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PHENOLIC-IODINE REDOX PRODUCTS
Mass spectrometry, thermal and other physico-chemical methods of analyses

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Abstract

Three interesting new compounds formed as a result of phenols-iodine redox reactions were investigated by mass spectral fragmentation (MS) and thermal analyses (TA) as well as some other physicochemical methods as microanalysis and infra-red spectroscopy to elucidate their structures. The characterization of the compounds was satisfactorily achieved by using the above analytical tools and their proposed general formulae, were found to be $C_{24}H_{15}O_8I$ (PC-IO_3^-), $C_{24}H_{14}O_{12}I_2$ (PG-IO_3^-) and $C_{12}H_8O_6I_2$ (PG-IO_4^-).

The fragmentation pathways of PC-IO_3^-, PG-IO_3^- and PG-IO_4^- have been examined using electron ionization (EI) mass spectrometry in comparison with thermal analyses (TG and DTA). Both decomposition modes were investigated, and the fragmentation pathways were suggested. The combined application of mass spectrometry and thermogravimetry (MS and TG) in the analysis of the products allowed the characterization of the fragmentation pathway in MS.

The major pathway in both techniques of PC-IO_3^- is due to the loss of CHO followed by CH_3I+2H_2O. It is due to the loss of $2H_2O$ followed by the loss of $2CH_3I$ for PG-IO_3^-. While for PG-IO_3^- it is related to the loss of $2H_2O$ followed by loss of $2CH_3I$ molecule stepwise. Different stabilities for initial products and some fragments are discussed.

Keywords: mass spectrometry, redox reactions, thermal analysis

Introduction

Mono-, di- and polyhydric phenols are of wide pharmaceutical and industrial applications. They can be used as antiseptic and disinfectants and also in preparation of dyes, drugs, bakelite, etc. due to their essential applications in life chemistry. It is of great interest to follow their structures via oxidation by oxidizing agents as IO_3^- and IO_4^-.

Structural determinations of phenols and their redox products are generally based upon pieces of information obtained from mass spectrometric techniques as electrospray mass spectrometry (ES-MS) with collision-induced dissociation-(CID) [1–6]. Spectral advantages in structure studies were obtained from combination be-

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tween mass spectrometry, infra-red spectroscopy and thermogravimetry [7]. Investigation of some phenolic compounds using mass spectrometry was the subject of many studies [8].

A number of phenolic compounds were determined via oxidation with iodine and its derivatives (iodate and periodate). These oxidants interacted with these phenolic compounds to give inner and/or outer intermediate complex compounds. The solids resulting from some redox reactions between iodine and some phenolic compounds were isolated and purified by Zayed *et al.* [9–11]. Three of these redox products are the subject of this work.

In mass spectrometry, the fragmentation of excited molecular ions consists in a series of unimolecular reactions that compete on the ground state mainfold [13]. Information concerning some of individual steps can be illuminated from the comparison of mass spectra with the fragmentation observed from thermal analyses (TA) technique, where only one decay channel was observed. This is very important in order to identify the chemical processes and proceeds of the fragmentation. EI and TA fragmentation did not necessarily follow the same pathways. The success of comparison between two techniques, in structure confirmation is based on the correct choice of the unimolecular fragmentation channel of decay in MS and TA.

The aim of the present work is the use of mass spectral fragmentation in comparison with the thermal decomposition and other physicochemical methods. This comparison aims chiefly to confirm and to illuminate the general and structural formulae of the separated solid products obtained from oxidation of catechol (PC) and pyrogallol (PG) with IO_3^- and IO_4^-. Also, studying the behavior of the three compounds PC-IO_3^-, PG-IO_3^- and PG-IO_4^- in mass spectral fragmentation and thermal analyses, helps the interpretation of the decompositions of these compounds and in selection of the correct thermal and mass spectral pathways.

Experimental

Materials and procedures

PC-IO_3^- and PG-IO_3^- were prepared by adding 100 mL of 0.1 M IO_3^- to 100 mL 0.1 M of PC and PG at temperatures 55 and 50°C , respectively and at pH 4–5. The formed precipitates were left in contact with mother liquid for 2 h, then the precipitates were filtered and washed with hot distilled water several times and finally with pure ethanol and dried in air. Meanwhile PG-IO_4^- was prepared by dissolving 0.785 g of PG in 100 mL of 0.025 M IO_4^- at 30°C and at pH 5.5. The formed redox products were recrystallized from ethanol.

