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A New Type of Induced Decomposition. II.[1] Decomposition of Phenylpropioloyl Peroxide and *t*-Butyl Phenylperoxypropiolate in Solution

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Decomposition of phenylpropioloyl peroxide and *t*-butyl phenylperoxypropiolate in cumene, toluene, and cyclohexane was investigated. Product analysis and kinetic study together with the findings that radicals separately generated caused the decomposition of these peroxides demonstrate of a new type of induced decomposition involving radical attack on the triple bond of these peroxides and subsequent β-scission.

Although the chemistry of carbon radicals such as alkyl, vinyl, and phenyl radicals are well documented, much less attention has hitherto been focussed on the ethynyl radical $R-C\equiv C\cdot$, in which it is expected the sp hybrid nature of the orbital carrying an odd electron may impart any special characteristics to the behaviour of this type of radicals. One fruitful method for generation of ethynyl radicals is the photolysis of ethynyl iodides.[2,3] An alternative approach to ethynyl radicals should be provided by homolysis of appropriate acetylenic peroxides. Thus we have studied the decomposition in solution of phenylpropioloyl peroxide and *t*-butyl phenylperoxypropiolate with the expectation that it would generate the phenylethynyl radicals. However, there did not appear to be strong indication of the generation of free phenylethynyl radicals, but evidence for a new type of induced decomposition was afforded as preliminarily reported elsewhere.[1] The present paper gives a detailed account of the study of this type of induced decomposition.

Results and Discussion

Phenylpropioloyl peroxide (I) and *t*-butyl phenylperoxypropiolate (II) were allowed to decompose in cumene, toluene, and cyclohexane at 80° and 110°C under a nitrogen atmosphere, and the products were examined (see Tables 1 and 2). Operation of a homolytic mechanism in the decomposition of these compounds is demonstrated by the formation of bicumyl and α-methylstyrene in cumene and of bibenzyl in toluene, all arising from radicals derived from the solvents. Moreover, the formation of acetone and *t*-butyl alcohol in the decomposition of the peroxy-ester (II) is characteristic of the intervention of the *t*-butoxyl radical. The peroxide (I) and the peroxy-ester (II) gave relatively small amounts of carbon dioxide and higher yield of the parent acid compared with common diacyl peroxides and *t*-butyl peroxyacetate. This fact may suggest that the phenylpropioloyloxyl radical if generated by homolysis from these peroxides may tend to abstract a hydrogen atom from a solvent molecule rather than to undergo fission to give carbon dioxide and a phenylethynyl radical. If the carbon dioxide had come solely from the phenylpropioloyloxyl radical, the phenylethynyl radical must have been generated in the corresponding amount, which in turn would have given rise to phenylacetylene by abstraction of a hydrogen atom from a hydrogen donor in the surroundings. Since the phenylethynyl radical is expected to abstract a hydrogen atom readily because of the large heat of formation of an sp C–H bond,[4] the very low yield of phenylacetylene actually found seems to indicate that this radical could have hardly been formed in these decompositions. Thus, the carbon dioxide actually found must have been evolved from some sourses other than the phenylpropioloyloxyl radical. In this connection, the formation of 1,3-diphenylpropyne in toluene and (phenylethynyl)cyclohexane in cyclohexane is of interest, since the combination of a radical derived from a solvent molecule and a

Table 1. Products from decomposition of phenylpropioloyl peroxide at 80 °C[a]

Products[b]	Solvent		
	Toluene	Cumene	Cyclohexane
CO_2	0.54	0.15	0.66
$PhC\equiv CCO_2H$	0.89	1.50	0.48
$PhC\equiv CCH_2Ph$	0.17		
$PhC\equiv CC_6H_{11}$			0.56
$[PhC(CH_3)_2]_2$		0.03	
$PhC(CH_3)=CH_2$		0.44	
$PhCH_2CH_2Ph$	0.05		

a) 3.20 mmol in 20 ml of solvent. b) In mol per mol of peroxide.

