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Thermal Decomposition of *t*-Butyl Heptafluoroperoxybutyrate

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Synopsis. The decomposition of *t*-butyl heptafluoroperoxybutyrate (TBH) was studied in both toluene and methanol. Kinetic and product studies from the thermolysis showed that this peroxy ester decomposes heterolytically in nonpolar solvents like toluene with homolysis, whereas in methanol this peroxy ester undergoes principally transesterification.

Although the mechanisms for the thermolysis of a series of peroxy esters have been extensively investigated,[1] studies of fluorinated peroxy esters have been few. Bartlett *et al.* reported that the *t*-butyl peroxy esters derived from strong organic acids might well undergo ionic cleavage in polar solvents[2] and *t*-butyl peroxytosylate decomposes heterolytically with Criegee rearrangement in absolute methanol to give acetone dimethyl acetal and toluenesulfonic acids.[3] Hedaya *et al.* reported that 1-methoxy-1-methylethyl *p*-nitroperbenzoate ($p\text{-}NO_2C_6H_4CO_2OC(CH_3)_2(OCH_3)$) decomposes heterolytically in methanol to give rise to Criegee-type products *via* 1,1-dimethoxyethylium ion intermediate.[4] These results suggest that *t*-butyl peroxy esters derived from perfluorinated organic acids ($R_fCO_2OC(CH_3)_3$, R_f=perfluorinated alkyl, aryl) would decompose similarly to give Criegee-type products. We wish to report herein on the results of the thermal decomposition of *t*-butyl heptafluoroperoxybutyrate (TBH) in both toluene and methanol.

Results and Discussion

The thermal decomposition of TBH was carried out in both toluene and methanol at 10.0—85.0 °C as shown in Table 1. For decomposition of TBH in toluene at 65.0—85.0 °C, autocatalysis was observed in the absence of pyridine and the first-order rate constants could not be obtained. However rates of decomposition following a first-order rate constant were obtained at 10.0—30.0 °C and autocatalysis was not observed. The values of the activation enthalpy and entropy for the thermal decomposition of TBH in toluene and in methanol were $\Delta H^{\neq}=89.5\pm4.2\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq}=-74.1\pm12.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and $\Delta H^{\neq}=44.4\pm2.1\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq}=-167.8\pm7.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively.

When TBH decomposed in toluene, 1,2-diphenylethane, which would result from radical cleavage, was obtained as shown in Table 2. Additionally the bulk polymerization of styrene initiated by TBH was studied at 50—60 °C. The thermal polymerization of styrene may be considered negligible at these temperatures. Bulk polymerization of styrene was observed and the rate constants of the polymerization were shown in Table 3. From the rate constants, the value of the activation energy of the polymerization was $94.6\pm9.2\,\mathrm{kJ\,mol^{-1}}$, which suggests that the polymerization of styrene initiated by TBH is not cationic but radical.[5] These results indicate that TBH would decompose homolytically in toluene.

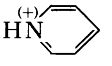
On the other hand, the activation parameters for the thermal decomposition of TBH in toluene have small values compared with those of *t*-butyl peroxy esters which are expected to decompose homolytically; for example, *t*-butyl peroxypivalate, in chlorobenzene, $\Delta H^{\neq}=125.5\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq}=46.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$.[6] The smaller values of the enthalpy and the entropy of activation suggest that TBH would decompose in part with heterolysis. The rates of decomposition followed a first-order rate equation in the presence of pyridine, however, the first-ordsr rate constants drifted upwards remarkably after about 60% reaction at 85 °C. From this result, it can be seen that the autocatalysis was not completely suppressed even when pyridine was present. Decomposition products in toluene at 85 °C in the presence of pyridine were studied and the results were shown in Table 2. Heptafluorobutyric acid resulted from the thermolysis of TBH and reacted with pyridine to give pyridinium heptafluorobutyrate (**3**). Furthermore, 2-methoxy-1-propene (**1**), which would

Table 1. Rate constants for the thermal decomposition of 0.10 M[a)] TBH in toluene and in methanol

Temp/°C	$k_d\times10^5/\mathrm{s^{-1}}$	Solvent
65.0	1.88±0.05	Toluene[b,c)]
75.0	4.66±0.15	
80.0	7.06±0.12	
85.0	12.03±0.46	
10.0	7.19±0.07	Methanol[d)]
15.0	9.37±0.31	
19.6	13.04±0.26	
30.0	26.04±0.99	

a) 0.10 M=0.10 mol $\mathrm{dm^{-3}}$. b) 0.10 M pyridine was added. c) Analysis by iodometry. d) Analysis by infrared spectra.

