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Comparative study on the fragmentation of some simple phenolic compounds using mass spectrometry and thermal analyses

M.A. Fahmey^a, M.A. Zayed^{b,*}, Y.H. Keshk^c

^aNuclear Physics Department, N.R.C., Atomic Energy Authority, Cairo 13759, Egypt

^bChemistry Department, Faculty of Science, Cairo University, Giza, A.R.E., Egypt

^cPhysics Department, Faculty of Education, Damanhour, El-Behera, Egypt

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Abstract

The fragmentation pathways of 2-hydroxyphenol and 2,3-di-hydroxyphenol have been examined using electron impact mass spectrometry in comparison with thermal analyses (TGA and DTA). Both the decomposition modes were investigated, and the fragmentation pathways were suggested. The combined use of mass spectrometry and thermogravimetry (MS and TG) in the analysis of 2-hydroxyphenol and 2,3-di-hydroxyphenol allowed the characterization of the fragmentation pathway in MS which was the objective of this research. The major pathway of hydroxyphenol includes successive loss of CHO, while 2,3-di-hydroxyphenol the major pathway involved loss of H₂O followed by CO.

There was virtually no ring disintegration until the majority of the attached groups were lost in 2-hydroxyphenol, while in 2,3-di-hydroxyphenol a complete decomposition occurred. On the other hand, an O atom remains attached to five-membered ring in a cyclopentanone form as a result of the stability of PG in comparison with PC. The thermal decomposition and mass spectral fragmentation of the hydroxybenzene are also correlated with the electron delocalization of their ring system.

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1. Introduction

The [C₆H₆O]⁺ ion has been the subject of extensive studies [1]. A number of techniques have been utilized among which are collision induced dissociation [2,3], metastable abundance ratios [4], isotope labeling studies [5], ion cyclotron resonance spectrometry [6]. This work has been motivated, in part by an interest in keto–enol tautomerism in gas phase [7]. The

tautomerism occurs as rate determining step in CO elimination from ionized phenol [8]. This investigation employed kinetic energy release measurements on metastable ions in reaching this conclusion [8].

Fragmentation of aromatic phenols are characterized by intense peaks for the molecular ion, and by little indication of dehydration from phenol groups unless there is an adjacent functional group [9]. The loss of neutral CO from the molecular ion of phenol produces a substantial peak at mass 66 in the mass spectrum. The appearance of this ion is due to the formation of intermediate structure of the phenol molecular ion which is easy to visualise as a process characterized by the loss of neutral CO, while CHO is

* Corresponding author. Tel.: +20-202-5676624;
fax: +20-202-5727556.

E-mail address: mazayed@chem-sci.cairo.eun.eg (M.A. Zayed).

lost more readily from the higher homologues [10]. In 2-hydroxyphenol, for instance, the ion due to $[M-CHO]^+$ is more abundant than $[M-CO]^+$ [10].

Mass spectra consist of a series of competitive and consecutive unimolecular fragmentations [11] in conjunction with thermal decomposition which provide additional data about the sample, and is very important in order to understand the chemical processes and mechanism of the fragmentation, since electron impact (EI) and thermal analysis (TA) fragmentation do not necessarily follow the same pathway.

The fragmentation in both EI and TA techniques [11] are similar in that rupture takes place at weak bonds. The loss of molecular species as CHO, CO and H₂O, all of which are known to occur preferentially in the preferred processes, have the lowest energy requirements. In TA, the molecules are continuously energised and deactivated by a gas evolution, and the distribution of energy can be described by a temperature. In EI, the ion produced is formed with specific amount of internal energy, which is conserved independently in all subsequent dissociations. During the ionization process, transitions to various states are possible leading to a collection of ions with a distribution of internal energies. This will be quite different from the thermal distribution, and will differ with electron energy and nature of the molecular species. In MS, the dissociation does not immediately follow ionization, but it is slow enough to permit the transfer of energy into the various degrees of freedom involved in the observed dissociation.

The aim of the present work is to study the collective behavior of some phenolic compounds in mass spectra and thermal analyses fragmentation to investigate the decomposition, and the fragmentation stability of the hydroxybenzenes by thermal and EI methods and the stability of the remaining fragment to further fragmentation.

2. Experimental

2.1. Materials

All chemicals employed in the present work were of the analytical grade supplied by two companies. These included phenol and 2-hydroxyphenol (PC) from ALDRICH, while 2,3-di-hydroxyphenol (PG) from Merck.