Table 2. Products from decomposition of *t*-butyl phenylperoxypropiolate at 110 °C

Solvent	Toluene	Cumene	Cyclohexane[a]	Cyclohexane[b]
Peroxy-ester, mmol	2.65	2.92	0.82	8.88
Solvent, ml	15.0	15.0	7.0	100.0
Products[c]				
CO_2	0.675	0.377		
$PhC\equiv CCO_2H$	0.268	0.442	0.199	0.12
$PhC\equiv CH$	0.011	0.003	nil	
$PhC\equiv CCH_2Ph$	0.385			
$PhC\equiv C-C_6H_{11}$			0.668	0.62
$(PhC(CH_3)_2)_2$		0.353		
$Ph(CH_3)C=CH_2$		0.366		
$PhCH_2CH_2Ph$	0.023			
t-BuOH	0.585	0.623	0.970	
Me_2CO	0.106	0.158	trace	

a) At 80 °C. b) Photolysis at room temperature. c) Mol per mol of peroxide.

phenylethynyl radical scarcely formed is improbable. These experimental results taken as a whole point to a decomposition pattern different from what is expected from simple homolysis at the peroxidic linkage, and an induced decomposition was suspected. This view is supported by a kinetic study of the decomposition. Kinetic runs were carried out in toluene under a nitrogen atmosphere and followed by iodometric titration. The peroxy-ester (II) disappeared apparently with first order kinetics, but change in the initial concentration of the peroxy-ester from 0.0085 M to 0.12 M resulted in a 1.3-fold increase in the rate of decomposition (Table 3), a fact indicative of the co-operation of an induced pathway. The decomposition of the peroxide (I) in toluene at 70° did not obey a first-order rate law, but approximately a 3/2-order rate law, $-d[p]/dt=k[p]^{3/2}$, where [P] is the concentration of the peroxide (I), the plot of $[P]^{-1/2}$ against time giving a more satisfactory straight line. The observed 3/2-order rate constants, *k*, are listed in Table 4. They varied with the initial concentration of the peroxide, and their plots against the inverse square root of the initial concentration of the peroxide (I), $[P_0]^{-1/2}$, gave a straight line, which is represented by $k=k_i+k_1[P_0]^{-1/2}$. Thus, the rate of decomposition is approximately expressed by

Table 3. Rate constants for thermal decomposition of *t*-butyl phenylperoxypropiolate in toluene at 110 °C

Initial concn, M	$k\times10^5$ s^{-1}
0.0085	2.15, 2.09
0.120	2.60, 2.79

Table 4. Observed 3/2-order rate constants, *k*, for phenylpropioloyl peroxide in toluene at 70 °C

Initial concn, M	$k\times10^{-3}$ s^{-1} M$^{-1/2}$
0.01	2.00, 2.32
0.05	1.89, 1.95
0.10	1.78, 1.64

$$-d[P]/dt = k_1[P] + k_i[P]^{3/2},$$

where k_1 and k_i were found to be 5.9×10^{-5} s^{-1} and 1.6×10^{-3} s^{-1} M$^{-1/2}$, respectively. The presence of a 3/2-order term together with the finding that the rate of decomposition is significantly diminished by traces of oxygen present in the reacting system supports the concurrence of an induced path.[5] Thus the following Reaction sequence 1—5, in which SH stands for a solvent molecule, may represent important pathways for the decomposition of the peroxide (I).

$$\underset{\text{(I)}}{(PhC{\equiv}CCO_2)_2} \xrightarrow{k_1} 2PhC{\equiv}CCO_2\cdot \qquad (1)$$

$$PhC{\equiv}CCO_2\cdot + SH \xrightarrow{k_2} PhC{\equiv}CCO_2H + S\cdot \qquad (2)$$

$$S\cdot + (I) \xrightarrow{k_3} Ph\dot{C}{=}C(\text{-}S)CO_2\text{-}O_2CC{\equiv}CPh \qquad (3)$$

$$Ph\dot{C}{=}C(\text{-}S)CO_2\text{-}O_2CC{\equiv}CPh \xrightarrow{k_4} PhC{\equiv}C\text{-}S + CO_2 + PhC{\equiv}CCO_2\cdot \qquad (4)$$

$$2S\cdot \xrightarrow{k_5} S\text{-}S \qquad (5)$$

A similar sequence of reactions will readily be written down for the peroxy-ester (II). Decomposition of the peroxide (I) produces phenylpropioloyloxyl radicals, which abstract a hydrogen from solvents. The newly formed solvent radical S· adds to the triple bond of the peroxide (I) to give vinylic radicals, which would then decompose into an acetylenic compound, a phenylpropioloyloxyl radical, and a molecule of carbon dioxide. Evidently the large heat of formation of carbon dioxide facilitates such a β-scission reaction. The major products of the decomposition are readily explained by reference to this reaction sequence. The absence of 1,3-diphenyl-3,3-dimethylpropyne from the decomposition in cumene is probably due to the circumstances that the α,α-dimethylbenzyl radical is very sluggish in the addition reaction to the triple bond because of its resonance stabilization and bulkiness. The rate law of the decomposition which includes a 3/2 power term[6] is also readily derived by the usual stationary state approximation with the reasonable assumption of Reaction 4 being much more rapid than Reaction 3.

