Thermochimica Acta, 179 (1991) 237–245
Elsevier Science Publishers B.V., Amsterdam

STRUCTURE ELUCIDATION OF AMINOPHENOLS–IODINE REDOX PRODUCTS BY EMANATION THERMAL ANALYSIS

M.A. ZAYED

Chemistry Department, Faculty of Science, Cairo University, Giza (Egypt)

V. BALEK

Nuclear Research Institute, REZ, Prague (Czechoslovakia)

(Received 27 July 1990)

ABSTRACT

The structures of polymers I and II and the dimer III that formed during the oxidation of *o*-, *p*- and *m*-aminophenol respectively with iodine have been studied previously by TGA, DTA, and elemental and spectral analyses. In the present work these structures were confirmed by emanation thermal analysis (ETA) of the compounds. The possible structural changes of these polymeric and dimeric forms were followed at different temperatures by measurement of emanation power under various conditions. The schemes representing the possible chemical and physical changes were suggested during gradual heating, isothermal heating and gradual cooling at different stages. The results were in good agreement with those of normal TGA and DTA. Detailed changes were detected and identified by the non-traditional technique of ETA which could not be identified by conventional methods of analysis.

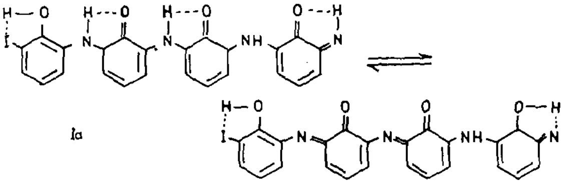
INTRODUCTION

New and sensitive methods for the investigation of solid substances are needed, mainly for checking the quality of raw materials, intermediate products and final products in the production of materials with defined properties and for the optimization of the associated technological procedures. In recent years some techniques based on non-traditional principles have been developed [1–5]. By the use of such techniques and of new methods of data evaluation [6,7] we can often obtain new information about solids. The aim of this work is the correlation of measurements obtained using conventional thermal analysis methods (TGA and DTA) [4] with those obtained using the non-traditional technique of emanation thermal analysis (ETA) on solid products obtained during oxidation of aminophenols with iodine in order to confirm their proposed structures. The ecological importance of oxidation of phenols with iodine lies in removal of their toxicity towards living things, such as the Egyptian carp fish [7]. It is important to study their redox products in order to confirm the mechanism of the redox reactions [8] and their stoichiometry and thus to suggest a suitable iodine dose for toxicity removal.

EXPERIMENTAL

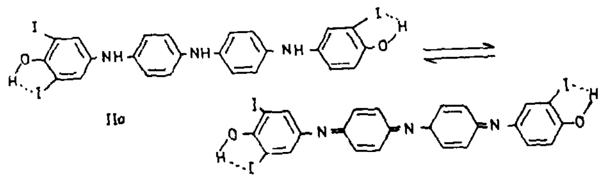
Preparation of solid samples and structural identification

The samples were prepared by addition of iodine solution to aminophenols under appropriately selected conditions, and then investigated by thermal (TGA and DTA) and spectral (UV and IR) analyses [4]; alternatively, they were obtained from the redox reaction medium in potentiometric monitoring of the iodine–aminophenol redox reactions [9]. The compounds obtained are the reddish-violet solid polymer product **I** from *o*-aminophenol (*o*-AP), m.p. 240 °C, the deep violet redox product **II** of *p*-aminophenol (*p*-AP), m.p. 250 °C, and the brown dimer **III** of *m*-aminophenol (*m*-AP), m.p. 138 °C. These products were named as recommended by IUPAC (Chemical Abstracts 1967–1971 index period) [10] and their structures were proposed as



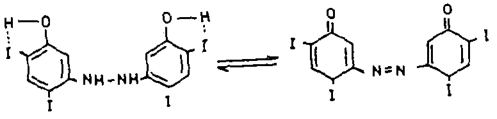
Ia

Ib



IIa

IIb



IIIa

IIIb

Emanation thermal analysis

ETA is defined [1,11] as "a technique in which the release of radioactive inert gases from a substance is measured as a function of temperature or time whilst the substances are subjected to a controlled temperature programme". Inert gases are used as indicators of the state of solids and their changes.

