset{\substack{|\\ OCH_3}}{C}{=}CH_2}} + \mathrm{C_3F_7CO_2H} \end{cases}$$

Scheme 2.

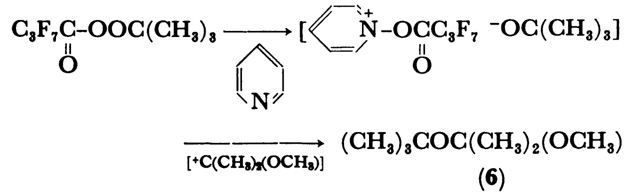
In the decomposition of TBH in pyridine, 2-*t*-butoxy-2-methoxypropane (**6**) was obtained in 21% yield. The formation of this product may be explained by a nucleophilic attack of the N-lone pair of pyridine on a peroxidic α-oxygen of peroxy ester to give *t*-butoxide ion which reacted with 1-methoxy-1-methylethylium ion. It was reported that a reaction of *t*-butyl perbenzoate with dimethyl sulfide occurred at the peroxidic α-oxygen of the benzoyloxyl group to form a dimethylbenzoyloxysulfonium ion, not at the *t*-butoxyl

TABLE 4. PRODUCTS FROM THE THERMAL DECOMPOSITION OF 0.10 M TBA IN NITROBENZENE[a] AT 70 °C FOR 7 h, IN PYRIDINE AT 50 °C FOR 12 h AND IN METHOXYBENZENE[a] AT 70 °C FOR 7 h

Product	$PhNO_2$ mol/mol	C_5H_5N mol/mol	$PhOCH_3$ mol/mol
$(CH_3O)C(CH_3)=CH_2$	0.19	0.46	0.14
$(CH_3)_2C(OCH_3)_2$	0.06	—	0.02
$C_3F_7CO_2C(CH_3)_3$	0.02	—	0.28
$C_3F_7CO_2C(CH_3)_2(OCH_3)$	0.05	—	0.02
$C_3F_7CO_2H$	0.90	0.97(0.91)[b]	0.59
$CH_3CO_2CH_3$	—	0.03	—
$(CH_3)_2CO$	—	—	0.07
$CH_3OC_6H_4CH_3$	—	—	0.10
$(CH_3)_2(CH_3O)COC(CH_3)_3$	—	0.21	—
$C_5H_5N\rightarrow O$	—	0.07	—

a) 0.1 M pyridine was added to suppress the acid-catalyzed decomposition. b) Isolated yield of pyridinium heptafluorobutyrate.

oxygen to form dimethyl-*t*-butoxysulfonium ion.[12] The peroxidic α-oxygen of a heptafluorobutyryloxyl group should be more electropositive than the *t*-butoxyl oxygen. α-Oxygen in a peroxy ester O–O bond is estimated to be more electropositive than α-oxygen according to a MO calculation.[13] Therefore, a nucleophilic attack of pyridine on the heptafluorobutyryloxyl peroxidic oxygen rather than on the *t*-butoxyl oxygen is expected to be favored.



(6)

In a thermal decomposition of TBH in methoxybenzene, the values of the activation enthalpy and entropy for the thermal decomposition of TBH were $\Delta H^{\ddagger}=95.4\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}=-37.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$. These values are larger than those for a thermal decomposition of TBH in nitrobenzene. Ionic Criegee type rearrangement products such as 2-methoxy-1-propene (**1**), 2,2-dimethoxypropane (**4**), and 1-methoxy-1-methylethyl heptafluorobutyrate (**5**) were obtained as the decomposition products in methoxybenzene. Furthermore, acetone (**7**), *t*-butyl heptafluorobutyrate (**8**), and methoxymethylbenzene (**9**), which would result from a homolytic cleavage, were also obtained as shown in Table 4. From these results, it may be concluded that the thermal decomposition of TBH in methoxybenzene is characteristic of mixed ionic and radical cleavages.