The incursion of an induced path of decomposition is further supported by the following experiments, in which radicals separately generated caused the decomposition of the peroxides at relatively low temperatures, at which they cannot otherwise undergo appreciable decomposition. The peroxide (I) or the peroxy-ester (II) was heated in toluene at 35 °C for 15 h under a nitrogen atmosphere in the presence of di-*t*-butyl diperoxyoxalate, which is known to decompose readily at low temperatures generating *t*-butoxyl radicals.[7] A considerable part of the peroxides decomposed and the characteristic product was 1,3-diphenylpropyne in each case (Table 5). Control experiments showed that these peroxides did not undergo homolytic fission to a measurable extent in the absence of the diperoxyoxalate under otherwise similar conditions. Evidently *t*-butoxyl radicals, generated from the diperoxyoxalate, abstracted

Table 5. Decomposition of phenylpropioloyl peroxide and *t*-butyl phenylperoxypropiolate in the presence of di-*t*-butyl diperoxyoxalate at 35 °C for 15 h under nitrogen

	Phenylpropioloyl peroxide	*t*-Butyl phenylperoxypropiolate
Peroxide taken, mmol[a)]	1.34	2.40
Peroxide decomposed, mmol	1.26	0.94
(t-BuOOCO)$_2$, mmol	1.76	2.43
Products, mmol		
CO_2	4.56	5.44
$PhC{\equiv}CCH_2Ph$	0.54 (0.43)[b)]	0.48 (0.51)[b)]
$PhCH_2CH_2Ph$	0.72	1.87

a) In 8 ml of toluene. b) Mol per mol of peroxide decomposed.

a hydrogen atom from toluene to give a benzyl radical, and this radical immediately attacked the triple bond in the acetylenic peroxides finally to afford 1,3-diphenylpropyne.

N-Nitrosoacetanilide, a generator of phenyl radicals,[8] also brought about the decomposition of the peroxy-ester (II) at room temperature, 1,2-diphenylacetylene being produced (Table 6).

Table 6. Decomposition of *t*-butyl phenylperoxypropiolate induced by the phenyl radical at room temperature for 16 h under nitrogen

Solvent	Hexane	Acetone
PhN(NO)COCH$_3$, mmol	2.44	2.45
Peroxide taken, mmol[a]	1.75	1.88
Peroxide decomposed, mmol	0.46	1.00
Products, mmol		
CO$_2$	0.371	0.836
PhC≡CPh	0.0578 (0.127)[b]	0.259 (0.259)[b]

a) In 8 ml of solvent. b) Mol per mol of peroxide decomposed.

A toluene solution of acetyl peroxide and *di-t*-butyl diperoxyoxalate was kept at 35 °C under a nitrogen atmosphere for 15 h and iodometric titration showed that the acetyl peroxide remained undecomposed, whereas the diperoxyoxalate is believed to have decomposed completely under such reaction conditions.[7] Under similar experimental conditions, benzoyl peroxide did not decompose at all, either (Table 7). Obviously the benzyl radical does not displace the carboxyl group of the peroxides which have no α,β-unsaturated bond.

Table 7. Behaviour of benzoyl and acetyl peroxide in the presence of decomposing di-*t*-butyl diperoxyoxalate in toluene at 35 °C under nitrogen

	(PhCOO)$_2$	(CH$_3$COO)$_2$
Peroxide taken, mmol[a]	1.88	1.92
Remaining Peroxide, mmol	1.86	1.99
(*t*-BuOOCO)$_2$, mmol	1.64	2.69
Time, h	18	15

a) In 8 ml of toluene at 35 °C, under nitrogen.

These results strongly support the addition-elimination mechanism shown in Reactions 3 and 4 for the induced decomposition of the peroxide (I). Similar addition-elimination mechanisms had been postulated in radical induced reaction of methyl propenyl ketone,[9] crotonaldehyde,[10] and phenyl azide[11] at rather high temperatures. Since the discovery of the induced decomposition of benzoyl peroxide by Bartlett and Nozaki,[5] numerous studies[12] have been made, but the present mechanism is unique in that radicals attack the site of unsaturation exclusively.

