Photochemical Benzoyloxylation with Labeled Benzoyl Peroxide

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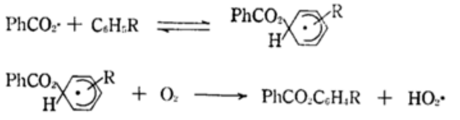
Nakata, Tokumaru and Simamura[1] studied the photochemical decomposition of benzoyl peroxide in aromatic solvents, and explained the formation of a considerable amount of aryl benzoate under oxygen atmosphere by the following mechanism.

All the experimental results were consistent with the above mechanism.

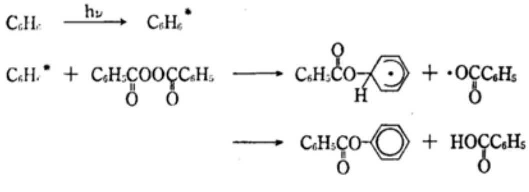


However, the mechanism of the photochemical excitation of benzoyl peroxide is not clear. On the basis of the findings that 1) very slow photolysis of benzoyl peroxide in cyclohexane was much accelerated by addition of benzene and 2) the decomposition of benzoyl peroxide was not retarded by the presence of oxygen, an effective quencher of triplet state excitation, they suggested that the decomposition of the peroxide in benzene was caused by the energy transfer from the benzene of an excited singlet state to the peroxide, followed by monomolecular decomposition of the peroxide, as shown in the following.

$$C_6H_6 \xrightarrow{h\nu} C_6H_6^*$$
$$C_6H_6^* + (C_6H_5COO)_2 \longrightarrow C_6H_6 + (C_6H_5COO)_2^*$$
$$(C_6H_5COO)_2^* \longrightarrow 2C_6H_5COO\cdot$$

Scheme 1

Another possible mechanism is the direct attack of the excited benzene molecule upon the peroxide as shown in the following.



Scheme 2

By an analogy to the attack of trityl radical[2] and α-ethoxy-ethyl radical[3] upon the peroxide, the attack of the excited benzene is expected to take place on the peroxidic oxygen of the peroxide. If the benzoyl peroxide labeled with ^{18}O in the carbonyl oxygen were used, the phenyl benzoate produced *via* Scheme 1 should contain scrambled oxygen-18, whereas the phenyl benzoate produced *via* Scheme 2 should contain non-scrambled oxygen-18.

In an attempt to clarify the mechanism of the photochemical benzoyloxylation, we studied the products of decomposition of the benzoyl peroxide labeled with oxygen-18 in the carbonyl oxygen. A solution of 2.7 g of the labeled benzoyl peroxide in 500 m*l* of benzene (0.0223 mol/*l*) was irradiated with a high pressure mercury lamp either under a nitrogen atmosphere or with bubbling of oxygen gas (41 m*l*/min) at 18—20°C for 12 hr. By a separate experiment the half life of the peroxide under these conditions was found to be 55 min. After the reaction was over, the solution was evaporated to dryness, and the column-chromatographic separation of the residue gave 700 mg (in O_2) or 170 mg (in N_2) of pure phenyl benzoate. The carbonyl oxygen of phenyl benzoate or the starting peroxide was separated from alkoxy oxygen or peroxidic oxygen by the reaction with hydrazine. Benzhydrazide obtained was pyrolyzed and carbon dioxide evolved was assayed for oxygen-18 by mass spectrometry. The results are shown in Table 1.

They indicate that direct attack of excited benzene upon benzoyl peroxide does not occur to any appreciable extent. Therefore, as mechanism of the photochemical decomposition of benzoyl peroxide, Scheme 1 appears to be most probable.

Table 1. Specificity of ^{18}O-labeling

Sample	%^{18}O-Excess	%^{18}O-Calcd
Starting BPO	0.627	0.618
Its hydrazide	1.236	(1.236)
	N_2 atmosphere	
PhCOOPh*	0.606	0.618
Its hydrazide	0.535	0.618
PhCOOH*	0.612	0.618
	O_2 bubble	
PhCOOH*	0.586	0.618
Its hydrazide	0.642	0.618

* Direct products of photolyses

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1) T. Nakata, K. Tokumaru and O. Simamura, *Tetrahedron Letters*, **1967**, 3303.

2) W. von E. Doering, K. Okamoto and H. Krauch, *J. Am. Chem. Soc.*, **82**, 3579 (1960).

3) D. B. Denney and G. Feig, *ibid.*, **81**, 5324 (1959).