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STRUCTURE IDENTIFICATION OF SUBSTITUTED PHENOL REDOX PRODUCTS BY: THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

The structure of separated pure products obtained by oxidation of bromo- and chlorophenols with iodine were investigated by microanalysis, infrared (IR) spectroscopy and by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) to elucidate their molecular formulae. DTA analysis together with the IR spectral studies support the picture developed from TGA. This indicates that not only the crystallization water was lost but also the functional decomposition of these parent halogenated phenols is necessarily needed (as sublimation of some native iodine molecules) to interpret the successive mass lost. This structure elucidation confirms the previously reported mechanism of such redox reactions.

INTRODUCTION

Only a small amount of information on the separation and identification of the oxidation products obtained by reaction of phenol derivatives with inorganic oxidants, such as iodate, periodate, iodic and periodic acids have been published previously [1–6]. Some of these trials refer to the presence of iodine in the separated products [6]. Reaction of iodine with aromatic compounds may lead to nucleophilic and/or electrophilic interaction with the aromatic ring [7,8]. Iodine also reacts with aromatic-oxygen containing compounds to form iodosobenzene (C_6H_5IO, a yellow basic solid compound) and iodoxybenzene ($C_6H_5IO_2$, solid m.p. > 230) [9].

In this laboratory, the products obtained by oxidation of phenol derivatives with iodine in aqueous iodide solution under various conditions [10] were separated but not identified, as is the usual procedure. The mechanism of such redox reactions between iodine and phenols was suggested and well explained by using potentiometric and kinetic studies [11–13]. The identification of the solid redox products obtained may confirm the suggested schemes. The aim of the present work is, therefore, the critical identification of such redox products by microanalysis, IR spectra and essentially by DTA and TGA measurements.

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EXPERIMENTAL

Materials and solutions

The chemicals used in this investigation were all of analytical grade. They included *o*-bromophenol (*o*-BP), *p*-bromophenol (*p*-BP) and *o*-chlorophenol (*o*-CP) and iodine (from Koch-Light). The water used was always twice distilled using all glass equipment.

The 0.025 M solution of iodine (6.35 g l^{-1}) in aqueous potassium iodide (10 g l^{-1}) was prepared and kept in a dark flask. Stock solutions of 0.025 M phenol derivatives were prepared by dissolving the accurately measured calculated weights in the required volume of double-distilled water. The 0.05 M sodium hydroxide solution was prepared from the carbonate-free stock solution used to adjust the pH of the redox reaction medium to pH 8–9. A pH/mV meter (Orion Research Model 701 A) and a digital ionizer with combined pH electrode (Orion Model 91-02) were used for pH adjustment.

Preparation of the solid redox products

Equal volumes of aqueous iodine and phenol derivatives solutions were mixed, with constant stirring whilst adjusting the pH to 8–9 by gradual addition of aqueous sodium hydroxide solution, until the solid redox product just appeared. At pH > 10 the solid product obtained may dissolve. The solid product coagulated rapidly within 5 min of gentle warming on a water bath. Then, the precipitate was filtered from the mother liquor through a porcelain Buchner funnel using a water pump. The precipitate was washed several times with hot distilled water. The dried solid redox products were recrystallized twice from an ethanol–water mixture. The m.p.'s of the solid products were 120 ± 2, 126 ± 1 and 102°C for the *o*-BP, *p*-BP and *o*-CP products, respectively. The same solid products were also collected from the redox reaction medium when the redox reaction of iodine and phenol derivatives [10] was followed potentiometrically at the same pH values.

Microanalysis of the redox products

The microanalysis for C, H, halogen and the molecular weight (MW) determination of the crystalline pure product were performed by the Microanalytical Center at Cairo University. From the microanalysis data, the possible general formula of the redox products of *o*-BP and *p*-BP is $C_6H_4I_2O \cdot 2H_2O$, which contains two molecules of water of crystallization (calc.: (C) 18.84, (H) 2.09, (I) 66.49, MW 382; found (C) 18.7, (H) 2.05, (I) 66.1, MW 385). The obtained solid product of *o*-CP takes the formula of $C_6H_4ClIO \cdot 2H_2O$ (calc.: (C) 24.8, (H) 2.75, (Cl) 12.2, (I) 43.7, MW 290.5; found: (C) 23.9, (H) 2.2, (Cl) 11.9, (I) 45.0, MW 299.1).

