## THERMAL DECOMPOSITION OF THE DIMETHYL ESTER OF PEROXYDIPHTHALIC ACID

# G. I. Nikishin, E. K. Starostin, and B. A. Golovin

UDC 541.11+542.92;547.584

The thermal decomposition of benzoyl peroxide in organic solvents has been investigated in detail. by a number of authors [1-4]. The decomposition of other aroyl peroxides containing functional or alkyl groups in the benzene ring has been considerably less studied. It was established that the benzoyloxy radicals, possessing substituents in the o-position, generated from certain peroxides, are inclined to undergo various rearrangements. Thus, the formation of individual products in the decomposition of otoluylbenzoyl and o-benzoylbenzoyl peroxides can be explained by intramolecular transfer of hydrogen atoms in the corresponding benzoyloxy radicals [5]. The thermal decomposition of o-phenoxybenzoyl peroxide is accompanied by a rearrangement of the o-phenoxybenzoyl radicals that arise to o- (carbophenoxy)phenoxyl radicals [6]. 3,4-Benzocoumarin is formed from o-phenylbenzoyl peroxide as a result of homolytic cyclization of o-phenylbenzoyl radicals [5].

This work was devoted to an investigation of the thermal decomposition of the dimethyl ester of peroxydiphthalic acid (DEPA) in solution; peroxydiphthalic acid itself is practically insoluble in organic solvents. The basic reactions products were identified, and the reaction kinetics in benzene and acetic acid was studied. According to the kinetic data, the decomposition of DEPA obeys a first-order equation with respect to the peroxide (Figs. 1 and 2). In acetic acid the reaction proceeds at a somewhat higher rate than in benzene, which is evidenced by the values of the rate constants at the temperature  $80^{\circ}$ ,  $1.97 \cdot 10^{-4}$  and  $1.47 \cdot 10^{-4}$  sec<sup>-1</sup>, respectively (Table 1). The activation energy of the decomposition in benzene is 24.0 kcal/mole, and in acetic acid 27.5 kcal/mole. It should be noted that the activation energy of the decomposition of benzoyl peroxide in benzene is 29.6 [7] and 31.0 kcal/mole [8] – it differs appreciably from the value that we found for DEPA.

The data obtained, in particular, the composition and structure of the reaction products (Table 2), permit us to assume that at the first step of the decomposition of DEPA there is a homolytic cleavage of



Fig. 1. Semilogarithmic plots of the kinetic curves of the decomposition of the dimethyl ester of peroxydiphthalic acid in acetic acid.

Fig. 2. Semilogarithmic plots of the kinetic curves of the decomposition of the dimethyl ester of peroxydiphthalic acid in benzene.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.5, pp. 946-950, May, 1971. Original article submitted August 1, 1969.

• 1971 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. TABLE 1. Rate Constants of the Decomposition of the Dimethyl Ester of Peroxydiphthalic Acid in Acetic Acid and Benzene

|                                                                      | Reaction rate constant $k \cdot 10^4$ |         |  |  |  |
|----------------------------------------------------------------------|---------------------------------------|---------|--|--|--|
| I, C                                                                 | acetic<br>acid                        | benzene |  |  |  |
| 95,4<br>90,0<br>85,0<br>80,3<br>80,0<br>76,0<br>75,0<br>72,0<br>69,5 | 10,13<br>5,62<br>3,40<br>1,97<br>     |         |  |  |  |
| E, kcal<br>/mole                                                     | 27,5                                  | 24,0    |  |  |  |

the O-O bond with the formation of o-(carbomethoxy)benzoyloxy radicals (I)



At the temperature  $80^{\circ}$  and DEPA concentration 0.045 M, these radicals undergo decarboxylation to a substantial degree: in acetic acid 1.35 moles of carbon dioxide per mole of the peroxide are liberated, and in benzene 1.16 moles of carbon dioxide

$$(11) \begin{array}{c} \text{COOCH}_3 \\ \text{COOC$$

The formation of other gaseous substances does not occur. Phthalic anhydride was detected somewhat unexpectedly in the decomposition products. Its formation can be explained if we assume that the radicals (I) are capable of cyclization with elimination of a methoxy radical