2.2. Mass spectral measurements and instruments

The mass spectra of phenol, 2-hydroxyphenol (PC) and 2,3-di-hydroxyphenol (PG) were recorded with EI technique at 70 eV on a Hewlett-Packard MS-5988GC instrument in the Microanalytical Center, Cairo University. The instrument was calibrated using perfluorotributylamine as standard material. The reproducibility of the readings was also checked by repeating experimental measurements twice as recommended in literature [12].

2.3. Thermal analyses (TGA and DTA)

The TGA and DTA studies were made with conventional thermal analyzer (Shimadzu system, Shimadzu 30 series thermal analysis instrument). The mass losses (5 mg samples) and heat responses of the changes in the sample were measured in the temperature range from 20 to 200°C for PC, and up to 300°C for PG. The heating rate was 10°C min⁻¹ in both TGA and DTA in an inert argon atmosphere. These instruments used were calibrated using indium metal as thermally stable material. The reproducibility of instrument reading was determined by repeating each experiment twice.

3. Results

3.1. Mass spectra

The 70 eV EI mass spectrum of phenol, PC and PG were studied and recorded. A typical spectrum (bar graph) is listed in Fig. 1, while the major fragmentation pathways of PC and PG are presented.

3.2. Thermal analyses

The samples were measured in the temperature range from 20 to 200°C for PC, and up to 300°C for PG. The calculated and estimated weight loss for PC are 52.7 and 52.67%, respectively, and also the calculated and estimated weight loss for PG are 36.5 and 36.45%, respectively. For PC, at 105°C: end peak, melt of PC and loss of CHO; at 165°C: end peak, loss of CHO, complete decomposition. For PG, at 80°C: end peak, loss of H₂O; at 134°C: end peak,

melt and loss of CO; at 211°C: end peak, complete decomposition.

4. Discussion

4.1. Mass spectral behavior of phenolic compounds

It is important to compare mass spectral fragmentation pattern of phenol as parent molecule (Fig. 1(A)) in comparison with its derivatives PC and PG (Fig. 1(B))

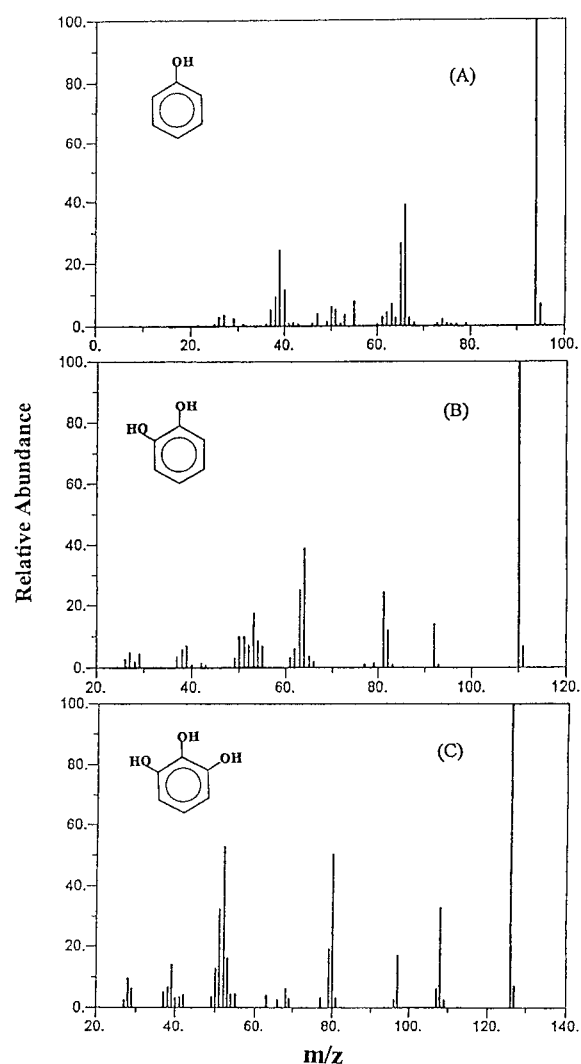
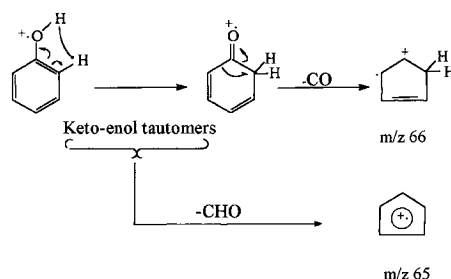


Fig. 1. Mass spectra (EI, 70 eV) of phenol (A), PC (B), and PG (C).