Sample labelling

Labelling was performed by impregnating the sample to be measured with a solution containing ^{228}Th and ^{224}Ra nuclides; ^{220}Rn is formed in the substance as a consequence of α-decay according to the sequence

$$^{228}\mathrm{Th} \longrightarrow {}^{224}\mathrm{Ra} \longrightarrow {}^{220}\mathrm{Rn} \longrightarrow \cdots\cdots$$

Equipment for ETA

The equipment produced [12] by Netzch (Selb, F.R.G.) for the measurement of radioactive inert gases released from solids permits the measurement of trace amounts of inert gases which are carried from the sample being studied to the radioactivity detector by a carrier gas. The heating rate was 4–5 °C min^{-1} and the cooling rate was -2.5 °C min^{-1} in an argon atmosphere. The emanation power E (real units) was measured at different temperatures (Figs. 1–3). Isothermal heating over selected narrow temperature ranges was also performed.

RESULTS AND DISCUSSION

*Emanation thermal analysis of **I***

The ETA of the labelled polymer **I** involved the measurement of emanation power E at different temperatures (Fig. 1). The figure shows a broad increase of E with temperature increase from 50–230 °C (Fig. 1a), followed by an abrupt decrease to a minimum value at 275 °C. This is related to the fragmentation of the solid polymer **I** into its original free radicals (quinoneimines, QI): $^{+}O{-}C_6H_4{-}N{=}C_6H_4{-}N{=}C_6H_4{-}N{=}C_6H_4O^{+}$, symbolized as $(o{-}\mathrm{QI})_4^{++}$ [8], and/or the loss of N_2 and H_2 from crosslinking groups, as confirmed by TGA (estimated mass loss 4.15%; calculated 4.0%) and DTA (by the appearance of endotherms and exotherms) over the same temperature range. The dissociation of polymer **I** increases the radioactive disintegration power E as a result of release of radioactive inert gas molecules from the moiety of the polymer **I**. The abrupt decrease of E at 230–270 °C may be related to the association of the fragments and free radicals to give a stable crystalline new compact form, **Ib**, which decreases E. The emanation power starts to increase slowly with the increase of temperature up to 350 °C, becomes approximately constant up to 390 °C, and finally abruptly increases within a narrow temperature range, 403–409 °C. The constancy of E within the temperature range 350–390 °C may be attributed to some crystalline rearrangements. The crystalline re-

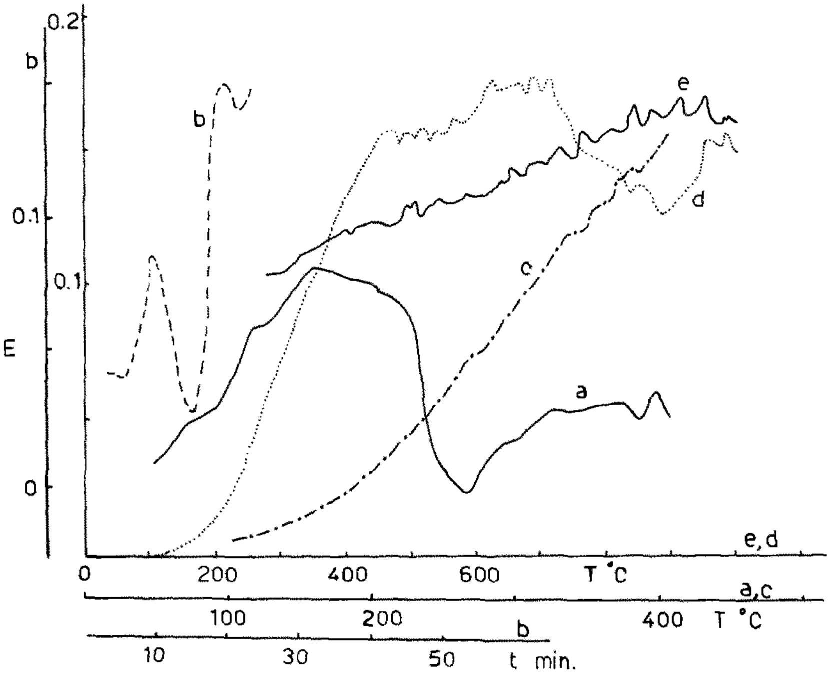


Fig. 1. Temperature dependence of emanating power of polymer I.