Microanalyses of the products

Microanalyses of C and H and molecular mass determinations of the pure products were performed by Micro-analytical Center of Cairo University.

Infra-red spectroscopy

IR spectra of the solid products were measured by KBr disc technique (at the same microanalytical center) in the wavenumber range 250–4000 cm^{-1}, using a Perkin Elmer model 1650 FT-IR.

Mass spectral measurements and instruments

All the mass spectrometric measurements were performed on a Hewlett Packard MS-5988 GC-MS instrument in Microanalytical Center, Cairo University. Electron ionization mass spectra were obtained at 70 eV. The instrument was calibrated by using perfluorotributylamine as a standard material. The reproducibility of the readings was also checked by repeating the experiment twice as recommended in literature [13].

Thermal analyses (DTA and TG)

DTA and TG studies were made with a conventional thermal analyzer (Shimadzu system, Shimadzu 30 series thermal analyses instrument). The mass losses (from 5 mg for each sample) and heat responses of the changes in the sample were measured in the temperature range from the ambient temperature to 1000°C with the heating rate 10°C min^{-1} both in TG and DTA in an inert argon atmosphere. These instruments were calibrated using indium metal as thermally stable material. The reproducibility of instrument reading was determined by repeating each experiment twice.

Results and discussion

The redox solid products (PC-IO_3^-, I, PG-IO_3^-, II, and PG-IO_4^-, III) were studied by means of mass spectrometry in comparison with the thermal analyses and other physicochemical methods as elemental analysis and IR spectroscopy, aiming to identify their actual structures.

Microanalysis of the products

The results of the elemental analyses of the three (I–III) compounds together with some of their properties as well as their formulae are shown in Table 1.

IR characteristics

IR spectra of the product PC-IO_3^- shows peaks at 3216, 3245, 3303, 3321, 3337 and 3380 cm^{-1}, which may be attributed to the modes of six OH groups as given in the proposed structures. The careful inspection of IR refers to the presence of the bands at 1613, 1492 and at 1462 cm^{-1}, which may be attributed to several modes of C–O groups present in the moiety of the proposed structure I. The bands detected between 755 to 1295 cm^{-1} may be assigned as different aromatic ring vibrations. The band at 630 may be assigned as another $\nu_{C=O}$ mode. The appearance of the intense broad band

Table 1 Microanalyses of solid products of (I)–(III)

Redox product	M.p./ °C	Colour	% C		% H		Molar mass/M		General molecular formula
			calc.	found	calc.	found	calc.	found	
PC-IO$_3^-$ (I)	>300	black	51.3	51.5	3.9	2.9	558	560–600	$C_{24}H_{15}O_8I$
PG-IO$_3^-$ (II)	>300	black	40.6	38.6	3.9	3.7	748	750	$C_{24}H_{14}O_{12}$ I_2
PG-IO$_4^-$ (III)	>300	black	30.1	28.7	4.1	3.6	502	502–520	$C_{12}H_8O_6$ I_2

(of intensity 85 to 86%) at 409 to 466 cm^{-1} may be attributed to the different modes of the C–I bond present in the terminal of the proposed structure I.

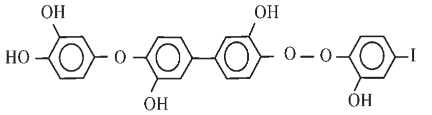
Table 2 The FT-IR spectra of the solid products (I)–(III)

