The Thermal Decomposition of 1-Methyl-1-phenylethyl 2,2-Dimethylperoxypropionate in Cumene

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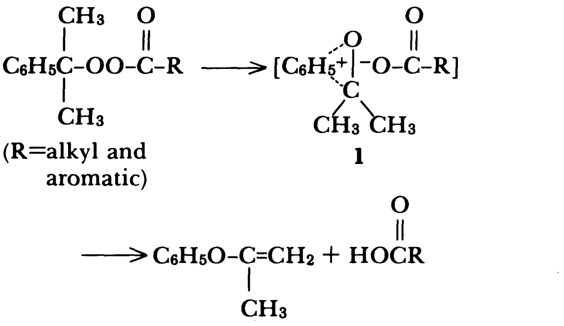
Synopsis. The thermal decomposition of 1-methyl-1-phenylethyl 2,2-dimethylperoxypropionate was studied in cumene. Based on the kinetic parameters and the decomposition products, it was concluded that the peroxyester was decomposed mainly by means of the radical process in cumene.

Most studies[1)] concerning the thermal decomposition mechanism of 1-methyl-1-phenylethyl peroxyesters have indicated that these peroxyesters are rather decomposed ionically as is shown in Eq. 1, compared with 1,1-dimethylethyl analogues which



$$C_6H_5C(CH_3)_2\text{-OO-}\overset{O}{\overset{\|}{C}}\text{-}R \longrightarrow \mathbf{1} \longrightarrow C_6H_5O\text{-}C(CH_3){=}CH_2 + HO\overset{O}{\overset{\|}{C}}R \qquad (1)$$

(R=alkyl and aromatic)

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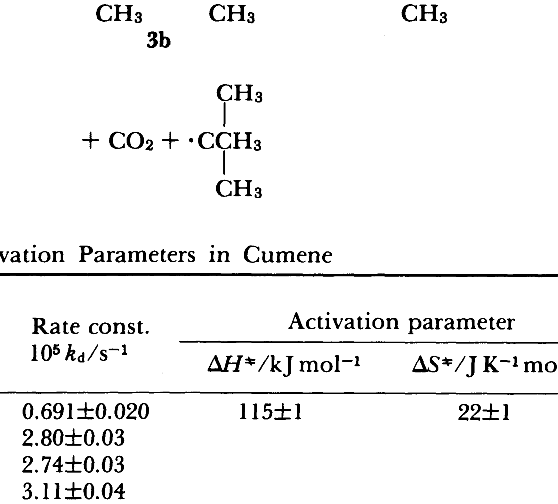
are decomposed by a radical process.[2)] Leffler and Scrivener[3)] have reported that 1-methyl-1-phenylethyl peroxyacetate is decomposed in toluene by means of competing radical (75%) and ionic (25%) pathways, based on the decomposition product. However, several reports[4)] and patents[5)] published more recently, have indicated that 1-methyl-1-phenylethyl 2,2-dimethylperoxypropionate (**2**) and 2,2-dimethylperoxyoctanoate can initiate the radical polymerization of vinyl monomers, such as methyl methacrylate, vinyl chloride, and ethylene. For the purpose of understanding this contradiction, we studied the thermal decomposition of **2** in cumene.

Results and Discussion

The rates of the thermal decomposition of **2** in cumene were determined by following the decrease in the peroxycarbonyl in the infrared spectra. The first-order rate constants were obtained with no appreciable change for a 10-fold increase in the peroxyester concentration. The results are given in Table 1 in order to compare them with those of the 1,1-dimethylethyl analogue.[2b)] The liquid part of the decomposition products was analyzed using GLC; the results are shown in Table 2. In a separate analysis with HPLC, phenol was detected, but the amount was only 0.004 mol per mol of the decomposed peroxyester. These results indicate that the **2** was decomposed almost quantitatively by means of the radical process in cumene. The first reason is that the activation parameters are similar to those of the 1,1-dimethylethyl analogue (Table 1). This means that **2** in cumene decomposes homolytically in the same



$$(CH_3)_3C\text{-OO-}\overset{O}{\overset{\|}{C}}\text{-}C(CH_3)_3 \longrightarrow [(CH_3)_3CO\cdot\ \overset{O}{\overset{\|}{C}}O\cdot C(CH_3)_3 \longleftrightarrow (CH_3)_3CO^-\ \overset{O}{\overset{\|}{C}}O\ {}^+C(CH_3)_3] \longrightarrow (CH_3)_3CO\cdot + CO_2 + \cdot C(CH_3)_3 \qquad (2)$$

