Decomposition of Phenylpropioloyl Peroxide and t-Butyl Peroxyphenylpropiolate in Solution. A New Type of Induced Decomposition

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PHENYLPROPIOLOYL PEROXIDE and t-butyl peroxyphenylpropiolate were expected to generate phenylethynyl radicals on decomposition in solution. We have prepared this peroxide, m.p. 94° (from methylene dichloride and methanol) and this perester (oil at room temperature, crystals from ether at $-78°$) from phenylpropioloyl chloride according to the usual methods, and have examined their decomposition in toluene and cyclohexane at 80°. Compared with common diacyl peroxides such as diacetyl and dibenzoyl peroxides, the amount of carbon dioxide (0·5—0·7 mole/mole of starting material) evolved was relatively small and the yield of phenylpropiolic acid (0·5—0·9 mole), the parent carboxylic acid, was higher. There did not appear to be strong indication of the generation of free phenylethynyl radicals, since the yield of phenylacetylene, which should be formed through the hydrogen abstraction by phenylethynyl radicals, was negligible or nil (by v.p.c.), and no 1,4-diphenylbuta-1,3-diyne was detected (by v.p.c. and u.v.), but the formation of 1,3-diphenylpropyne (0·2 mole) or phenylethynylcyclohexane (0·5—0·7 mole) was observed, which have structures corresponding to the combination of the phenylethynyl radical with the radical derived from a solvent by hydrogen abstraction. These findings are remarkable and an induced decomposition was suspected.

Kinetic measurements showed that the decomposition of t-butyl peroxyphenylpropiolate in toluene at 110° obeys a first-order rate law, but the observed rate constants increased with the initial concentration of the perester ($k_1 = 2{\cdot}7 \times 10^{-5}$ sec.$^{-1}$ and $2{\cdot}1 \times 10^{-5}$ sec.$^{-1}$ for initial concentrations of $0{\cdot}12\,\text{M}^{-1}$ and $0{\cdot}009\,\text{M}^{-1}$, respectively.) The rate of decomposition of phenylpropioloyl peroxide ($0{\cdot}01$—$0{\cdot}10\,\text{M}^{-1}$) in toluene at 70° was found to be expressed by the formula

$$\text{rate} = 5{\cdot}9 \times 10^{-5}[\text{P}] + 1{\cdot}6 \times 10^{-3}[\text{P}]^{3/2}\ \text{M/sec.}$$

where [P] is the concentration of peroxide. The presence of a 3/2-order term supports the concurrence of an induced decomposition.

Di-t-butyl peroxyoxalate,[1] which is known to undergo homolytic fission at relatively low temperatures, was found to cause the decomposition of phenylpropioloyl peroxide and t-butyl peroxyphenylpropiolate in toluene at 35°, the characteristic product being 1,3-diphenylpropyne (0·4—0·5 mole). At this temperature, these peroxides do not decompose to a measurable extent in the absence of the peroxyoxalate. Evidently, t-butoxy-radicals, generated by the peroxyoxalate, abstracted a hydrogen atom from toluene to give benzyl radicals, and these radicals immediately attacked the triple bond in the acetylenic peroxides to afford 1,3-diphenylpropyne. *N*-Nitrosoacetanilide, a generator of phenyl radicals, also brought about the decomposition of t-butyl peroxyphenylpropiolate at room temperature, 1,2-diphenylacetylene (0·3 mole) being produced. Similarly, the decomposition of dicinnamoyl peroxide and t-butyl peroxycinnamate was accelerated by di-t-butyl peroxyoxalate in toluene and by *N*-nitrosoacetanilide in acetone, giving rise to 1,3-diphenylpropene (0·6—0·9 mole) and stilbene (0·2 mole), respectively. Under similar experimental conditions, in the presence of decomposing di-t-butyl peroxyoxalate, diacetyl and dibenzoyl peroxide did not change at all.

These findings suggest that radicals derived from solvent by a hydrogen-abstraction reaction or directly from a radical generator can add to the unsaturated bond of these peroxides, and it is concluded that the decomposition of the acetylenic peroxides in a solvent (SH) includes such a radical addition as a step of the induced decomposition. Important pathways may be represented for phenylpropioloyl peroxide as follows:

$$(\text{PhC}{\equiv}\text{C}{\cdot}\text{CO}_2)_2 \rightarrow 2\,\text{PhC}{\equiv}\text{C}{\cdot}\text{CO}_2{\cdot} \qquad (1)$$

$$\text{PhC}{\equiv}\text{C}{\cdot}\text{CO}_2{\cdot} + \text{SH} \rightarrow \text{PhC}{\equiv}\text{C}{\cdot}\text{CO}_2\text{H} + \text{S}{\cdot} \qquad (2)$$

$$\text{S}{\cdot} + (\text{PhC}{\equiv}\text{CCO}_2)_2 \rightarrow \text{Ph}\dot{\text{C}}{=}\text{C}({-}\text{S})\text{CO}_2{-}\text{O}_2\text{C}{\cdot}\text{C}{\equiv}\text{CPh} \qquad (3)$$

$$\text{Ph}\dot{\text{C}}{=}\text{C}({-}\text{S})\text{CO}_2{-}\text{O}_2\text{C}{\cdot}\text{C}{\equiv}\text{CPh} \rightarrow \text{PhC}{\equiv}\text{C}({-}\text{S}) + \text{CO}_2 + \text{PhC}{\equiv}\text{C}{\cdot}\text{CO}_2{\cdot} \qquad (4)$$

$$2\text{S}{\cdot} \rightarrow \text{S}{-}\text{S} \qquad (5)$$

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[1] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.