Compound	The band/$\nu_{\text{cm}^{-1}}$	Intensity/%	Assignment
PC-IO_3^-	3216 to 3380	16 to 17.16	ν_{OH} of five phenolic groups
	1613.4	10.13	$\nu_{\text{C–O}}$ peroxide and biphenylether
	1492	34.068	ring system different modes
	1462	39.60	
	1259	22.97	
	755.9	75.52	
	630 to 460	81.6 to 85.1	$\nu_{\text{C–O}}$ of different phenolic groups
	409.4 to 434	86 to 96.95	different modes of C–1 bond
PG-IO_3^-	3751	29.16	ν_{OH} of the phenolic group in the compound
	3405	19.08	
	2368	73.70	
	1718.6	14.6	ν_{C} of semiquinone conjugate tetramer
	1616	7.91	$\nu_{\text{C–O}}$ of the peroxide form in a symmetrical polymer
	745 to 1253	74.3 to 20.9	different modes of ring system
	421.5	86	due to modes of C–I of two bonds in terminal of the polymer
PG-IO_4^-	2364.9 to 3186.9	22.75 to 58.24	due to different modes of ν_{OH}
	1200.5	50.2	due to the carbonyls of the semiquinone system of the dimer
	1613.8	11.98	due to $\nu_{\text{C–O}}$ of the peroxide system
	595 to 1423.5	67.99 to 21.34	due to the different modes of ring system
	433.9	69.61	due to the modes of vibration of two identical C–I groups

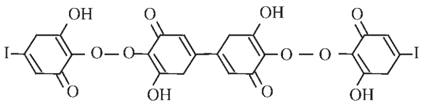
IR spectra of the product PG-IO_3^- shows a very broad band at 3216 cm^{-1} of intensity 89.16%; which may be assigned as ν_{OH} of different modes of four OH groups in the proposed structure of the separated tetramer II. The sharp band at 1718 cm^{-1} may be attributed to $\nu_{\text{C=O}}$ of the quinone or semiquinone isomer of the proposed structure. The band at 1616 cm^{-1} may be assigned as $\nu_{\text{C–O}}$ occurring between two phenyl rings and/or that present in peroxide part of this polymeric form. The three bands between 755 to 1492 cm^{-1} may be assigned as different aromatic rings vibrations. The two bands at 754 cm^{-1} may be assigned as the $\nu_{\text{C-O}}$ aromatic peroxides part in the entity of the investigated polymer. The small broad band centered at 421.5 cm^{-1} of intensity 86% may refer to the $\nu_{\text{C–I}}$ of the substituted iodine atoms at terminals of the compound II.

IR spectra of the product PC-IO_4^- show a broad band of different peaks. These peaks appear at 2364 cm^{-1} (58.24%) and 3186.9 (22.75). These peaks may be attributed to the frequencies of two OH groups of the symmetrical dimer III. The small sharp band appeared at 1700 cm^{-1} (50.21%) may be attributed to the $\nu_{C=O}$ of the symmetrical conjugate system in the proposed structure under investigation. The sharp band occurs at 1613.8 cm^{-1} may be attributed to another modes of two carbonyl groups in the moiety of the product. The bands occurred at 1423.5, 1327 cm^{-1} may be assigned as the ν_{C-O} of peroxide dimer. The bands appeared at 831 cm^{-1} (67.20%) and 595 cm^{-1} (67.99%) may be related to the different modes of conjugated ring systems of the product III. The intense band at 433.9 cm^{-1} (69.61%) may be attributed to the different modes of symmetrical C–I bonds in the proposed structure.

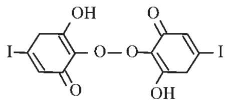
The proposed structure of the present compounds (I–III) as suggested by the results of the microanalyses and infrared are given by,



PC-IO_3^- (I)



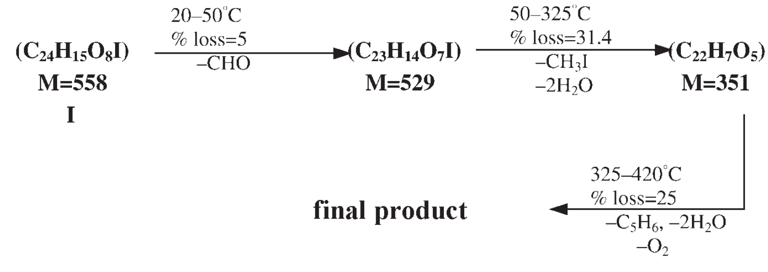
PG -IO_3^- (II)



PG-IO_4^- (III)

Thermal analyses (TG and DTA)

TG curve (Fig. 1A) corresponding to the product of PC-IO_3^- reaction refers to three stages (Scheme 1). The first occurs between 20 to 50°C, the second present between 50 to 350°C and the third is found between 350 to 450°C. These stages are accompanied by practical mass losses of 5, 31.4 and 25%, (the calculated total mass losses 61.8%), respectively. The observed mass losses may correspond to the possible elimination of species: CHO, $2H_2O$ and CH_3I, H_2O, cyclopentene and/or O_2 as given by the proposed Scheme 1. The DTA curve (Fig. 1A) refers to three exothermic peaks, the first is weak; at 40, the second peak is strong relative broad at 350 to 450 with its maximum located at 425 and the third is sharp one with its maximum at 454°C. This means that all three stages of mass losses occur during three endothermic processes.