Experimental

Materials. Toluene, cumene, cyclohexane, and hexane were washed successively with concentrated sulphuric acid and water, dried with calcium chloride, and distilled over sodium, and middle fractions were used. Acetone was purified by distillation after drying with potassium carbonate. Benzoyl peroxide was purified by dissolving in dichloromethane and precipitating with methanol. *t*-Butyl hydroperoxide was purified by distillation, bp 32 °C/12 mmHg.

Product Analysis by Vapour-phase Chromatography. VPC analyses were carried out on a Perkin Elmer Vapor Fractometer Model 154-D using helium as a carrier gas and the following stainless steel columns: 1) a 4 m column packed with polyethylene glycol (15%) at 120° for analysis of acetone, *t*-butyl alcohol, phenylacetylene, and 2-phenylpropene; 2) a 0.4 m column packed with silicone grease SE 30 (15%) at 193°C for analysis of cyclohexylphenylacetylene; 3) a 1 m column packed with silicone grease SE 30 (15%) at 199 °C for analysis of bibenzyl, 1,3-diphenylpropyne, and 2,3-dimethyl-2,3-diphenylbutane. Commercial products were used for comparison of common compounds, but authentic samples of 1,3-diphenylpropyne[13] and cyclohexylphenylacetylene[14] were prepared according to the directions described in the literature.

Phenylpropioloyl Peroxide. Sodium peroxide (2.0 g) was added to a solution of phenylpropioloyl chloride[15] (5.0 g) in ether (50 ml) at −5 °C. The mixture was stirred for 10 min, and then a little water was added dropwise, the temperature being kept at 0—−5 °C. After a vigorous reaction subsided, a further 5 ml of water was added and the mixture was allowed to warm to room temperature. The ether layer was separated and the aqueous layer was extracted with three 10 ml portions of ether. The combined ether solution was washed with 5% sodium carbonate solution and then with water, dried with sodium sulphate and concentrated under reduced pressure. The residue was washed with cold methanol and dissolved in a small amount of dichlomethane. Precipitation by addition of a large quantity of cold methanol gave 3.8 g of crystals, mp 94.1—94.2 °C (Found: C, 73.54; H, 3.32%. Calcd for $C_{18}H_{10}O$: C, 74.48; H, 3.47%. Purity, 99.8% by iodometric titration[16]).

t-*Butyl Peroxyphenylpropiolate.* Phenylpropioloyl chloride[15] (5.03 g) and 10 ml of water containing 2.09 g of potassium hydroxide were added simultaneously over a period of 40 min to a stirred solution of 2.91 g of *t*-butyl hydroperoxide in 20 ml of water. The temperature was maintained at 8—10 °C during the addition. The reaction mixture was stirred overnight at room temperature. The organic layer was separated and washed successively with 10% aqueous sodium carbonate and saturated sodium chloride solution. The viscous oil obtained (8.3 g, 68%) was dissolved in ether and the solution dried with anhydrous sodium sulphate. Crystallization from ether at −78 °C gave a pure specimen (Found: C, 71.74; H, 6.36%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%. Purity, 99% by iodometric titration[16]).

Decomposition of Phenylpropioloyl Peroxide and t-*Butyl Phenylperoxypropiolate in Solutions.* A typical run was as follows. A solution of the peroxide (3.20 mmol) in 20 ml of solvent was placed in a two-necked reaction flask equipped with a gas inlet-tube and a reflux condenser which was connected to a trap cooled with solid carbon dioxide–acetone. The other end of the trap was attached to a tube containing Ascarite–magnesium perchlorate. Nitrogen gas was passed through the solution for a while to remove dissolved oxygen. The flask was placed in a bath kept at 80 °C and the peroxide was allowed to decompose completely, a slow stream of nitrogen being passed through the solution. The reaction mixture was diluted to 25.0 ml with the same solvent. A ten millilitre aliquot of the solution was extracted with 5% aqueous sodium carbonate solution. The extract was acidified with hydrochloric acid and the phenylpropiolic acid liberated was extracted with ether and weighed. The residual solution was washed with 5% aqueous sodium carbonate solution and examined by VPC. The products were identified by comparing their retention times with those of authentic samples. Carbon dioxide was absorbed in an Ascarite–magnesium perchlorate tube and the tube weighed.