Scheme 1. Principal mass spectral fragmentation of phenol.

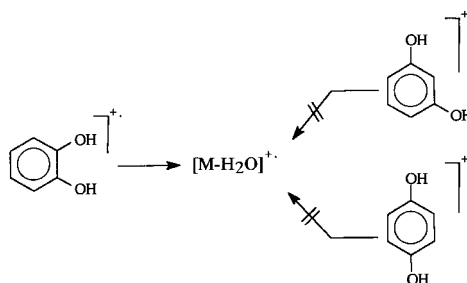
and (C)). This is considering a solid bar to help the explanation of fragmentation pattern of PC and PG to elucidate the course of the chemical change. The mass spectra of phenol already reported [13] illustrate a number of fragmentations characteristic of the hydroxyl group on an aromatic ring. The $[M-CO]^+$ peak, which is usually accompanied by $[M-CHO]^+$ is especially useful in recognizing this functionality.

The apparent mechanism of phenol mass fragmentation (Scheme 1) involves elimination of oxygen with its adjacent ring carbon, while deuterium labeling [13] indicate that CHO loss is accompanied by substantial hydrogen scrambling [13].

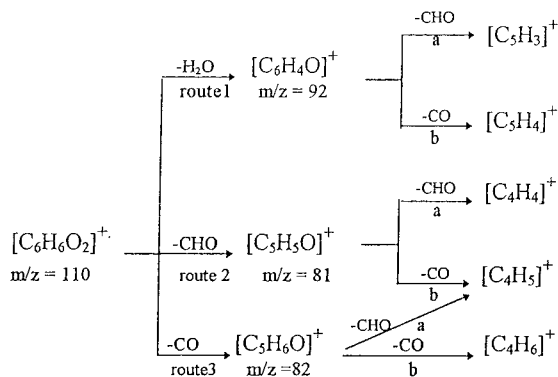
4.2. Fragmentation of PC

PC exhibits elimination of H₂O during analysis by electron impact (EI) ionization mass spectrometry, in contrast to the other two isomeric hydroxy phenols [14,15]. This specific behavior suggests the occurrence of H-migration from the 1- to 2-hydroxy group in the molecular ion of PC (Scheme 2).

The appearance of $[M-H_2O]^+$ ($m/z = 92$) fragment ion in the mass spectrum of PC with its subsequent



Scheme 2. Elimination of H₂O from hydroxyphenol isomers.



Scheme 3. Fragmentation pathway of principal ions from PC.

loss of CHO and CO forming $[M-H_2O-CHO]^+$ ($m/z = 63$) and $[M-H_2O-CO]^+$ ($m/z = 64$) ions (Scheme 3, route 1a,b) are due to “ortho effect” of the two adjacent OH groups.

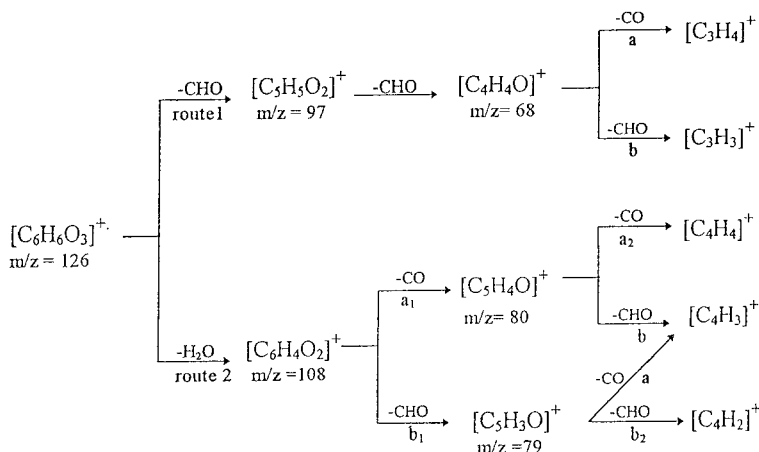
Also, the spectrum of PC molecular ion illustrates a number of fragmentation characteristics of the presence of OH groups in aromatic ring, i.e. CHO and CO loss forming $[M-CHO]^+$ ($m/z = 81$) with RI = 24.5% and $[M-CO]^+$ ($m/z = 82$) with RI = 12%. Subsequent loss of CHO of these ions leads to the formation of masses 52, 53 and 54. The proposed fragmentation patterns at 70 eV are outlined in the following Scheme 3.

