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Study on Scrambling in Decomposition of Labeled Acetyl Benzoyl Peroxide

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Acetyl benzoyl peroxide [acetyl-^{18}O] and acetyl benzoyl peroxide [benzoyl-^{18}O] were decomposed in 0.1 M benzene solutions at 78° for 160 min (48% decomposition; its half life, determined by gas evolution, was 168 min.), and the undecomposed ABP-^{18}O was recovered and purified. The contents of oxygen-18 at the acetyl or benzoyl carbonyl were determined by converting the recovered ABP-^{18}O into acethydrazide or benzhydrazide. The results are shown in Table 1 and 2.

TABLE 1. OXYGEN-18 ANALYSIS OF ACETYL BENZOYL PEROXIDE [BENZOYL-^{18}O]

Sample	^{18}O excess atom %	
	Found	Calcd
$PhCON_2H_3$ derived from the starting ABP-^{18}O[a]	0.901[b]±0.007	(0.901)
$PhCON_2H_3$ derived from the recovered ABP-^{18}O	0.892[b]±0.016	0.901
Products of Decomposition		
$PhCO_2H$	0.466	0.451
$PhCO_2CH_3$	0.428	0.451
CO_2	0.196	—

[a] When the starting ABP-^{18}O itself was directly subjected to pyrolysis, the ^{18}O excess atom % of the carbon dioxide formed was 0.252 %.
[b] The average of the values obtained by two experiments.

TABLE 2. OXYGEN-18 ANALYSIS OF ACETYL BENZOYL PEROXIDE [ACETYL-^{18}O]

Sample	^{18}O excess atom %	
	Found	Calcd
$CH_3CONHN{=}CHPh$ derived from the starting ABP-^{18}O[a]	1.228	(1.228)
$CH_3CONHN{=}CHPh$ derived from the recovered ABP-^{18}O	1.169[b]+0.029	1.228
Generated CO_2 during decomposition	0.363[b]±0.003	—

[a] When the starting ABP-^{18}O itself was directly subjected to pyrolysis, the ^{18}O excess atom % of the carbon dioxide formed was 0.365 %.
[b] The average of the values obtained by two experiments.

Data in Table 1 and 2 indicate that scrambling of acetyl oxygen-18 appears to take place to small extent and that of benzoyl oxygen-18 was much less; these findings are in parallel with the results that scrambling of the labeled acetyl peroxide was extensive[1] whereas that of the labeled benzoyl peroxide was very small.[2,3]

Recently Goldstein and Judson[4] reported that oxygen scrambling of acetyl peroxide in isooctane was much more extensive than that in cumene. Therefore it is possible that scrambling of ABP is greater in solvents other than aromatic solvents. Further investigation is desirable in order to establish whether or not scrambling of the label of ABP is much affected by solvents.

Experimental

Benzaldehyde-^{18}O. A solution of 31 g of benzylideneaniline (0.17 mol) in 150 m*l* of ether was mixed with 11.0 g of ^{18}O-enriched water (1.3 atom % excess oxygen-18) and 19.7 g of concentrated sulfuric acid. After hydrolysis was complete, precipitates formed were filtered and the ether was evaporated under reduced pressure. The residue was distilled under reduced pressure, and 11.5 g of benzaldehyde-^{18}O was obtained at 61.0—63.5°C/14 mmHg.

Acetic anhydride-^{18}O. The method described by Oae, Kitao, and Kitaoka was used with some modification.[5] To a solution of 250 m*l* of anhydrous ethanol and 40 g of water enriched with 1.3 atom % excess oxygen-18, 23 g of sodium metal (1 mol) was added slowly with cooling. To this solution 41 g (1 mol) of acetonitrile was added, and the mixture was refluxed for 4 days. After hydrolysis was completed, the solvent was evaporated and the white crystals obtained was heated under reduced pressure until they melted. Sodium acetate formed amounted to 75.5 g (92%).

Then, 41 g (0.5 mol) of sodium acetate-^{18}O was treated with 89 g (0.75 mol) of thionyl chloride, and distillation yielded acetyl chloride-^{18}O (32.1 g; 82%). A mixture of 32.1 g (0.41 mol) of acetyl chloride-^{18}O and 34.5 g (0.42 mol) of sodium acetate-^{18}O was let to react at 140°C for 3 hr. Distillation of the mixture and the redistillation of the distillate yielded 24.5 g (57%) of acetic anhydride-^{18}O at 135—139°C.

