No Scrambling in the Decomposition of Labeled Benzoyl Peroxide

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Taylor and Martin[1] showed that *ca.* 38% of all radical pairs formed in the decomposition of acetyl peroxide recombined in the solvent cage to give acetyl peroxide with scrambling of label. We have investigated a similar reaction with benzoyl peroxide labeled with oxygen-18 in the carbonyl oxygen. We wish to report on a rather surprising finding that the scrambling of the label does not occur during the decomposition of the labeled benzoyl peroxide.

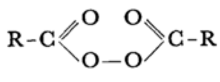
The labeled benzoyl peroxide was prepared from the labeled benzoyl chloride and sodium peroxide. A solution of 120 m*l* of benzene containing 8.00 g of the benzoyl peroxide was refluxed at 78°C for 340 min (a half life of the peroxide). The carbon dioxide evolved was collected in a liquid nitrogen trap. The reaction mixture upon 50% decomposition was cooled and separated into benzoyl peroxide, benzoic acid and an ester fraction, from which phenyl benzoate was isolated by elution chromatography.

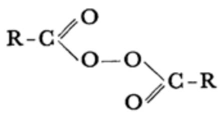
These products were converted into carbon dioxide which were assayed for oxygen-18 by mass spectrometry. Several methods were investigated in order to separate the carbonyl oxygen and the peroxidic oxygen in the benzoyl peroxide, and the best method found was converting it into benzhydrazide by the reaction with hydrazine. The hydrazide obtained from the starting peroxide contained all the oxygen-18 that was present in the peroxide. It is interesting to note that hydrazine attacks the carbonyl carbon of benzoyl peroxide, whereas dimethylaniline attacks the peroxidic oxygen.[2] The results are shown in Table 1.

TABLE 1. SPECIFICITY OF ^{18}O-LABELING

Sample	% ^{18}O-excess	% ^{18}O Calcd
Starting BPO	0.696	0.673
Its hydrazide	1.345	(1.345)
Recovered BPO	0.708	0.673
Its hydrazide	1.314	1.345
PhCOOH	0.682	0.673
PhCOOPh	0.628	0.673
CO_2	0.669	0.673

The hydrazide produced from the peroxide recovered after 50% decomposition contained all the oxygen-18 that was present in the starting peroxide (within the experimental error). This finding clearly shows that the scrambling of the label does not occur in the decomposition of the ^{18}O-labeled benzoyl peroxide in contrast to the case of acetyl peroxide.[1] It is difficult to determine the reason for the difference of the behavior of these two peroxides, but following explanation seems to be possible. There are two limiting conformations, I and II, for peroxides. Conformation I is favorable for the scrambling upon decomposition. Because of the resonance with the benzene ring, the carbonyl oxygen of benzoyl peroxide is negatively charged to a greater extent than that of acetyl peroxide. Due to the repulsion of the greater charge on the oxygen, the conformations of the decomposing benzoyl peroxide probably do not contain Conformation I. The majority of the peroxide will be decomposing from the conformations similar to Conformation II.


I


II

In order for the radicals produced from Conformation II to scramble, the carboxyl group must rotate. The bond between the methyl carbon and the carboxyl carbon is not restricted, whereas the bond between the benzene ring and the carboxyl carbon is somewhat restricted because of the resonance. The rotation of the benzoyloxy radical as a whole is also expected to be more difficult than the acetoxy radical which is much smaller. However, further investigation is necessary for the clarification of these points.

1) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966).

2) C. Walling, " Free Radicals in Solution," John Wiley, New York (1957), p. 590—595.