4.3. Fragmentation of PG

The major fragmentation process occurring in the molecular ion of PG leads to the formation of $[M-H_2O]^+$ ($m/z = 108$) with relative intensity 32.4% in comparison with that obtained from PC with relative intensity (RI = 14.4%). Elimination of H_2O in PG is a result of H-transfer between vicinal hydroxy groups. The highly specific dehydration process observed in the molecular ion PG is due to the proximity of three OH groups in benzene ring. A subsequent loss of CO and CHO affording $[M-H_2O-CO]^+$ ($m/z = 80$) with RI = 50.5% with less abundant $[M-H_2O-CHO]^+$ ($m/z = 79$) with RI = 19.5%. Masses at 50, 51 and 52 are due to secondary decomposition. The proposed possible fragmentation pathways of PG at 70 eV are outlined in the following Scheme 4.

4.3.1. Thermal decomposition behavior of PC and PG

The TGA and DTA curves obtained for PC are shown in Fig. 2. The TGA curve of PC in Fig. 2(A) involves three stages. The first stage extended from 20 to 115°C, the second from 115 to 135°C and the third from 135 to 170°C. These stages are accompanied by mass losses of 26.4, 26.4 and 46%, respectively. These mass losses may be attributed to the removal of successive two CHO groups of mass 29 in two steps, and the third step involves the complete



Scheme 4. Fragmentation pathway of principal ions from PG.

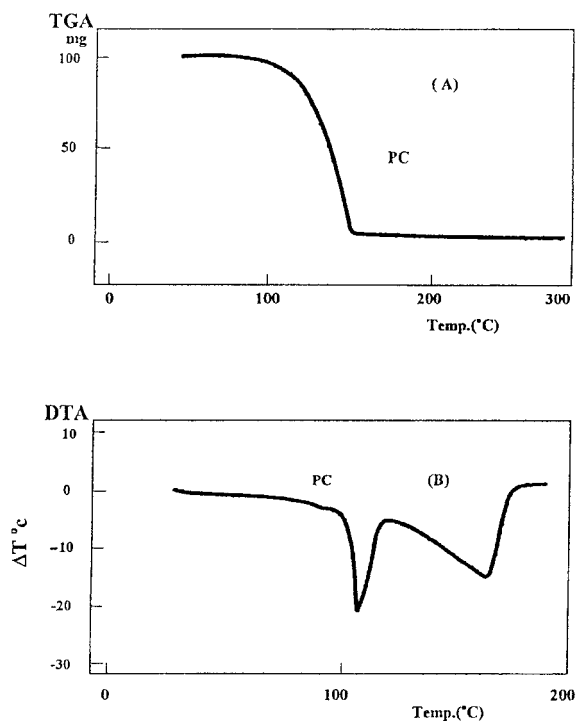


Fig. 2. TGA (A) and DTA (B) curves of PC.

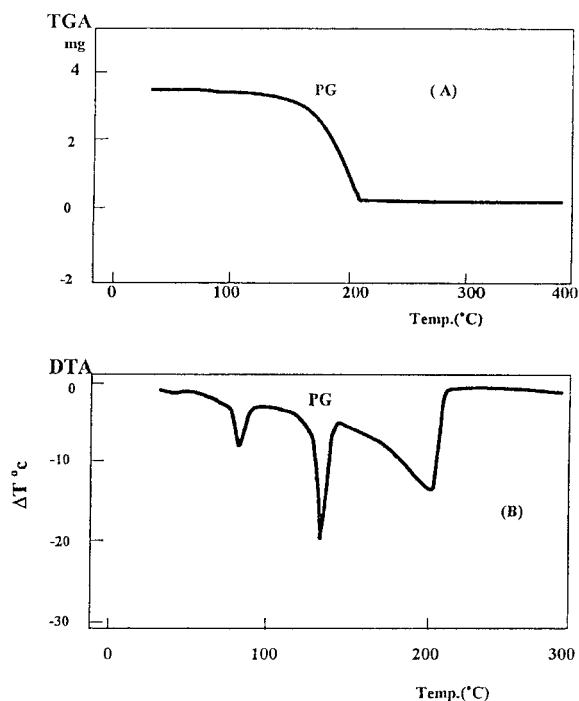
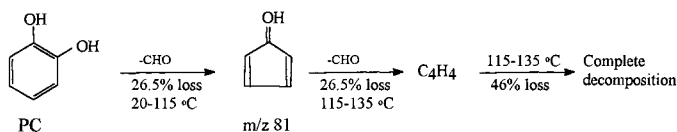


Fig. 3. TGA (A) and DTA (B) curves of PG.