Scheme 1 Thermal decomposition behavior of PC–IO_3^-

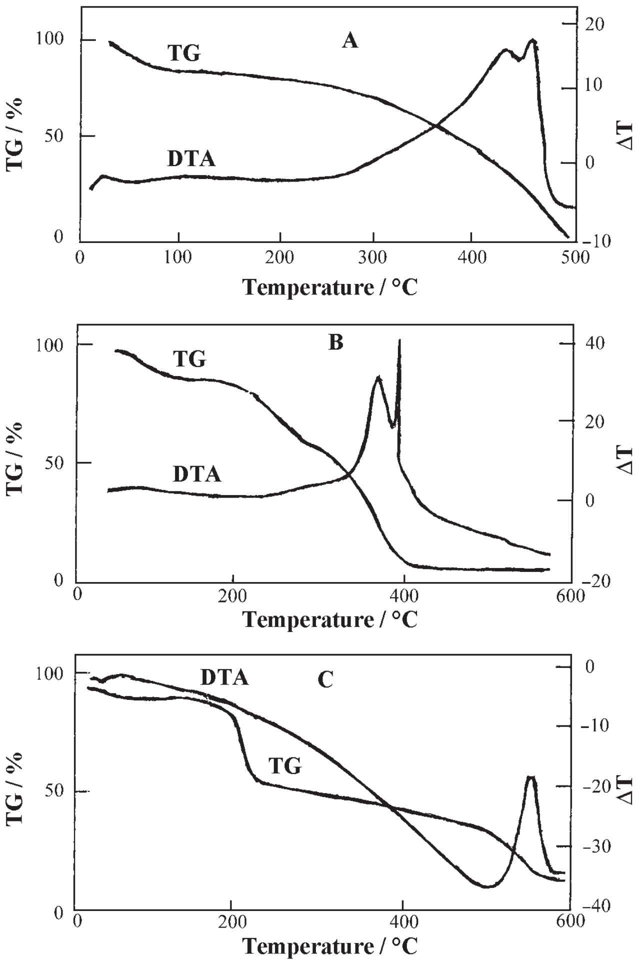
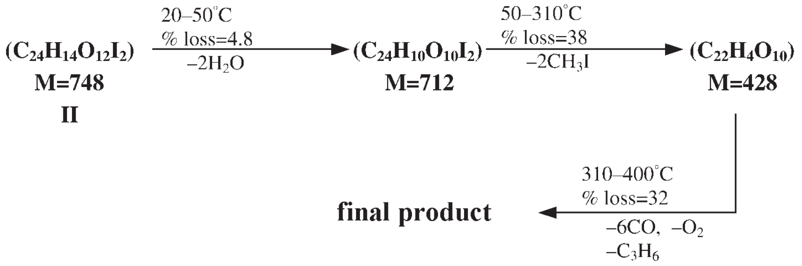


Fig. 1 TG and DTA curves of the reaction products A – PC-IO_3^-, B – PG-IO_3^- and C – PG-IO_4^-

The obtained TG and DTA curves of II are given in Fig. 1B. The obtained TG is composed of three stages at temperature ranges between 20 to 50, 50 to 310 and 310 to 400°C and accompanied by mass losses 4.8, 38 and 43%, respectively. These stages correspond to the loss of $2H_2O$, $2CH_3I$, 6CO, O_2 and propene. DTA curve consists of a broad endothermic peak at 40°C together with two strong and sharp exothermic peaks at 381 and 410°C. This means that the mass losses are exothermic and accompanied by chemical reactions like oxidation of CO with O_2 to give CO_2. TG and DTA data (Table 3) enabled us to suggest the following thermal decomposition Scheme 2.