IR spectra

The IR spectra of the solid redox products obtained was measured by the KBr disc technique (at the same microanalytical unit) in the range 250–4000 cm^{-1}. The IR spectra show [14] a band at 3420 cm^{-1}, which refers to the presence of a hydrogen-bonded OH group, with the other frequencies in the range 3480–3510 cm^{-1}, which refer to the water molecules of crystallization. The peak at 860 cm^{-1} refers to two vacant adjacent positions in the aromatic ring and the peak at 880 cm^{-1} refers to the position which is occupied by the second iodine atom, obtained by the electrophilic attack on the aromatic ring by iodine.

Thermal analysis (DTA and TGA)

The DTA and TGA studies were made by using a conventional thermal analyser (Shimadzu system, Shimadzu 30 series thermal analysis instrument). The weight losses (from 2.5 mg sample) and heat response of the changes in the sample were measured in the range from room temperature to 350 °C. The heating rate was 10 °C min^{-1} in both TGA and DTA.

RESULTS AND DISCUSSION

DTA curves for the oxidation products of *o*-BP, *p*-BP and *o*-CP are represented graphically in Fig. 1, graphs (a), (b) and (c), respectively. Curve (a) indicates the appearance of a finite exotherm at 82 °C, a very strong endothermic peak at 182 °C and a strong broader endotherm which is centered at 282 °C but essentially starts at about 250 °C. A small exotherm, following the last decomposition peak, was found to be centered at about 290 °C.

The finite exotherm at 82 °C might be related to the secondary interactions between the sample and environmental moisture and might be subjected to some aggregation effects of the sample multiples or particulates.

The second deep endothermic peak at 182 °C follows the conventional crystallization-water loss. The relatively weak endotherm located at 250–282 °C might be reasonably attributed to the significant decomposition of the oxidation product of *o*-BP with sublimation of some constitutional iodine molecules. This might tentatively follow the crystallization of decomposition products which is related to the weak exotherm located at about 290 °C. The relatively weak endothermic peak centered at 282 °C might be partially compensated for by the consequent liberation of lattice energy by the existing molecular species.

The DTA curve obtained for the oxidation products of *p*-BP (Fig. 1, curve b) is not dissimilar to that obtained for the products of *o*-BP. The

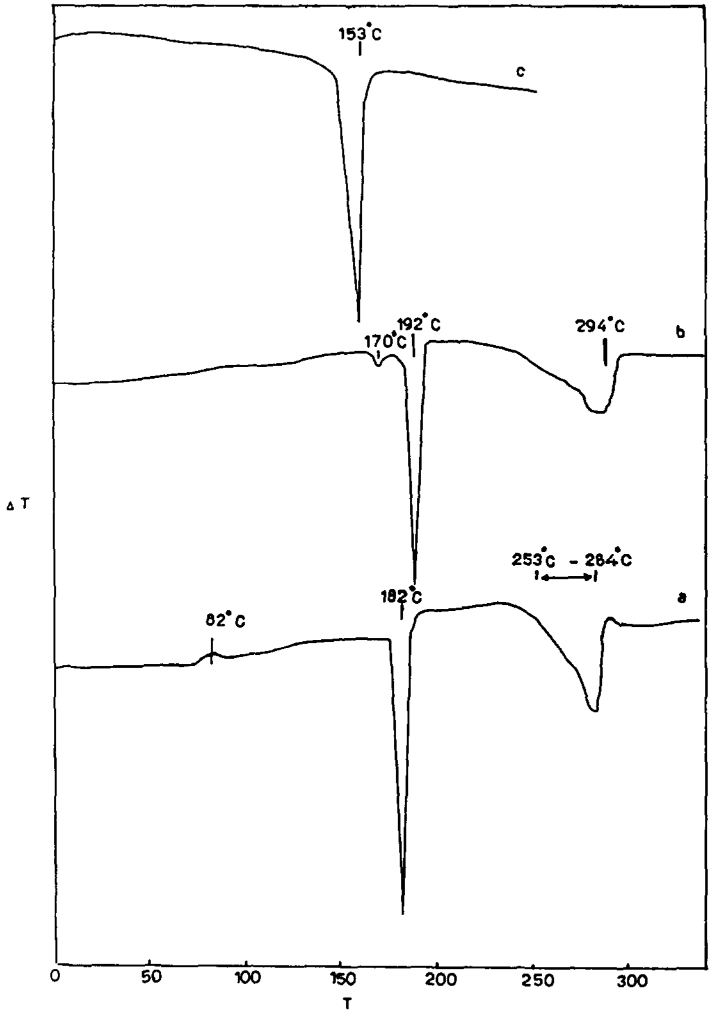


Fig. 1. Differential thermal analysis of the redox products of the iodine interaction with: (a) *o*-BP; (b) *p*-BP; (c) *o*-CP.