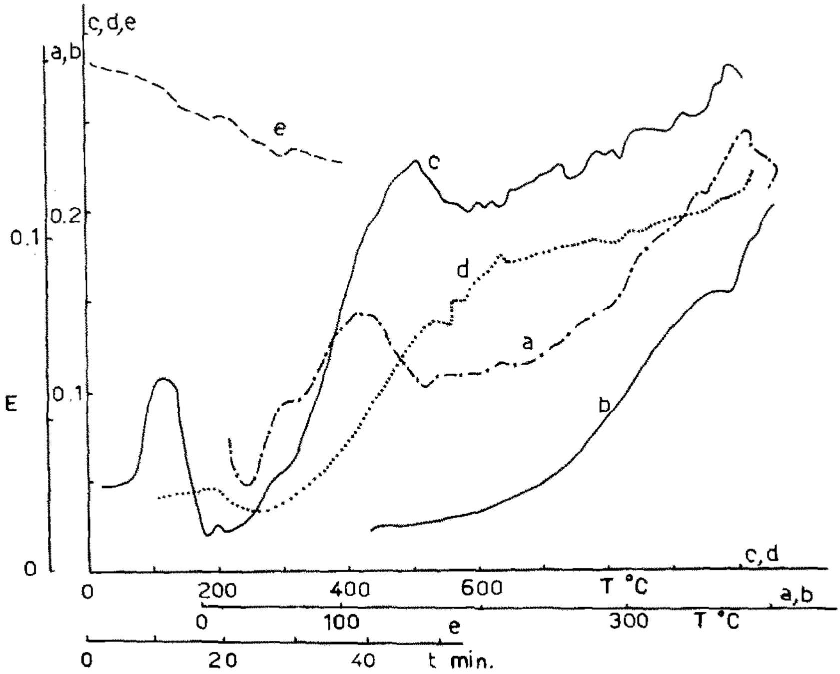


Fig. 2. Temperature dependence of emanating power of polymer II.

arrangements are apparent as two peaks after 5 and 25 min on studying the isothermal changes at 403–409 °C (Fig. 1b). The effect of cooling on the emanation power of **Ib** within the temperature range 425–100 °C (Fig. 1c) leads to a gradual decrease of E as the temperature decreases, which means a gradual solidification and/or decrease of porosity to form a new compound. In order to test the stability of this polymer **Ic** it is reheated from 100 up to 1100 °C (Fig. 1d). The E–T curve shows a steady regular increase of E with T up to 400 °C, which is the reverse behaviour to cooling (Fig. 1c). This increase of E may relate to the increase of porosity of this polymer. On continuous heating from 400–750 °C, the curve shows a gradual increase of E involving some peaks. These peaks may be related to holes and lattice defects which help to increase the radiation power. Starting from 750 °C, E decreased up to 850 °C, which may be related to crystalline rearrangement of the second form to give a third polymer **Ic**. The porosity of this polymer increases with the increase of T from 850 to 1100 °C, as shown by an increase of E. The stable final form **Ic** shows approximately constant emanation power on cooling from 1100 to 200 °C (Fig. 1e), including some peaks, which may be related to decreases in porosity. All the above changes of polymer **I** are summarized in Scheme 1.

$$\text{Polymer } \mathbf{I} \xrightarrow{100\text{–}270\,^\circ\text{C}} (o\text{-QI})_4^{++} \text{ or } N_2 \text{ and } H_2 + \mathbf{Ib}$$

$$\alpha\text{-}\mathbf{Ib} \underset{100\text{–}425\,^\circ\text{C}}{\overset{270\text{–}290\,^\circ\text{C}}{\rightleftharpoons}} \beta\text{-}\mathbf{Ib} \xrightarrow{100\text{–}400\,^\circ\text{C}} \alpha\text{-}\mathbf{Ic} \underset{200\text{–}1100\,^\circ\text{C}}{\overset{400\text{–}1100\,^\circ\text{C}}{\rightleftharpoons}} \beta\text{-}\mathbf{Ic}$$

Scheme 1.