TG curve of the reaction product III consists of four stages. They are ranged between room temperature to 190, 190 to 225, 225 to 510, and 510 to 575°C, respec-



Scheme 2 Thermal decomposition behavior of PG–IO_3^-

tively. The four stages correspond to mass losses of 7.2, 28.4, 28.4 and 6.3%, respectively. TG stages may be due to the removal of $2H_2O$ and stepwise loss of two CH_3I molecules and O_2 respectively. The obtained DTA curve (Fig. 1C) consists also of four endothermic peaks comparable to the four stages of mass losses. The first and second peaks are weak. They occur at 45 and 210°C. The third and fourth peaks are strong and sharp and located at 490 and 570°C, respectively. The results of thermal behavior of the product III can be tentatively represented by the following Scheme 3.

The thermal analyses can be summarized in Table 3.

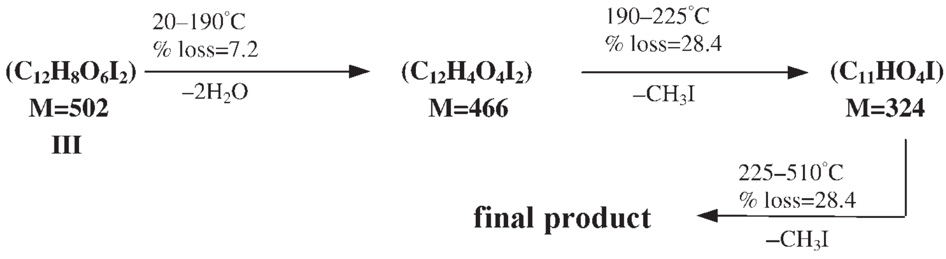
Table 3 Thermal analyses of compound (I)–(III)

Compound	Temp. range/°C	Mass loss/% calc.[a]	Mass loss/% found[b]	Possible fragments	DTA
PC-IO_3^- (I)	20–470	61.8	61.85	CHO, CH_3I, $4H_2O$, O_2 and cyclopentadiene	40°C: exo. peak refers to loss of CHO. 425°C: exo. peak, loss of CH_3I, $2H_2O$. 454° : exo. peak, loss of O_2, $2H_2O$, cyclopentadiene
PG-IO_3^- (II)	20–430	85.8	85.8	$2H_2O$, $2CH_3I$, 6CO, O_2, propene	40°C: end peak, loss of $2H_2O$ 381°C : exo. peak, loss of $2CH_3I$ 410°C: exo. peak, loss of 6CO, O_2, propene
PG-IO_4^- (III)	20–600	69.3	71	$2H_2O$, $2CH_3I$, O_2	45°C: end peak, loss of $2H_2O$ 210°C: end peak, loss of CH_3I 490°C: end peak, loss of CH_3I 570°C: end peak loss of O_2

[a] Calculated mass loss from the molar mass of the compound
[b] Estimated percent loss from experimental work

Mass spectral fragmentation

70 eV EI mass spectra of the redox compounds (I)–(III) were studied and record. The mass spectra of the three products (Fig. 2) demonstrate molecular ions of m/z=558, 748 and 502 for (I)–(III) respectively. It is worth noting that the mass spectra of the main compounds i.e. PC and PG were previously studied [14] in this laboratory. Typical spectra (bar graphs) are presented in Fig. 2. The important peaks and their rela-



Scheme 3 Thermal decomposition behavior of PG–IO_4^-

tive intensities in mass spectra are listed in Table 4 for the molecular ions up to *m/z* 55 (only prominent and important ions are recorded for simplification). The main fragmentation pathways used for comparison with TA is also reported in this work.

All spectra of the studied compounds are characterized by very small molecular ion signals (<1%) at 70 eV. The abundance of the molecular ion, depends mainly on its stability and the amount of energy needed to ionize the molecule [15]. Particular structure features tend to show characteristic values of these properties, so the magnitude of $[M]^{+\cdot}$ provides an indication of the structure of the molecule [15]. Also, the compounds, PC-IO_3^-, PG-IO_3^- and PG-IO_4^- are characterized by very high relative intensity (base peak, R.I.=100%) at fragment ion *m/z* 55. This fragment ion is reasonably formed from $[C_5H_7O]^+$ (*m/z* 83) and $[C_5H_5O]^+$ (*m/z* 81) by CO and C_2H_2 loss respectively.