The probability of such cyclization is confirmed by a qualitative identification of methanol in the reaction mixture (by the method of mass spectrometry on an MI-1305 instrument according to the characteristic peaks of the ions with mass numbers 32 and 31). The latter is readily obtained on account of stripping of hydrogen atoms from the solvent by methoxy radicals [9]. However, reaction (3) cannot be considered a priori as the only pathway of synthesis of phthalic anhydride and methanol from DE PA. Together with the homolytic cyclization of radicals (I), we should also have assumed the possibility of occurrence of reactions (4) and (5)



Our investigations permitted us to establish that under the experimental conditions that we used, methanol and phthalic anhydride are not formed from the monomethyl ester of phthalic acid, i.e., reaction (5) does not take place. In addition to participation in monomolecular processes of decarboxylation and cyclization, radical (I) is also capable of interacting with the solvent.

| · · · · · · · · · · · · · · · · · · · |          |                   |                         |                                    |                                         |                                              |                                                |                                            |  |
|---------------------------------------|----------|-------------------|-------------------------|------------------------------------|-----------------------------------------|----------------------------------------------|------------------------------------------------|--------------------------------------------|--|
| Solvent                               | T, °C    | Carbon<br>dioxide | Phthalic<br>anhydride   | Methyl ester<br>of benzoic<br>acid | Dimethyl<br>ester of di-<br>phenic acid | Methyl ester<br>of o-phenyl-<br>benzoic acid | Methyl-<br>phenyl ester<br>of phthalic<br>acid | Monomethyl<br>ester of<br>phthalic<br>acid |  |
| Benzene                               | 80<br>80 | $1,16 \\ 1,35$    | 0, <b>5</b> 56<br>0,236 | $0,240 \\ 0,970$                   | 0,096                                   | 0,557                                        | 0,001                                          | 0,085<br>—                                 |  |

TABLE 2. Yield of Decomposition Products of the Dimethyl Ester of Peroxydiphthalic Acid, Moles per Mole of the Peroxide



Fig. 3. IR spectrum of the dimethyl ester of peroxydiphthalic acid in carbon tetrachloride.



Fig. 4. IR spectrum of peroxydiphthalic acid in a pressing with KBr.

In the decomposition of DEPA in benzene, the methylphenyl ester of phthalic acid was detected among the reaction products; it is probably formed as follows:



However, this pathway is realized with a very negligible contribution to the summary process of chemical conversions of the radicals (I) – the yield of the monophenyl ester of phthalic acid is only 0.001 mole per mole of the peroxide. It may be assumed that an analogous reaction takes place between benzene and the radicals (II), generated according to Eq. (2). As a result, the methyl ester of o-phenylbenzoic acid is obtained

$$(7)$$

In Eqs. (6) and (7), X' undoubtedly represents radicals (II), and evidently radicals (I) and CH<sub>3</sub>O. We have already noted the presence of methanol, formed from CH<sub>3</sub>O, in the decomposition products of DEFA.

As for the radicals (I), they should be converted to the monomethyl ester of phthalic acid according to schemes (6) and (7). However, the monomethyl ester of phthalic acid could not be identified by the method of gas — liquid chromatography under the conditions that were used as applied to the analysis of the other esters presented in Table 2.

For this reason, the reaction products were preliminarily methylated with diazomethane, then analyzed for the content of the dimethyl ester of phthalic acid.

In the decomposition of DE PA in acetic acid, the radicals of (II) that arise enter into a reaction with the solvent, giving the methyl ester of benzoic acid, and recombine, forming the dimethyl ester of diphenic acid

 $2 \xrightarrow{\text{COOCH}_3} \xrightarrow{\text{COOCH}_3} \xrightarrow{\text{COOCH}_3} (8)$ 

#### EXPERIMENTAL

Peroxydiphthalic acid was synthesized according to the method of Bayer [10, 11]: 20 g of thoroughly ground phthalic anhydride was added to a vigorously mixed cooled mixture of 150 ml of 3% hydrogen peroxide and 75 ml of 10% sodium hydroxide. After 5 min of filtration, the unreacted anhydride was removed, the filtrate acidified with sulfuric acid, the white crystals precipitated, filtered off, washed with water, acetone, and dried under vacuum; mp 168° (with decomp.).