weak shoulder at 72–84 °C (Fig. 1b) replaces the peak at 82 °C (Fig. 1a). The very strong endotherm centered at 182 °C in curve (a) is qualitatively split to the endotherms at 170 °C and 192 °C in curve (b). This might reflect a similar nature of the loss of crystallization water with a less significant demarkation in the nature of crystallization water.

The relatively broad peak, 250–294 °C, might reflect some qualitative differences in the nature of the bonding of the iodine entities with the benzene rings; in curve (b), no crystallization exothermic peak was obtained at 290 °C.

The nature of the functional groups existing in the redox products of *o*-BP, *p*-BP and in *o*-CP were identified by IR spectroscopy, see Figs. 2a, 2b

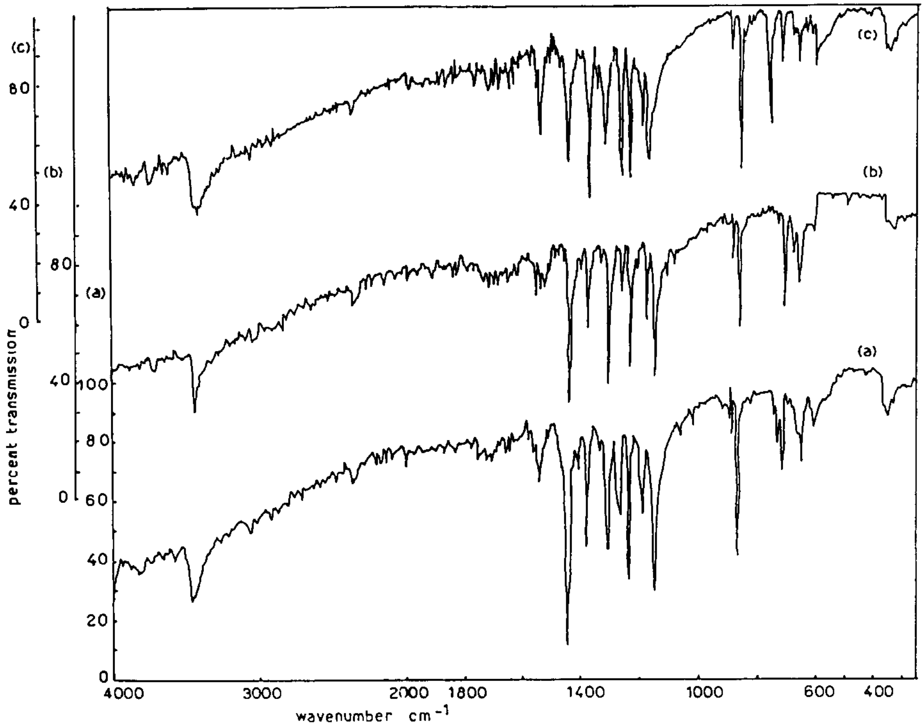
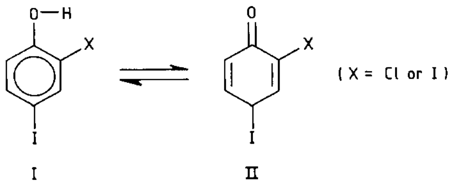


Fig. 2. Infrared spectra of the redox products of iodine interaction with: (a) *o*-BP; (b) *p*-BP; (c) *o*-CP.

and 2c, respectively. Spectra (a) and (b), for *o*-BP and *p*-BP redox products, respectively, are almost identical apart from some bands in the range 1500–1100 cm^{-1} which characterizes the aromatic ring frequencies. Complementary band characteristics for various functional groups are listed in Table 1. The differences between the IR spectra and DTA curves of the redox products of *o*-BP and *p*-BP suggest that a hybrid structure exists between these two canonical forms. The weak endothermic peak at



253–284°C (centered at 282°C) of Fig. 1a suggests that the *o*-BP redox products contain mostly the canonical form **I** and only a minor amount of **II**. However in Fig. 1b the broad weaker endotherm at 250–298°C (centered at 294°C) suggests that the cannonical form **II** predominates in the redox products of *p*-BP with only a minor amount of structure **I**. This finding agrees with the previously established reaction mechanisms [10].

