## THE MECHANISM OF OXIDATION OF DERIVATIVES OF AMINOALKYLPHENOLS BY BENZOYL PEROXIDE COMMUNICATION II. PRODUCTS OF THE OXIDATION OF THE METHYL ETHER OF o-AMINO-p-tert-BUTYLPHENOL

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UDC 541.124+542.943+547.564.4

In an earlier communication [1] we described the radicals formed in the oxidation of the methyl ether of o-amino-p-tert-butylphenol (MEABP) by a nonequivalent molar quantity of benzoyl peroxide (BP). In this paper we describe the nonradical products in the oxidation of MEABP by BP in equimolar ratio.

The method of workup for these oxidation products was changed somewhat. First of all, a crystalline product (I) precipitated from the reaction mixture upon standing. Benzoic acid (BA) was removed from the benzene solution by repeatedly washing with water. Finally, the washed benzene solution was chromatographed on  $Al_2O_3$ . After chromatography and recrystallization two additional products were isolated: cream-colored needles (II), mp 138.2-139.2°C, and red crystals (III), mp 321-323°C. Besides this, there were stable radicals which had some ionic character, as reported earlier [1]. Obviously, there are many products in the oxidation of MEABP by BP. Considering also the repeated chromatographies and purification steps, the yield of isolated products is very small, and determination of their structures is quite difficult.

The ammonium salt of benzoic acid (I), mp  $180-186^{\circ}$ C, precipitates out as white scales. In spite of its simple composition, there is a problem in determining its structure. The reaction product always had benzoic acid as an impurity, in various amounts depending on the experiment. Benzoic acid can be formed either in the oxidation reaction or by decomposition of (I). The product remains impure even after re-crystallization. Vacuum sublimation of (I) gave the acid salt  $C_6H_5COONH_4C_6H_5COOH$ ; this transformation of ammonium salts is described in other work [2]. The composition of (I) was determined by the quantity of NH<sub>4</sub>Cl formed upon the addition of gaseous HCl to an alcohol solution of (I), which showed an equimolar ratio of benzoic acid to NH<sub>3</sub>. The identity of (I) as ammonium benzoate was finally proven by synthesis from NH<sub>3</sub> gas and BA in benzene solution, which gave a product identical to (I) by IR spectroscopy.

The formation of ammonium benzoate in the reaction of MEABP with BP was somewhat surprising to us. Other workers [3, 4] have noted the cleavage of the amino group as  $NH_3$  in the peroxidase oxidation of 4-methoxy-2,6-dimethylaniline and p-anisidine in the presence of  $H_2O_2$ . The authors propose several possible mechanisms for the cleavage with  $H_2O_2$  playing a basic role. It is still not clear how the amino group is cleaved in our case.

Benzoic acid can easily be formed by the abstraction of a hydrogen atom from the amino group by a radical of a peroxidic residue or by benzoyl peroxide itself.

Compound (II), mp 138.2-139.2°C by its elemental analysis and molecular weight seems to be the product of the addition of the benzoic acid residue to the starting material. There is no reaction when gaseous HCl is bubbled into a benzene solution of (II), inferring that the addition occurs on the amino group. We thus conclude that compound (II) is benzoyloxy-(2-methoxy-5-tert-butylphenyl)amine



A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1097-1099, May, 1970. Original article submitted November 14, 1968.

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The IR-spectrum of (II) had absorption bands characteristic for OCH<sub>3</sub> (~2840 cm<sup>-1</sup>), tert-butyl group (~2900 cm<sup>-1</sup>), NH (~3240 cm<sup>-1</sup>), as well as other bands we could not explain. It was verified that no (II) is formed by reaction of starting material MEABP with BA during chromatography. This experiment involved chromatography on  $Al_2O_3$  of a mixture of MEABP and BP (1:1 molar ratio) which had been left for 20 h. The MEABP was eluted quantitatively from the column while BA was adsorbed. The appearance of (II) in the products of the oxidation reaction can be explained using a mechanism proposed earlier [1]. The initially formed radical (IV) is unstable and undergoes further reaction with a benzoic acid radical or with BP to form the addition product (II)



Compound (III), mp 321-323°C from its molecular weight and elemental analysis contains two residues of the starting amine and one residue of BP. No structure for (III) was determined, as it seems to be a product of later stages of the oxidation of MEABP.