Decomposition of Phenylpropioloyl Peroxide and t-*Butyl Phenylperoxypropiolate in the Presence of Di*-t-*butyl Diperoxyoxalate.* A typical run was as follows. A solution of the phenylperoxypropiolate (2.40 mmol) in 8.0 ml of toluene was placed in a two-necked reaction flask equipped with a gas inlet-tube and a reflux condenser which was connected to a trap cooled with acetone and solid carbon dioxide. The other end of the trap was attached to a tube containing Ascarite–magnesium perchlorate. Nitrogen was bubbled through the solution vigorously for a while to remove dissolved oxygen, and di-*t*-butyl diperoxyoxalate[7)] (2.43 mmol) was added to the solution. The flask was placed in a constant-temperature bath kept at 35 °C and the peroxy-ester were allowed to decompose, a very slow stream of nitrogen being passed through the reaction mixture. After 15 h (5 half-life period of *t*-butyl diperoxyoxalate), the reaction mixture was diluted to 10.0 ml with toluene in a measuring flask. A 1.0 ml portion of this solution was pipetted out for determination of undecomposed peroxy-ester by iodometry.[16)] The remainder of the solution was treated with 10% sodium carbonate solution, and the aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. The ether was removed under reduced pressure and the acidic residue was weighed. The organic layer was treated with 5 ml of acetic acid containing a very small quantity of iron(III) chloride and 1 g of sodium iodide, and the mixture was allowed to stand for 20 min at room temperature in order to decompose the remaining peroxypropiolate; the liberated iodine was reduced with sodium thiosulphate solution, and the organic layer was washed with 10% aqueous sodium carbonate, dried with anhydrous sodium sulphate, and analyzed by VPC. Carbon dioxide was absorbed in an Ascarite–magnesium perchlorate tube and the tube weighed.

Reaction of Acetyl Peroxide or Benzoyl Peroxide in the Presence of Decomposing Di-t-*butyl Diperoxyoxalate in Toluene.* A solution of acetyl peroxide (1.92 mmol) and di-*t*-butyl diperoxyoxalate (2.69 mmol) in 8.0 ml of toluene was kept at 35 °C for 15 h under a nitrogen atmosphere. The reaction mixture was diluted to 10.0 ml with toluene. Three 1.0 ml portions of the mixture were taken to determine undecomposed acetyl peroxide by iodometric titration.[16)]

Experiments with benzoyl peroxide were carried out similarly.

Decomposition of t-*Butyl Phenylperoxypropiolate in the Presence of* N-*Nitrosoacetanilide.* A typical run was as follows. A solution of the peroxypropiolate (1.75 mmol) and *N*-nitrosoacetanilide (2.44 mmol) prepared according to Grieve and Hey's procedure[8)] in 8 ml of hexane was allowed to decompose for 16 h at room temperature under a nitrogen atmosphere. The reaction mixture was diluted to 10 ml with hexane and a 1.0 ml portion of the mixture was withdrawn to determine the undecomposed peroxy-ester by iodometric titration.[16)] The remaining solution was treated with sodium iodide (1 g) and 10 ml of acid acetic solution of iron(III) chloride (0.002%). (In the case of acetone solution, the solvent was removed under reduced pressure, and replaced by 10 ml of chloroform. The chloroform solution was then treated with sodium iodide in a way similar to the above.) The mixture was allowed to stand for 15 min, and the liberated iodine was reduced with aqueous thiosulphate solution. The aqueous layer was separated and extracted with benzene. The extracts were combined with the organic layer, washed successively with a 10% sodium carbonate solution and a satruated sodium chloride solution, and dried with anhydrous sodium sulphate. After removal of most of the solvent, the residue was diluted to 2.0 ml with benzene and analyzed by VPC.

Kinetics Measurements. The decomposition of the peroxide (I) or the peroxy-ester (II) was followed by iodometric titration according to Swern's method.[16)] In a reaction vessel fitted with a gas inlet-tube and a reflux condenser was placed 50 ml of purified toluene. The vessel was heated in a thermostatted oil bath, and nitrogen was bubbled through the solution for more than two hours. The peroxide (I) of the peroxy-ester (II) was then added to the solution, and allowed to decompose, a slow stream of nitrogen being passed. Aliquots were withdrawn periodically, quenched by chilling to −78 °C, treated with NaI–$CHCl_3$–AcOH (containing 0.002% $FeCl_3$-$6H_2O$), and titrated with a standard sodium thiosulphate solution.

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