TABLE 1

Identification of the important frequencies of the IR spectra of the oxidation products of *o*-BP and *p*-BP with I_2

Important bands [a] (cm^{-1})		Identification
o-BP	*p*-BP	
860 vsh	860 vsh	*p*-Substituted two adjacent
880 vsm	880 vmsh	Isolated-H
1150 vsh	1150 vsh	C–O (stretched)
1260 sh	1260 smsh	O–H bending
1540–1560 b	1500–1560 b	Aromatic ring bands
1640–1650 smb	1640–1650 smb	Water of crystallization
3390–3420 smb	3350–3420 shb	Intramolecular and weakly bonded O–H
3780–3740 smb	3650–3700 smb	H-bonded OH in solid

[a] vsh, very sharp; smsh, small sharp; b, broad; smb, small broad; sh, sharp; shb, sharp broad.

The DTA curve for the oxidation products of *o*-CP (Fig. 1c) exhibits a strong endothermic peak at 153°C which may be reasonably interpreted as corresponding to the loss of crystallization water without any further losses confined to the decomposition of the chloride derivative redox product.

As has been previously reported [9], the bond energies for C–Cl, C–Br and C–I are 393.3, 274.5 and 414.2 kJ mol^{-1}, respectively. The order of magnitude of these bond energies does not fit with the nature of the pre-explained DTA curves of the redox products obtained. The fractional decomposition process is, therefore, integrally fulfilled by the total of bond energies and the polarizability [15] of these bonds at the onset of the

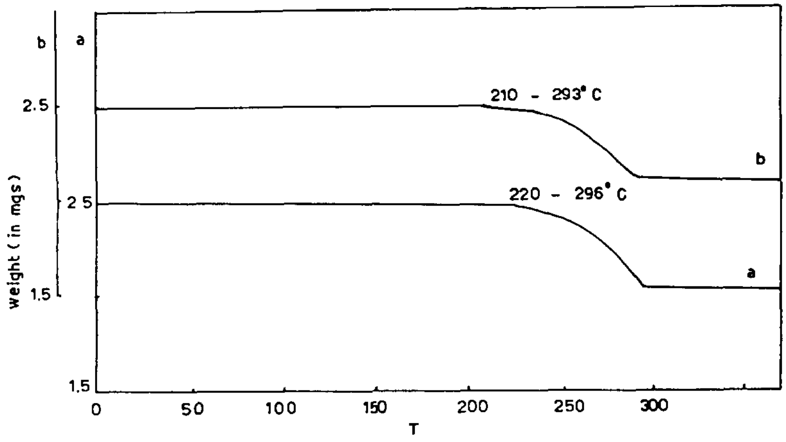


Fig. 3. Thermogravimetric analysis plots of the redox products of the iodine interaction with: (a) *o*-BP; (b) *p*-BP; (c) *o*-CP.

decomposition process (i.e., detachment of the halide from the parent moeity).

Figure 3 illustrates TGA for *o*-BP and *p*-BP redox products (curves (a) and (b), respectively) which show similar trends of mass loss with the consequent increase of temperature. The temperature range 220–296°C indicates a 17.2% mass loss for the *o*-BP redox products, which was found to exceed the loss of two water molecules of crystallization (from chemical analysis 9.45%). This indicates that crystallization water loss is also accompanied by a fractional mass loss of the halide content from the parent material. Similarly, in case of the *p*-BP redox products, the TGA mass loss (12.2%, withing the range 210–293°C) exceeds the total mass loss chemically determined (i.e., 9.45%).

The foregoing discussion of DTA and IR spectral studies supports the picture developed from thermogravimetric analysis. This indicates that not only is the crystallization water lost but the fractional decomposition of these parent phenol derivatives (as sublimation of some native iodine molecules) is necessarily needed to interpret the excessive mass lost.

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