Table 4 Relative intensities of the prominent peaks in the mass spectra of three precursors (relative to the base peak=%)

Compound	*m/z*/R.I.%									
PC-IO_3^- (I)	558 (<1%)	529 (2.1)	387 (2.1)	351 (2.5)	320 (7.6)	223 (4.3)	156 (49.5)	83 (70.7)	66 (23.4)	55 (100)
PG-IO_3^- (II)	748 (<1%)	712 (1.3)	428 (1.6)	392 (1.6)	214 (3.10)	111 (23.3)	90 (14.0)	69 (46.5)	55 (100)	
PG-IO_4^- (III)	502 (<1%)	466 (<1)	324 (14.1)	182 (13.3)	142 (42.2)	127 (34.4)	109 (29.7)	83 (56.3)	66 (25.0)	55 (100)

The characteristic feature of the primary fragmentation pattern of the product PC-IO_3^- is due to the successive loss of CHO, followed by CH_3I+2H_2O loss and forming fragment ion at *m/z*=529, and 351, respectively. Also, the spectrum observed as peaks (Table 4) corresponds to the presence of three and two attached aromatic rings at *m/z*=320 and *m/z*=156, respectively. The spectra of PG-IO_4^- product are characterized by very low relative abundance at higher mass above *m/z*=111. The appearance of masses at *m/z*=466, 324 and 182 is mainly due to the successive loss of dehydration and $2CH_3I$ stepwise. The spectrum of the products PG-IO_4^- is characterized by moderate intensities of all the ions in the mass spectra in comparison with the spectrum of PC-IO_3^- and PG-IO_3^-. The fragmentation schemes of the three products (I)–(III) may be tentatively given by Schemes 4–6.