Dimethyl Ester of Peroxydiphthalic Acid. DEPA was produced by methylation of peroxydiphthalic acid with an ether solution of diazomethane, prepared from nitrosomethylurea [12]. The product, recrystallized from ether, was isolated in the form of white crystals with mp 101.5°. Found: C 60.35; 60.36; H 4.17; 4.22%.  $C_{18}H_{14}O_8$ . Calculated: C 60.34; H 3.91%. The content of active oxygen, according to the data of iodometric titration [13], is 98-100% of the theoretical.

The kinetic results were obtained in the decomposition of DEPA in a thermostatically controlled reactor  $(\pm 0.1^{\circ})$  in an atmosphere of purified argon. The initial peroxide concentration was 0.075 M. The decomposition of DEPA for a determination of the composition and yield of the products obtained was conducted in a two-necked flask, equipped with a reflux condenser, a tube for introduction in inert gas, and a trap with alkali for the trapping of CO<sub>2</sub>. The peroxide concentration in such experiments was 0.045 mole per mole of the solvent. Temperature of the reaction  $80^{\circ}$ .

The composition of the decomposition products of DEPA was determined by the method of gas -liquid chromatography, using an internal standard and standard samples produced by counter synthesis. Conditions of analysis: temperature 140-160°, column length 2 m, diameter 4 mm, 10% polyethylene glycol adipate and 15% silicone SE-30 on Chromosorb P. The detector was a katharometer, the carrier gas helium. The amount of the monomethyl ester of phthalic acid was calculated as the difference between the total content of the dimethyl ester of phthalic acid in the products of methylation of the reaction mixture and the amount of dimethyl phthalate corresponding to the content of phthalic anhydride (the latter is methylated by diazomethane together with the carboxylic acid [12]). The IR spectra cited in Figs. 3 and 4, corresponding to peroxydiphthalic acid and its dimethyl ester, were taken in a pressing with KBr and in a solution of carbon tetrachloride, respectively. The spectra were taken on a UR-10 instrument.

### CONC LUSIONS

1. The kinetics of the thermal decomposition of the dimethyl ester of peroxydiphthalic acid in acetic acid and benzene was studied.

2. The basic reaction products were identified, and the mechanism of their formation was proposed.

#### LITERATURE CITED

- 1. D. H. Hey and J. Peters, J. Chem. Soc., 79 (1960).
- 2. H. Gellison and P. H. Hermans, Ber., 58, 285, 476, 765 (1925).
- 3. H. Gellison and P. H. Hermans, Ber., 59, 63, 662 (1926).
- 4. D. F. De Tar and R. C. Lamb, J. Amer. Chem. Soc., 81, 122 (1959).
- 5. F. D. Greens, G. R. Vannorman, J. C. Cantrill, and R. D. Gilliom, J. Organ. Chem., 25, 1790 (1960).
- 6. F. De Los, D. F. De Tar, and A. Hlynsky, J. Amer. Chem. Soc., 77, 4411 (1955).
- 7. C. A. Kamenskaya and S. S. Medvedev, Zh. Fiz. Khimii, 14, 922 (1940).
- 8. K. Nozaki and P. D. Bartlett, J. Amer. Chem. Soc., 68, 1686 (1946).
- 9. U. C. McBay and O. Tucker, J. Organ. Chem., 19, 1003 (1954).
- 10. A. Bayer and V. Villiger, Ber., 34, 762 (1901).
- 11. V. Karnozhintskii, Organic Peroxides [Russian translation], IL (1961), p. 66.
- 12. In: New Methods of Preparative Organic Chemistry [Russian translation], IL (1950).
- 13. F. Kritchfield, The Analysis of the Basic Functional Groups in Organic Compounds [Russian translation], Mir (1965), p. 189.