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Scrambling of Oxygen in the Diester Produced from Labeled Diacyl Peroxide-Olefin Reaction

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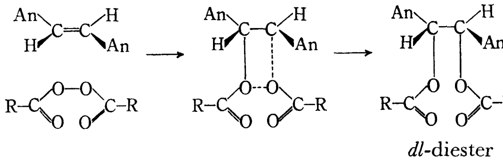
dl-Dihydroanisoin bis-*m*-bromobenzoate produced from the reaction between *p,p'*-dimethoxy-*trans*-stilbene and *m,m'*-dibromobenzoyl peroxide labeled with oxygen-18 at the carbonyl oxygen was found to possess completely equilibrated oxygens, and this finding indicated that a four-centerd mechanism was unlikely.

Formation of cyclohexyl acetate from the decomposition of diacetyl peroxide in cyclohexene was explained by the direct attack of cyclohexene on peroxidic oxygen,[1] but such mechanism was ruled out by a later publication describing the formation of cyclohexyl acetate and 1,2-diacetoxycyclohexane having completely scrambled oxygen-18 from the acetyl peroxide labeled specifically at the carbonyl oxygen.[2]

We have recently reported that phenyl benzoate formed from the photochemical decomposition in benzene of the benzoyl peroxide labeled with oxygen-18 at the carbonyl oxygen possesses completely scrambled oxygen and that direct reaction between benzoyl peroxide and benzene must be denounced.[3] Greene, Adam and Cantrill studied the decomposition of *m,m'*-dibromobenzoyl peroxide in benzene containing, *p,p'*-dimethoxy-*trans*-stilbene, isolated *meso*-dihydroanisoin bis-bromobenzoate (28%) and the *dl*-diester (57%), and proposed that the major course of the reaction proceeded by direct reaction between peroxide and olefin according to the four-centered mechanism shown below.[4]



($An = p\text{-}CH_3O\text{-}C_6H_4$, $R = m\text{-}Br\text{-}C_6H_4$)

We have investigated this reaction by use of oxygen-18, and have obtained evidence against such four-centered mechanism.

Experimental

m-Bromobenzaldehyde-^{18}O. *m*-Bromobenzylideneaniline (bp 135°C/0.5 mmHg) was prepared by the reaction with *m*-bromobenzaldehyde and aniline. When a mixture of $H_2{}^{18}O$ (5 g) (^{18}O atom % 1.52) and 9.8 g of concentrated sulfuric acid was added to 26.5 g of *m*-bromobenzylideneaniline, a slightly exothermic reaction took place and white crystals of anilinium sulfate precipitated. After the precipitates were filtered off, 50 m*l* of benzene was added. The organic layer was separated and dried over magnesium sulfate. After the solvent was removed in vacuum, the residual yellow-brown liquid was distilled under reduced pressure and 15.2 g of *m*-bromobenzaldehyde-^{18}O (bp 80.5°C/5 mmHg) was obtained.

m,m'-Dibromobenzoyl Peroxide Carbonyl-^{18}O. Chlorine gas was bubbled through a mixture of 50 m*l* of carbon tetrachloride and 15.2 g of *m*-bromobenzaldehyde-^{18}O at room temperature for 85 min. After the solvent was removed in vacuum, the residual liquid was distilled to give 13 g of *m*-bromobenzoyl chloride-^{18}O; yield, 73.0%.

According to the procedure described by Doering, Okamoto and Krauch[5] 13 g of *m*-bromobenzoyl chloride-^{18}O was let to react with sodium peroxide, and 8.7 g of *m,m'*-dibromobenzoyl peroxide was obtained; mp 117.8°C, yield, 79.5%.

Reaction between m,m'-Dibromobenzoyl Peroxide Carbonyl-^{18}O and p,p'-Dimethoxy-*trans*-stilbene. A benzene solution (35 m*l*) containing *m,m'*-dibromobenzoyl peroxide-^{18}O (1.33 g) and *p,p'*-dimethoxy-*trans*-stilbene (0.88 g) was frozen and degassed for three times in vacuum (10^{-2}—10^{-3} mmHg), and then was heated in a sealed ampoule at 78°C for 24 hr. According to the procedure described by Greene *et al.*,[4] the reaction mixture was treated with alkali for removal of *m*-bromobenzoic acid, and the *meso*-diester was obtained as crystals from ether. The main component of the residue was the *dl*-diester which was then purified by elution chromatography on silica gel. The carbonyl oxygen of the *dl*-diester was separated from the ether

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[1] J. C. Martin and E. H. Drew, *J. Amer. Chem. Soc.*, **83**, 1232 (1961).

[2] J. C. Martin, J. W. Taylor and E. H. Drew, *ibid.*, **89**, 129 (1967).

[3] M. Kobayashi, H. Minato and Y. Ogi, This Bulletin, **42**, 2737 (1969).