The nature of the new polymers **Ib** and **Ic** required separation and further structural investigation.

Emanation thermal analysis of polymer II

Polymer **II** is originally formed by the redox reaction between iodine and p-aminophenol (p-AP) by the mechanism [8]

$$\underset{p\text{-AP}}{H_2NC_6H_4OH} \rightleftharpoons \underset{p\text{-QI}^+}{HN{=}C_6H_4O^+} + 2H^+ + 2\,e^-$$

$$2HN{=}C_6H_4O^+ \overset{OH^-}{\rightleftharpoons} \underset{(p\text{-QI})_2^+}{NH{=}C_6H_4{-}N{=}C_6H_4O^+} + H_2O$$

$$2(p\text{-QI})_2^+ \rightleftharpoons (p\text{-QI})_4^{++}$$

$$(p\text{-QI})_4^{++} + 2\,I_2 \rightleftharpoons \left[(p\text{-QI})_4^{++}, I_2, I^+\right]I^-$$

$$\overset{OH^-}{\rightleftharpoons} \text{Polymer } \mathbf{II} + NH_3 + IOH + H_2O$$

The ETA of polymer **II** is shown in Fig. 2. The figure shows an abrupt decrease of emanation power at lower temperature (Fig. 2a) as a result of contraction of this polymer, which is indicated by an exothermic baseline shift in DTA [4] relating to the change of heat capacity. This is followed by a gradual increase in E with the increase of temperature up to 160 ° C, involving a peak at 90–120 ° C. The increase of E and the appearance of the peak are related to the thermal decomposition of this polymer to give a new one, **IIb**, as a result of loss of N_2 and NH_3 gases, as confirmed by TGA (estimated mass loss 6.0%; calculated 5.88%) and DTA (appearance of several exotherms) [8] over the same temperature range. On further heating of **IIb** up to 410 ° C, E continues to increase and some peaks appear, with a distinct one at 409 ° C. These changes may relate to the formation of holes and lattice defects, through crystalline rearrangements increasing emanation power. The gradual cooling of **IIb** from 410–120 ° C (Fig. 2b) leads to an abrupt decrease of emanation power up to 360 ° C followed by a gradual decrease up to 120 ° C. These changes on cooling may relate to solidification and crystallization of the polymer **IIb**, leading to a decrease in its porosity and consequently a decrease in E. The reheating of **IIb** in the temperature range 20–1100 ° C (Fig. 2c) results in a peak at 95–190 ° C, which may be attributed to partial crystalline damage leading to the escape of radioactive inert gas. This escape gradually increases with the increase of temperature up to 400 ° C. The appearance of another peak at 400–480 ° C may relate to another crystalline damage of **IIb**, its release of free radicals and/or its melting to give a new possible form **IIc**. This new polymer starts to compact, melt or recrystallize, involving some holes, as indicated by a slight increase of E and the appearance of some very small peaks in the temperature range 480–1080 ° C, followed by the appearance of a distinct peak at 1090 ° C. On cooling polymeric form **IIc** from 1100–100 ° C (Fig. 2d), a gradual decrease of E is observed with decreasing T within the temperature range 1100–600 ° C, followed by a more rapid decrease of E from 600–250 ° C and increase of E on cooling to 100 ° C. In general, all changes that occur for **IIc** on heating also occur on cooling, which can be explained only by the existence of two possible reversible forms of **IIc**, i.e. α-**IIc** and β-**IIc**. All the above changes are summarized in Scheme 2.