Table 2. Main products from the thermal decomposition of 0.10 M TBH and 0.10 M pyridine in toluene at 85 °C for 7 h

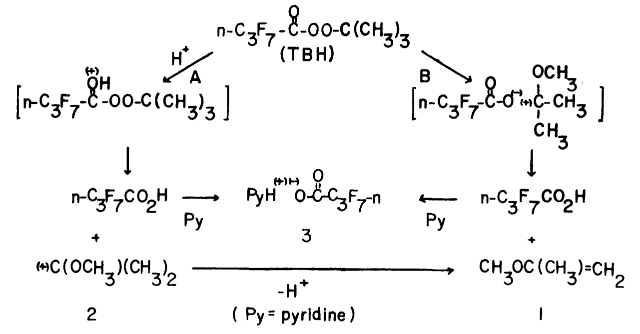
Product	Peroxy ester(mol/mol)
$CH_2=C(CH_3)_2$	0.02
$CH_3OC(CH_3)=CH_2$	0.08
$CF_3CF_2CF_2CO_2C(CH_3)_3$	0.07
$CF_3CF_2CF_2CO_2^{(-)}$ 	0.81[a)]
$PhCH_2CH_2Ph$	0.08

a) Isolated yield.

Table 3. Rate constants for the bulk polymerization of styrene initiated by 0.03 M TBH

Temp/°C	$R_P\times10^2/\mathrm{mol\ l^{-1}h^{-1}}$
50	7.77±0.64
55	12.16±0.84
60	22.43±0.64

result from ionic cleavage, was obtained as shown in Table 2. Olah *et al.* reported that the 1-methoxy-1-methylethylium ion (**2**) can also be isolated by the reaction of *t*-butyl peracetate with magic acid in SO_2ClF at −78 °C.[7] These results indicate that TBH would decompose partially with homolysis and partially with heterolysis which might contain both the autocatalysis (path A) and Criegee rearrangement (path B) according to the Scheme 1.


Scheme 1.

In the thermal decomposition of TBH in methanol, it is of interest that the entropy of activation for the decomposition has a large negative value compared with those of *t*-butyl peroxy esters derived from strong organic acids; TBH $\Delta S^{\neq} = -167.8 \pm 7.1\ \mathrm{J\ K^{-1}\ mol^{-1}}$; *t*-butyl *p*-nitroperbenzoate, in methanol, $\Delta S^{\neq} = -28.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$;[8] *t*-butyl peroxytosylate, in metanol, $\Delta S^{\neq} = 3.8\ \mathrm{J\ K^{-1}\ mol^{-1}}$.[3] From this large negative value of the entropy of activation and the observation of *t*-butyl hydroperoxide in decomposition products as shown in Table 4, it may be concluded that the thermal decomposition of TBH in methanol is principally dependent upon the following transesterification.

$$n\text{-}C_3F_7CO_2OC(CH_3)_3 + CH_3OH \longrightarrow n\text{-}C_3F_7CO_2CH_3 + (CH_3)_3COOH$$

On the other hand, 2,2-dimethoxypropane (**5**) in Table 4, which would result from nucleophilic attack of methanol on the 1-methoxy-1-methylethylium ion (**4**) as shown in Scheme 2, was obtained in 33% yield. The formation of 2,2-dimethoxypropane (**5**) also suggests that TBH would decompose in part with Criegee rearrangement. From the fact that methyl heptafluorobutyrate (**6**) can be quantitatively obtained by the reaction of heptafluorobutyric acid with methanol even at room temperature, **6** in Scheme 2 would result from the methyl-esterification of heptafluorobutyric acid as well as transesterification.

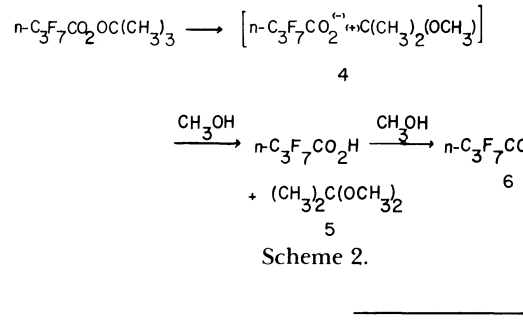

Scheme 2.

Table 4. Products from the thermal decomposition of 0.10 M TBH in methanol at 40 °C for 3 h

Product	Peroxy ester(mol/mol)
$CF_3CF_2CF_2CO_2CH_3$	0.93
$(CH_3)_3COOH$	0.65 (0.66)[a]
$(CH_3)_2C(OCH_3)_2$	0.33
$(CH_3)_2CO$	trace

a) Yield by iodometric analysis.

Experimental

TBH was prepared by the reaction of *t*-butyl hydroperoxide with heptafluorobutyryl chloride in the presence of pyridine and distilled carefully, bp 39.5—40.0 °C/17 mmHg (1 mmHg = 133.322 Pa). The infrared spectra showed the characteristic peroxy ester carbonyl band at 1815 cm^{-1}. ^{1}H-NMR($CF_2ClCFCl_2$) $\delta = 1.36$ (9H s). Mass *m/z* 286(M$^+$), 271, 197, 169, 150, 119, 100, 73, 69, 58, 57 (base), 55, 50, 45, 43, 42, 41, 39, 31, 29, 27, and 15; Calcd for $C_8H_9O_3F_7$: C, 33.58; H, 3.17%. Found: C, 32.50; H, 2.99%. The rates of decomposition of TBH were measured by iodometric titration or disappearance of the carbonyl stretching peak of the peroxy ester at 1815 cm^{-1}. The products of complete decomposition of TBH in both toluene and methanol were identified from the result obtained by GC/MS and the retention times of GLC compared with authentic samples.

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