## EXPERIMENTAL

Oxidation of MEABP by BP (1:1). MEABP (7.27 g) and BP (10.40 g) were dissolved in a minimal volume of dry benzene (85 ml). To avoid the strong initial heating and spattering of the reaction mixture the BP was added in small portions and the reaction mixture was cooled in ice. The mixture immediately turned dark brown in color, with a tinge of red. After 65 h a precipitate was removed by filtration (0.5248 g, 2.97% based on starting material). Washing of the precipitate on the filter with ethyl ether gave white scales of (I), mp 180-186°C. Found: C 60.78; 60.64; H 6.52; 6.30; N 6.88%.  $C_6H_5COONH_4$ . Calculated: C 60.40; H 6.5; N 10.05%.

From the ethyl ether washings BA, mp 120°, was isolated. Sublimation of (I) in vacuum (2 mm Hg) gave an acid salt. Found: C 64.04; 64.36; H 5.76; 5.62; N 4.99; 4.97%.  $C_{14}H_{15}O_4N$ . Calculated: C 64.45; H 5.8; N 5.37%.

Gaseous HCl was bubbled into an alcohol solution of 0.1520 g of (I), precipitating 0.0529 g of  $NH_4Cl$ , mp 340°C (337°C [5]).

The filtered benzene solution was washed repeatedly with hot water. The washing was deemed complete when ether extraction of the water washings and subsequent evaporation gave no residue of BA. One liter of the total water washings (10.325 liters) was extracted with ether ( $6 \times 130$  ml). After drying the solution over CaCl<sub>2</sub> and evaporating the ether, BA (0.6519 g, mp 114-116°C) was isolated. For the total water washings this would be 6.6472 g, or 64% based on BP, 37.6% based on starting material. Recrystallization from water gave BP mp 121°C, which did not show a mp depression when mixed with authentic pure BA.

The washed benzene solution underwentchromatography on  $Al_2O_3$  (particle size 50-140 mesh) on a column with successively decreasing diameter  $(37 \times 250 \text{ mm}) + (24 \times 220) + (10 \times 800 \text{ mm})$ . Elution solvents were benzene (2750 ml), ethyl ether (1500 ml), acetone (500 ml), ethanol (300 ml) and ether (300 ml). The various fractions had different colors, and gave powdery products upon removal of solvent.

Compound (II) separated from the orange first fraction upon workup of the dark brown powder with petroleum ether. The product was obtained as a sandy-colored precipitate, mp 129-139.5° (1.53% of total products). Recrystallization from petroleum ether gave cream needles of (II), mp 138.2-139.2°C, insoluble in water, slightly soluble in petroleum ether, soluble in alcohol and ether, and very soluble in benzene and  $CCl_4$ . Found: C 72.00; 71.84; H 7.13; 7.02; N 4.54; 4.77%; mol. wt. 291.75 (cryoscopic) and 297.5 (Rast).  $C_{18}H_{21}NO_3$ . Calculated: C 72.23; H 7.07; N 4.68%; mol. wt. 299.35.

Compound (III) was isolated from a red fraction by continuous extraction and subsequent precipitation from ethyl ether, to give clear red crystals with mp 321-323°C (Kopfler). Compound (III) is slightly soluble in alcohol, ether, CCl<sub>4</sub>, and benzene, and more soluble in CHCl<sub>3</sub>. Gaseous HCl bubbled into a benzene solution of (III) changes its color to cinnamon, and with conc.  $H_2SO_4$  the color changes to emerald green, which becomes brick-red when diluted with water. This reverts to the clear red crystals of (III) after a few days. Catalytic reduction of (III) in CHCl<sub>3</sub> over Pt/C gives a colorless solution which becomes brick-red in air. Found: N 5.77; 6.07%; mol. wt. 576 (Rast).

## CONCLUSIONS

Four products of the oxidation of o-amino-p-tert-butylphenol by benzoyl peroxide (1:1 molar ratio) were isolated and characterized. Structures of three of these were established.

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