$$\text{Polymer } \mathbf{II} \xrightarrow{20\text{–}150\,^{\circ}\mathrm{C}} \mathrm{NH_3} + \mathrm{N_2} + \alpha\text{-}\mathbf{IIb}$$

$$\alpha\text{-}\mathbf{IIb} \xrightleftharpoons[120\text{–}410\,^{\circ}\mathrm{C}]{120\text{–}410\,^{\circ}\mathrm{C}} \beta\text{-}\mathbf{IIb} \xrightarrow{20\text{–}480\,^{\circ}\mathrm{C}} \alpha\text{-}\mathbf{IIc} \xrightleftharpoons[100\text{–}1100\,^{\circ}\mathrm{C}]{400\text{–}1100\,^{\circ}\mathrm{C}} \beta\text{-}\mathbf{IIc}$$

Scheme 2.

The distinct peak occurring at 1024 ° C (Fig. 2c) was studied by tracing the isotherm of β-**IIc** at 1024–1012 ° C (Fig. 2e), which shows a decrease of E

with time as a result of crystalline rearrangement of *β*-**IIc** into *α*-**IIc**, which has fewer holes and lower porosity.

Emanation thermal analysis of compound III

The dimer **III** was suggested as being formed by oxidation of *m*-aminophenol (*m*-AP) with iodine [8] according to

$$\underset{m\text{-AP}}{H_2N{-}C_6H_4{-}OH} \longrightarrow \underset{m\text{-QI}^+}{HN{=}C_6H_4O^+} + H^+ + 2e^-$$

$$\underset{2m\text{-QI}^+}{2HN{=}C_6H_4O^+} \longrightarrow \underset{(m\text{-QI})_2^{2+}}{O^+{-}C_6H_4{-}NH{-}NH{-}C_6H_4O^+} \longrightarrow$$

$$\longrightarrow \text{dimer } \mathbf{III}$$

The heating of compound **III** over the temperature range 25–500 ° C (Fig. 3a) shows a gradual increase of emanation power with temperature increase up to 160 ° C, involving some peaks at 60–160 ° C. These peaks are essentially attributed to the partial decomposition of dimer **III** to give N_2 and H_2 gases, as confirmed by TGA (estimated mass loss 4.0%; calculated 4.44%) and the appearance of a series of endo- and exotherms in DTA over this temperature range. This partial decomposition increases the emanation power as a result of radioactive inert gas release, and results also in the formation of a new form **IIIb**. Starting from 160 ° C, the emanation power of **IIIb** slowly increases up to 430 ° C, involving particular peaks. These changes may be attributed to internal rearrangements such as crystallization or aggregation of sample multiples or particulates. On cooling of form **IIIb** from 430–100 ° C (Fig. 3b) all changes appear to be reversible. This means that the newly formed compound is chemically and physically stable. The isothermal behaviour of this compound (Fig. 3c) at 412–409 ° C over a period of 40 min is associated with constant emanation power, which is plausibly attributed to the stability of **IIIb** at this temperature. The reheating of **IIIb** from 100–1100 ° C (Fig. 3d) is accompanied by approximate constancy of E with the temperature increase up to 400 ° C. Starting from 410 ° C the radioactive disintegration abruptly increases up to 710 ° C; it appears as a broad peak and is attributed to crystalline rearrangement to form *α*-**IIIb**. The appearance of some peaks at 710–1100 ° C may be attributed to the formation of lattice defects and/or holes during crystalline rearrangement of *α*-**IIIb** to give *β*-**IIIb**. The stability of this final *β*-form is demonstrated by the isothermal constancy of E (Fig. 3e) over 50 min at 1027–1005 ° C. On cooling the stable *β*-**IIIb** form (Fig. 3f) in the temperature range 1100–100 ° C, reversible behaviour is observed, which means that