Thus, the decomposition of TBH was affected by the polarity of the solvents; the rate of decomposition increased with the dielectric constant of a solvent (ε). In a nonpolar solvent such as octane ($\varepsilon=1.90$) and benzene ($\varepsilon=2.27$), the decomposition proceeds homolytically and the ionic decomposition becomes dominant in a polar solvent such as nitrobenzene ($\varepsilon=34.6$), and pyridine ($\varepsilon=12.3$). In methoxybenzene ($\varepsilon=4.30$), the decomposition is characteristic of mixed ionic and radical cleavages. Although the dielectric constant of nitrobenzene is larger than that of pyridine, the decomposition in pyridine is faster than that in nitrobenzene. This may be due to a nucleophilic attack of pyridine to the O–O bond of TBH.

Experimental

The ^{1}H-NMR spectra were taken with a JEOL JNM-MH-100 spectrometer. The mass spectra were measured with a JEOL JMS-D300 spectrometer. ESR signals were taken with a JES-PE-3X spectrometer. GLC analyses were performed on a Shimadzu GC-4APTF gas chromatograph. IR spectra were recorded on a JASCO A-3 spectrophotometer. Benzene, octane, nitrobenzene, pyridine, and methoxybenzene were purified according to conventional methods. Heptafluorobutyryl chloride was prepared by a reaction of heptafluorobutyric acid and phosphorus pentachloride. The pure acid chloride had a bp of 39—40 °C/760 mmHg (1 mmHg=133.322 Pa), (38—39 °C/740 mmHg[14]) and $\nu_{C=O}$ 1795 cm^{-1}. *t*-Butyl hydroperoxide (commercial grade of Nippon Oil & Fats Co.) was distilled prior to use, bp 32—35 °C/15 mmHg.

Preparation of t*-Butyl Heptafluoroperoxybutyrate (TBH).* Heptafluorobutyryl chloride (77 g, 0.33 mol) was added to *t*-butyl hydroperoxide (35 g, 0.39 mol) in pentane (55 g) at −2 °C and the mixture was cooled to −10 °C. Dry pyridine (31 g, 0.39 mol) was added dropwise with stirring over a period of 20 min while the temperature was maintained below 0 °C. The reaction mixture was then kept at −5 °C—−10 °C for an additional 40 min. The resulting mixture containing a white precipitate was poured into 100 mL of cold aqueous 10% hydrochloric acid and was thoroughly stirred. The pentane layer was separated, washed twice with 100 mL of cold aqueous 5% sodium hydroxide, and finally with 100 mL of cold water. After being dried over anhydrous magnesium sulfate, the solution was concentrated to give 42 g of a crude colorless peroxy ester. This was carefully distilled to give a pure colorless peroxy ester, bp 39.5—40.0 °C/17 mmHg. The infrared spectra exhibited the characteristic peroxy ester carbonyl band at 1815 cm^{-1}. ^{1}H-NMR ($CF_2ClCFCl_2$) $\delta=1.36$ (9H, s). MS *m/z* 286 (M$^+$), 271, 197, 169, 150, 119, 100, 73, 69, 58, 57 (base), 55, 45, 43, 42, 39, 31, 29, 27, and 15; Anal. Calcd for $C_8H_9O_3F_7$: C, 33.58; H, 3.17%. Found: C, 32.50; H, 2.99%.

Kinetic Measurement. A solution of TBH in a degassed sealed tubes were immersed in a constant-temperature bath. Each sample tube was taken out after appropriate time intervals and immersed in a Dry Ice–acetone bath to quench the reaction; the amount of the residual TBH was estimated by iodometric titration.

Decomposition Products of TBH. The products of the decomposition of TBH were identified by GC–MS and by their retention times of GLC compared with those of authentic samples. The yield of heptafluorobutyric acid was determined by titration after hydrolysis of the reactants. Yields of the other products were determined by GLC using internal standards.

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