3a **3b**

Table 1. Decomposition Rates and Activation Parameters in Cumene

R in $R\overset{O}{\overset{\|}{C}}(CH_3)_2OOCC(CH_3)_3$	Concn M[a)]	Initial temp °C	Rate const. $10^5 k_d/s^{-1}$	Activation parameter ΔH^{*}/kJ mol^{-1}	Activation parameter ΔS^{*}/J K^{-1} mol^{-1}
C_6H_5	0.051	40	0.691±0.020	115±1	22±1
	0.019	50	2.80±0.03		
	0.051	50	2.74±0.03		
	0.217	50	3.11±0.04		
	0.051	60	10.32±0.24		
	0.051	70	35.7±1.64		
CH_3[b)]	—	60	2.95	118±1	23±3

a) 1 M=1 mol dm^{-3}. b) See Ref. 2b.

Table 2. Decomposition Products of **2** in Cumene[a)]

Product	Amount mol/mol of **2**
2-Phenyl-2-propanol	0.94
Acetophenone	0.04
1-Methyl-1-phenylethyl 1,1-dimethylethyl ether	0.02
2,3-Dimethyl-2,3-diphenylbutane	0.63
2-Phenyl-1-propene	0.005

a) Decomposition conditions: initial concentration of **2**, $0.050\ \mathrm{mol\ dm^{-3}}$; decomposition, 96 h at 50 °C under a nitrogen atmosphere.

fashion to the 1,1-dimethylethyl analogue (Eq. 2), because the ionic decomposition of peroxyesters has a considerably smaller activation entropy than does the radical one.[1d)] The second reason involves the decomposition products. That is, the products in Table 2 can be explained as having been obtained from the 1-methyl-1-phenylethoxyl radical. Criegee rearrangement products, such as 2-phenoxypropene, phenol and 2,2-dimethylpropionic acid, could be detected in only small amounts; not at all. The higher yield of 2-phenyl-2-propanol compared with Leffler's results may be explained by the decomposition temperature and the disproportionation of the radicals in the solvent cage. Our experiment was done at a lower temperature (50 °C). The ratio of the β-scission of the alkoxyl radical to the hydrogen abstraction increased with the reaction temperature.[6)] The alkoxyl radical is much more likely to disproportionate with the 1,1-dimethylethyl radical than with the methyl radical in the solvent cage.[7)]

The peroxyester **2** decomposes more homolytically than does 1-methyl-1-phenylethyl peroxyacetate.[3)] This may be correlated with the acidity of the parent acids. Because the dissociation constant[8)] of 2,2-dimethylpropionic acid (8.91×10^{-6}) was smaller than that of acetic acid (1.23×10^{-5}), the peroxyester **2** is less acceptable as an ionic intermediate **1**, as is shown in Eq. 1. The rate constants in the decomposition of 1,1-dimethylethyl and 1-methyl-1-phenylethyl peroxyacetates in diphenylmethane and toluene at 100 °C were 1.23×10^{-5}[9)] and $3.43\times10^{-5}\ \mathrm{s^{-1}}$,[1d)] respectively, and the later decomposed about 2.8 times faster than the former. However, the peroxyester **2** decomposed about 3.5 times faster than the 1,1-dimethylethyl analogue (Table 1). These differences indicate that the polar structure of **2**, similar to **3b**, may be stabilized by the electron-withdrawing phenyl substituent and that the contribution of the exothermic decarboxylation to the transition state may accelerate the homolitic decomposition of **2**.[10)]

Experimental

The peroxyester **2** was prepared by the reaction of 2,2-dimethylpropionyl chloride with 1-methyl-1-phenylethyl hydroperoxide in the presence of a 20% KOH aqueous solution in a method similar to that in the reference.[10)] The cumene was purified by the method described in Ref. 11. The decomposition rates were determined by following the carbonyl band of **2** at $1767\ \mathrm{cm^{-1}}$. The decomposition products were determined by means of standard analytical techniques[10)] using gas-liquid chromatography (GLC) and high-performance liquid chromatography (HPLC).

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