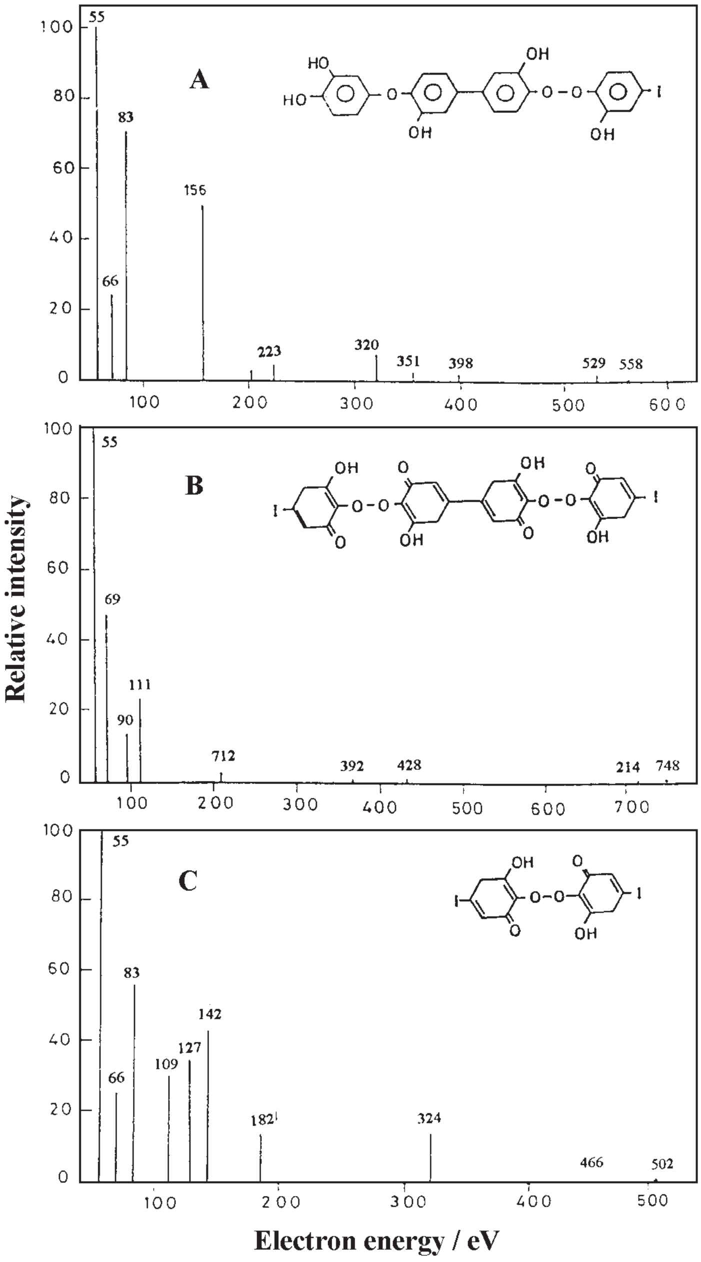
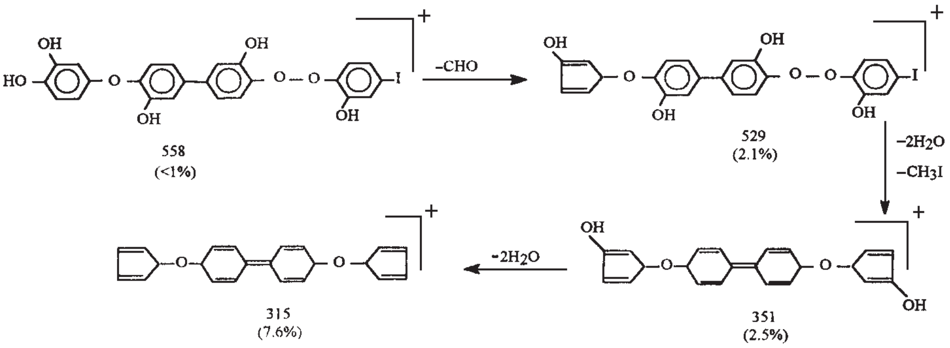
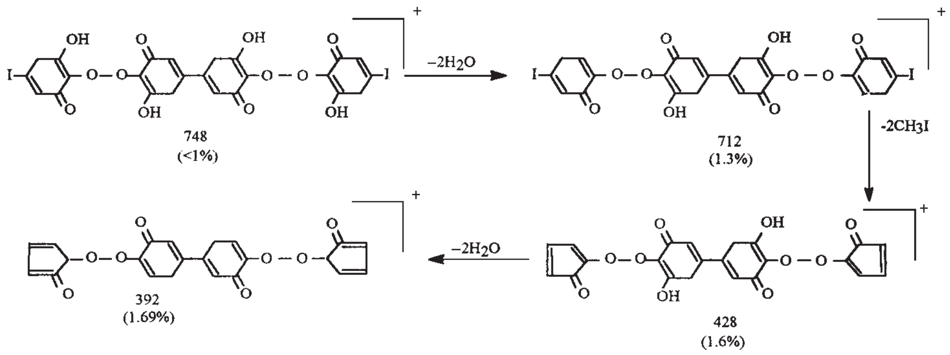


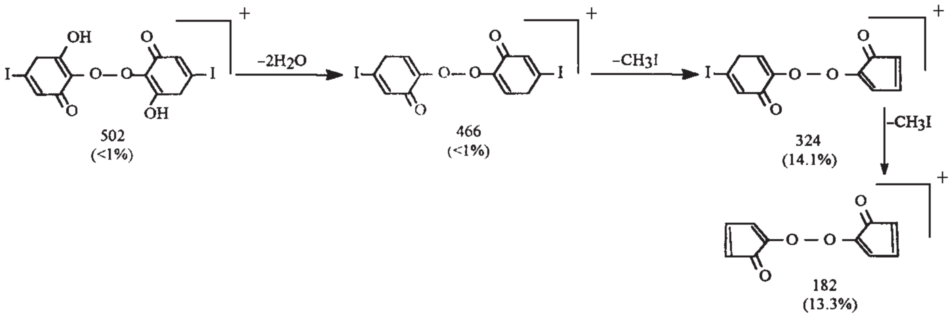
Fig. 2 Mass spectra (EI, 70 eV) of A – PC-IO_3^-, B – PG-IO_3^- and C – PG-IO_4^-



Scheme 4 Fragmentation pathway of principal ions from PC-IO_3^-



Scheme 5 Fragmentation pathway of principal ions from PG-IO_3^-



Scheme 6 Fragmentation pathway of principal ions from PG-IO_4^-

Comparative study between MS and TA of the products

In our previous study [14], the fragmentations of 2-hydroxyphenol (PC) and of 2,3-di-hydroxyphenol (PG) were investigated in both MS and TA. In the present work three compounds forming as a result of reaction of these simple phenolic compounds (PC and PG) with IO_3^- and IO_4^- were investigated. The behavior on fragmentation in two techniques was discussed.