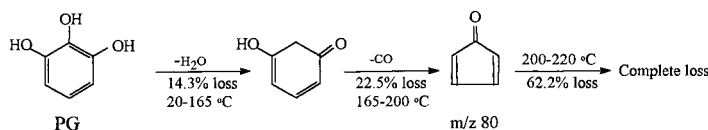
decomposition of the remainder part, i.e. C_4H_4 fragment. The results of thermal behavior of PC can be explained by the proposed Scheme 5. The DTA curve (Fig. 2(B)) refers to the presence of two endothermic peaks. The first peak is sharp and centered at $105^\circ C$, and the second is intensely broad and occurs from 120 to $180^\circ C$ with its maximum centered around $165^\circ C$. The first peak corresponds to melting of PC and the removal of CHO, and the second one is due to the escape of CHO from the entity of PC, and the complete decomposition occurs at the third step. The exothermic base shift at $180^\circ C$ is attributed to the increase in heat capacity of the residual reaction

product of the PC before going to complete decomposition in the third step (Scheme 5).

The TGA curve of PG (Fig. 3(A)) refers to the three stages. These stages are extended from 20 to 165 , 165 to 200 and 200 to $220^\circ C$, respectively. The found consecutive mass losses are 14.3 , 22.2 and 62.2% , respectively. The calculated mass losses are 14.7 , 22.5 and 62.5% . These mass losses are due to removal of H_2O , CO and the complete decomposition of PG. The DTA curve (Fig. 2(B)) shows three sharp endothermic peaks which may refer to the three sharp endothermic peaks at 80 , 134 and $211^\circ C$, respectively, which may refer to the three mass losses in TGA. These mass



Scheme 5. Thermal decomposition behavior of PC.



Scheme 6. Thermal decomposition behavior of PG.

losses can be tentatively represented by the proposed Scheme 6.

4.3.2. Comparative study between MS and TA of PC and PG

The important primary decomposition process of PC in TA is due to CHO loss from the original enol-form (Scheme 5). The thermal cracking can undergo bond rupture at a weak bond [11], and this leads to the formation of (C_5H_5O) $m/z = 81$. In MS, the keto–enol tautomerism was observed, i.e. appearance of $[M-CHO]^+$ and $[M-CO]^+$, while the loss of CHO preferentially occurs rather than loss of CO [10]. The fragment $m/z = 81$ is unstable enough in TA techniques which can undergo subsequent CHO loss and form four-membered ring.

The initial sequences of decomposition of PG in TA involves dehydration followed by decarbonylation (Scheme 6) and formation of (C_5H_4O) $m/z = 80$. This behavior is in agreement with the results obtained by using MS for dehydration (Scheme 4, route 2) followed by decarbonylation (Scheme 4, route 2a₁). The $[C_5H_4O]^+$ fragment ion, i.e. $[M-H_2O-CO]^+$ and its subsequent competitive fragments are stable in MS, i.e. observed in mass spectra with relatively high intensity. On the other hand, the fragment $[C_5H_4O]^+$ in TA is completely decomposed, while oxygen atom remains attached to five-membered ring in cyclopentanone form.

Finally, the fragmentation of PC and PG are comparable in both techniques, except the behavior of decomposition five-membered ring in PC ($m/z = 81$), indicating a high stability of the ion in gaseous phase at the energy considered, while it is unstable in neutral state. This stability may be attributed to the fragmentation of keto–enol tautomerism, which stabilized the fragment ion. The neutral enols [16] are thermodynamically less stable isomers, while upon ionization more stability is encountered. This encountered stability may arise from the greater unsaturation and greater electron delocalization in the ionized forms.

5. Conclusion

In this work, the investigation of 2-hydroxyphenol and 2,3-di-hydroxyphenol (PC and PG) using thermal decomposition and mass spectral fragmentation was performed. Comparative study of the fragmentation by MS and decomposition by TA for PC and PG shows a similarity, except the behavior of five-membered ring in TG of PC. This investigation concluded that both MS and TA are complementary techniques, and used to declare the thermal decomposition of hydroxybenzenes on heating, and the mass spectra helps the selection of their suitable thermal decomposition mechanisms.

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