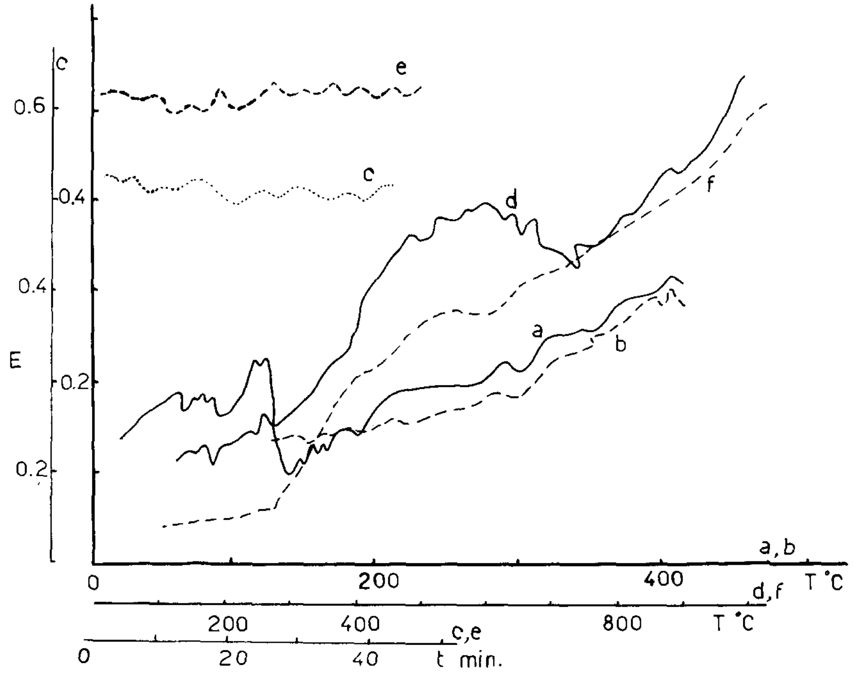


Fig. 3. Temperature dependence of emanating power of dimer III.

β-**IIIb** returns to the original form α-**IIIb**. The reversibility of heating and cooling of compound **III** can tentatively be represented by Scheme 3.

$$\text{dimer } \mathbf{III} \xrightarrow{60\text{–}1600\,°\mathrm{C}} \mathbf{IIIb} + N_2 \text{ and } H_2$$

$$\mathbf{IIIb} \underset{100\text{–}430\,°\mathrm{C}}{\overset{160\text{–}400\,°\mathrm{C}}{\rightleftharpoons}} \alpha\text{-}\mathbf{IIIb}$$

$$\alpha\text{-}\mathbf{IIIb} \xrightarrow{100\text{–}400\,°\mathrm{C}} \alpha\text{-}\mathbf{IIIb} \underset{100\text{–}1100\,°\mathrm{C}}{\overset{410\text{–}1100\,°\mathrm{C}}{\rightleftharpoons}} \beta\text{-}\mathbf{IIIb}$$

Scheme 3.

REFERENCES

1 V. Balek, Thermochim. Acta, 22 (1978) 1.
2 V. Balek and I. Tolgyessy, Emanation Thermal Analysis and Other Radiometric Emanation Methods, Elsevier, Amsterdam, 1984.
3 V. Balek and J. Rouquerol, Thermochim. Acta, 110 (1987) 221.
4 M.A. Zayed, Thermochim. Acta, 111 (1987) 103.
5 M.A. Zayed and F.A. Nour El-Dien, Thermochim. Acta, 128 (1988) 105.
6 I.N. Beckman, A.I. Shviryaev and V. Balek, Thermochim. Acta, 104 (1986) 255.

7 M.M. Ali, Analytical studies on the reaction between iodine and some phenolic compounds, M.Sc. Thesis, Cairo University, 1990.
8 M.A. Zayed, Thermochim. Acta, 159 (1990) 43; Egypt. J. Chem., 31(2) (1988) 187.
9 H. Khalifa, M.A. Zayed, M.S. Rizk and F.A. Nour El-Dien, Egypt. J. Chem., 27(6) (1984) 723.
10 M.A. Zayed and F.A. Nour El-Dien, Egypt. J. Chem., 32 (1990), in press.
11 R.C. Mackenzie, in G. Lombardi (Ed.), For Better Thermal Analysis, Rome, 1979.
12 W.D. Emmerich and V. Balek, High Temp. High Pressures, 5 (1973) 67.
13 I.L. Finar, Organic Chemistry, Toppan Printing, Singapore, 1985, Vol. 1, p. 700.