The primary decomposition process of the product PC-IO_3^- (I) is due to CHO loss from the original molecule in TA (Scheme 1) and MS (appearance of fragment ion at m/z=529 $[C_{23}H_{14}O_7I]^+$). The initial product is unstable in both TA (decompose at 40°C by CHO loss) and MS (R.I. of $[M]^+$<1%). The rest after CHO loss is stable enough in TA (wide temperature range 50–325°C) before subsequent loss of CH_3I molecule and dehydration (2 molecules of H_2O) (Scheme 1). In MS, the fragment ion $[M–CHO]^+$ also follows the same behavior as TA but forms an unstable $[M–CHO–CH_3I–2H_2O]^+$ fragment ion (m/z=351, R.I.=2.1%). This remainder is stable in the temperature range 325–420°C before the cleavage of the bonds between rings (loss of C_2H_6+$2H_2O$+O_2) in TA, whereas in MS the unstable four cyclic rings can undergo dehydration before bond cleavage. The major pathway of decomposition of the main group i.e. (PC) [14] includes successive loss of CHO group, since thermal cracking can undergo bond rupture at the weakest bond [15], therefore CH_3I is the second weakly bound in the moiety of the molecule not the second CHO group.

The initial product (PG-IO_3^-) (II) is unstable in TA and MS (Schemes 2 and 5) . The primary loss by two techniques includes dehydration (loss of 2 molecules of H_2O). This behavior is in agreement with the initial fragmentation of the second main group i.e. PG [14]. The remainder i.e (M–$2H_2O$) is stable up to 310°C in TA before losing two CH_3I molecules, while in MS, this fragment ion forms with very low stability (R.I.=1.3%). Finally, the remainder (M–$2H_2O$–$2CH_3I$) can undergo dehydration in MS while in TA bond cleavage and loss of $6CO+O_2+C_3H_6$ occur.

PG-IO_3^- (III) is stable enough in TA and can resist dehydration up to 190°C, in MS the dehydration forms a fragment ion at m/z=466 (R.I.<1%). Subsequent fragmentation leading to the stepwise release of CH_3I followed by another molecule. The first CH_3I needs 35°C to release while the second CH_3I needs high temperature (285°C). In MS, relatively small fragments are observed at m/z=324 $[M–2H_2O–CH_3I]^+$ (R.I.=14.1%) and at m/z=182 $[M–2H_2O–2CH_3I]^+$ (R.I.=13.3%).

Finally, we have demonstrated in this paper that PC-IO_3^- and PG-IO_4^- (four attached rings) are unstable in both techniques, while PG-IO_4^- (two attached rings) are stable in TA but not in MS. Subsequent fragmentation produces fragments with high stability in comparison with the corresponding fragments produced in MS in case of 4-attach rings, a relatively small in 2-attach rings. This low stability in case of electron ionization mass spectrometry can be interpreted on the basis of charge localization concepts [15]. The non-bonding orbitals available on oxygen atom is surely the site of electron expulsion upon ionization. The unpaired electron has a strong tendency for electron pairing and denoted to form a new bond. Hence, the partial localization of unpaired electron density in a certain orbital can reduce the activation energy for cleavage of certain bonds. Also, from the results obtained the two techniques are comparable until all OH and CH_3I disintegrated. After this the remaining can undergo different pathways.

Conclusions

Finally, it is concluded that the mass spectra fragmentation (MS), thermal analyses (TA) as well as IR-spectroscopy and elemental analyses are combined to study three redox products (PC-IO_3^-, PG-IO_3^- and PG-IO_4^-). Structural elucidation of these compounds can be satisfactorily achieved by using the above tools.

Also, the behavior of the three products using thermal decomposition and mass spectral fragmentation are performed. Comparative study of the fragmentation by MS and decomposition by TA for the three products shows similarity of the primary processes in both techniques until all OH groups and CH_3I molecules are released. The stability of the initial products and some fragments are discussed in both techniques. All the obtained results confirm the proposed structures of the redox products.

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