Acetyl Benzoyl Peroxide [Acetyl-^{18}O] and Acetyl Benzoyl Peroxide [Benzoyl-^{18}O]. The method described by Juračka and Chromeček was used with some modification.[6] To a mixture of 10.6 g (0.1 mol) of benzaldehyde-^{18}O or benzaldehyde, 24.5 g (0.24 mol) of acetic anhydride or acetic anhydride-^{18}O and 6.3 g of magnesium carbonate, oxygen gas was bubbled for 7 hr at 40°C. After the reaction was over, 400

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[5] S. Oae, T. Kitao, and Y. Kitaoka, *ibid.*, **84**, 3359 (1962).
[6] F. Juračka and R. Chromeček, *Chem. Prumysl.*, **6**, 27 (1956); A. Yamamoto, N. Inamoto, H. Morikawa, and O. Simamura, Abstracts of the 19th Anual Meeting of the Chemical Society of Japan, 3F202, 113 (1966).

m*l* of cold water was added and the mixture was extracted with 100 m*l* of ether. The ether extract was washed with a 5% sodium hydrogen carbonate solution and water, and then dried over anhydrous magnesium sulfate. Evaporation of the ether under reduced pressure yielded yellowish white crystal . After three recrystallization from *n*-hexane 11.8—12.5 g of white crystals was obtained (65—70%); mp 37.5—38.0°C.

Decomposition of ABP-^{18}O in benzene. A 0.1 mol/*l* solution of ABP-benzoyl-^{18}O or ABP-acetyl-^{18}O in benzene was degassed, and then decomposed for 160 min at 78°C. The carbon dioxide evolved was measured by a gas buret, and then collected in a liquid nitrogen trap and analyzed for excess oxygen-18.

About 40% of benzene was removed from the reaction mixture under reduced pressure. The benzene solution was washed with a 5% sodium hydrogen carbonate solution, which upon acidification yielded precipitates of benzoic acid. The benzene solution was washed further with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. When the residue was distilled *in vacuo* at room temperature, methyl benzoate was present in the distillate. The residue was recrystallized twice from *n*-hexane, and white crystals of undecomposed ABP were recovered.

Determination of Oxygen-18 Contents. *(1) Oxygen-18 Content in Benzoyl Oxygen of ABP*: To an ice-cooled solution of 1.5—2.0 g of anhydrous hydrazine and 15 m*l* of dry benzene a solution of 1.5—2.0 g of ^{18}O-enriched ABP in 15 m*l* of dry benzene was added drop by drop. Benzene and unreacted hydrazine were evaporated from the reaction mixture under reduced pressure, and other volatile compounds were removed under a reduced pressure of 8×10^{-4} mmHg at 70°C. The residue was recrystallized from benzene, and the crystals obtained were further purified by repeating recrystallizations three times from ether. The benzhydrazide-^{18}O obtained melted at 109—111°C (lit,[7] 112.5°C). This sample was converted by pyrolysis to carbon dioxide, which was subjected to mass spectrometric analysis for the determination of the oxygen-18 content in the benzoyl oxygen of ABP.

(2) Oxygen-18 Content in Acetyl Oxygen of ABP: In a way similar to that described above in (1) ^{18}O-enriched ABP was let to react with anhydrous hydrazine. After benzene and unreacted hydrazine were removed under reduced pressure, the residue was subjected to distillation at 40°C under a reduced pressure of 8×10^{-4} mmHg. The distillate was dissolved in dichloromethane, and freshly distilled benzaldehyde was added to this solution. The dichloromethane was removed under reduced pressure and the residue was recrystallized three times from ether. *N*-Benzylideneacethydrazide obtained melted at 134—135°C (lit,[8] 134°C). This sample was converted to carbon dioxide, which was analyzed for the determination of the oxygen-18 content in the acetyl oxygen of ABP.

(3) Mass-spectrometric Determination of Oxygen-18 Content. Samples of ABP, benzhydrazide, *N*-benzylideneacethydrazide, benzoic acid, and methyl benzoate were converted by the method of Rittenburg and Ponticorvo[9] to carbon dioxide, and the peak ratio 44/46 was determined by use of a Hitachi RMU-6E Type mass spectrometer.

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7) R. Stollé, *J. Prakt. Chem.*, **69**, 145 (1904).

8) T. Curtius and H. Franzen, *Ber.*, **35**, 3234 (1902).

9) D. Rittenburg and L. Ponticorvo, *Int. J. Appl. Radiat. Isotopes*, **1**, 208 (1956).