[4] F. D. Greene, W. Adam and I. E. Cantrill, *J. Amer. Chem. Soc.*, **83**, 3461 (1961).

[5] W. E. Doering, K. Okamoto and H. Krauch, *ibid.*, **82**, 3579 (1960).

oxygen by reaction with hydrazine in ethanol.[6] The content of oxygen-^{18}O was determined by mass-spectrometric analysis of the carbon dioxide obtained by pyrolysis of a sample.

Results and Discussion

The oxygen-18 analysis were performed for the starting peroxide, two products of the peroxide-olefin reaction (*m*-bromobenzoic acid and the *dl*-diester) and *m*-bromobenzhydrazide derived from the *dl*-diester. The results are summarized in Table 1.

Table 1. Specificity of ^{18}O labeling

Sample	Atom % ^{18}O-excess	% ^{18}O-calcd
Starting peroxide	0.516	(0.516)
m-Br-C_6H_4COOH	0.518	0.516
dl-Diester	0.459	0.516**
m-Br-$C_6H_4CON_2H_3$*	0.525	1.032**

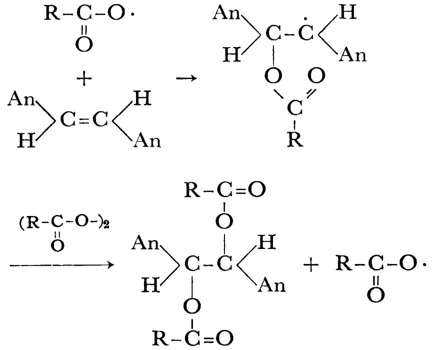
* Derived from the *dl*-diester by reaction with N_2H_4.

** Calculated according to Greene's mechanism.

The fact that oxygen-18 content of the benzhydrazide is approximately the same as that of the *dl*-diester indicates that carbonyl oxygen and ether oxygen of the *dl*-diester are almost completely equilibrated. If the peroxide decomposes *via* the four-centered mechanism corresponding to the direct reaction, the oxygen-18 of the peroxide must be completely retained at the carbonyl oxygen of the *dl*-diester, and the ^{18}O content of the benzhydrazide must be twice that of the *dl*-diester.

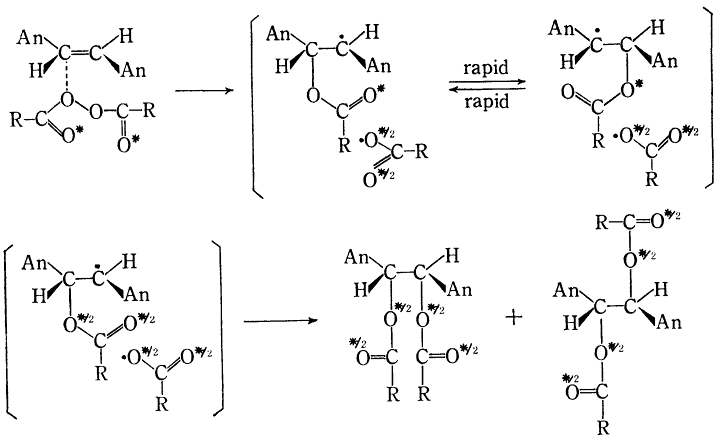
The possibility of the scrambling of the ^{18}O of the starting peroxide due to the recombination of benzoyloxy radicals in cage must be considered since such scrambling occurs in the cage of acetyl peroxide,[7] but we have recently demonstrated that such scrambling does not take place in the case of benzoyl peroxide labeled with oxygen-18 at the carbonyl oxygen.[8]

Thus the mechanism of the molecule-induced homolysis does not appear to be so straightforward as usually written.[9] The following radical-induced mechanism is rejected, at least as the major reaction, of the basis of the isotopic results in Table 1 and the finding of Greene *et al.* that in the presence of galvinoxyl the rate of the peroxide-olefin reaction was reduced by only 25%.



A mechanism which is consistent with various data obtained so far seems to be the following one, in which the diester is produced by combination of two radicals in a cage.

Certainly more detailed study is necessary in order to clalify the mechanism of this reaction completely. However, the above mechanism is consistent with the finding of Greene *et al.* that an



dl (57%) *meso* (27%)

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[6] D. Z. Denney, T. M. Valga and D. B. Denney, *ibid.*, **86**, 46 (1964).

[7] J. W. Taylor and J. C. Martin, *ibid.*, **88**, 3650 (1966).

[8] M. Kobayashi, H. Minato and Y. Ogi, This Bulletin, **41**, 2822 (1968).

[9] For instance, W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y. (1966), p. 119.

almost identical products mixture (29% *meso*-diester and 57% *dl*-diester) was obtained from the reaction between *p,p′*-dimethoxy-*cis*-stilbene and *m,m′*-dibromobenzoyl peroxide. The above mechanism is also similar to the mechanism proposed for the reaction between acetyl peroxide and cyclohexene.

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