

Thermal and Electron Impact Decomposition of 4-hydroxy-4'-cyano-azobenzene

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In the present work 4-hydroxy-4'-cyano-azobenzene (HCA) azo dye was investigated by means of differential thermal analyses (DTA) and thermogravimetry (TG) in comparison with electron impact (EI) mass spectral (MS) fragmentation at 70 eV.

Keywords: 4-phenylazo-phenols, azo dyes, mass spectra, electron impact ionization thermal decomposition

4-Hydroxy-4'-cyano-azobenzene (HCA) is an azoic dye with various applications in organic synthesis.

Thus, its derivatives attracted great attention in the last two decades due to their employment in the synthesis of photoresponsive azobenzene polymers. They have possible applications in non linear optics and optoelectronics and for optical information storage, thanks to laser-induced trans-cis-trans photoisomerization cycles of azobenzene chromophores [1]. Thus, certain teams used the HCA synthon in the synthesis of azobenzene side-chain-type copolymers with improved photoinduced anisotropy and long-term stability [2-4]. The photoinduced anisotropy in polythiophenes containing HCA derivatives was studied [5]. Recently, it was synthesised a photoresponsive polymer gel employing the coupling of HCA derivatives to α -cyclodextrin ring by esterification [6]. Azocellulose polymers [7] have also been synthesized by coupling 4-cyanophenylazophenol to the primary hydroxyl group of D-glucopyranose units of natural cellulose of ultrahigh molecular weight by the Mitsunobu reaction. Another class of polymers with application in holographic information storage was reported in [8] where a family of azobenzene peptides containing HCA was synthesized.

HCA has also been integrated in photoresponsive trisurea compounds [9]. They act as self-assembled materials with light-induced photoswitchable properties due to the azo linkages.

An interesting application of HCA was reported by [10] using this compound in the preparation of a new liquid crystal that can be used as stationary phase in gas-chromatography.

The structural formula of this azo dye was thoroughly investigated by several authors using different techniques (NMR, IR, UV-VIS) [1, 8, 9,11]. The mass spectrometry is important because it provides a lot of structural information with little expenditure of the sample. In electron impact (EI) mass spectra, the fragmentation consists of competitive and consecutive unimolecular fragmentation pathways [12,13]. The TG/DTA provides quantitative information on weight losses due to decomposition and/or evaporation of low molecular materials as a function of time and temperature. Due to the usage of azo dyes in special domains that require high temperatures, the investigation of their thermal stability is very important. Given this reason, the azo dyes were studied using thermogravimetric analysis [14-17]. The interpretation of thermal degradation processes can be supported by mass

spectrometric analysis because the nature of the released volatiles may be thus deduced.

The structure of 4-hydroxy-4'-cyanoazobenzene (HCA) is given in figure 1.

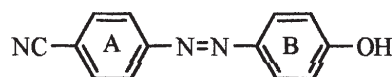


Fig. 1. The structure of HCA

The main purpose of the present work is to carry out experimental studies on HCA using thermal analysis measurements including kinetic analysis of the dye and EI mass spectral fragmentation at 70 eV.

Experimental part

Materials

4-Phenylazo-phenol analyzed in this work was synthesized by coupling the diazonium salt of *p*-amino-benzonitrile with phenol [8]. The obtained azo compound was purified by recrystallization from ethanol and its purity was examined by thin-layer chromatography and was checked by noting the melting points after successive recrystallizations. Chemicals (phenol, *p*-amino-benzonitrile) used in azophenol synthesis were purchased from Merck Company and were used without further purification.

Techniques

The mass spectrum has been obtained using a HPGC-MS 5890 MD 5971 spectrometer at 70eV, with carrier gas He at 2 mL/min.

The compound sample (2 mg) was analyzed using TG/DTA measurements in nitrogen atmosphere using a Perkin-Elmer TG/DTA analyzer with Pyris software. Thermogravimetric measurements were carried out in a temperature range (20 to 500°C) with a heating rate of 5 °C·min⁻¹.

Results and discussions

The reactivity of HCA is of great interest in organic synthesis. Knowledge on this topic can be obtained by studying the thermal and electron impact decomposition mechanisms of the azo dye, which is very important for understanding the chemical processes that might take place. As it is difficult to establish the exact major fragmentation pathway using only EI, we decided to

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combine the two above techniques. This makes possible to understand the following topics:

- the stability of the dye under thermal degradation in solid state and mass spectral fragmentation in gas phase;
- prediction of the primary site of the fragmentation, which helps to rationalize subsequent bond cleavage.

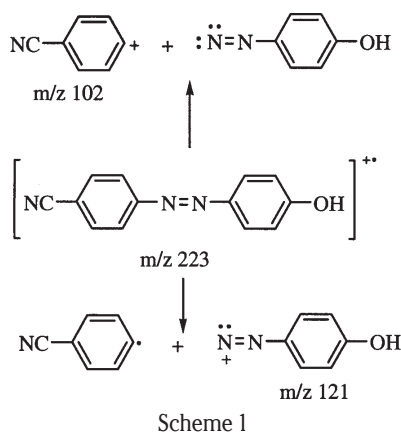
Mass spectra

The mass fragments of HCA displayed in its mass spectrum obtained by EI are presented in table 1.

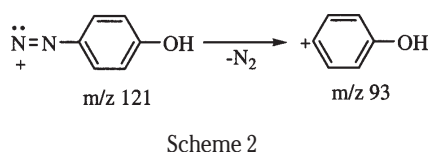
Table 1
THE MASS FRAGMENTS OF HCA

m/z	Ion formula	RI (%)
39	C ₃ H ₃	12.8
65	C ₅ H ₅	36.2
93	C ₆ H ₅ O	100
102	C ₇ H ₄ N	33.8
107	C ₆ H ₅ NO	69
121	C ₆ H ₅ N ₂ O	44.8
223	C ₁₃ H ₉ N ₃ O	59

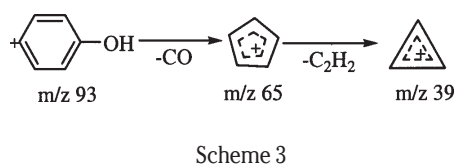
The mass spectrum of HCA contains a molecular ion peak M⁺ at m/z = 223 of relative intensity 59%, as a proof of its quite elevated stability. The molecule undergoes cleavage of the C-N bond to give fragments at m/z 102 and m/z 121 (scheme 1).



In a subsequent fragmentation, m/z 121 loses N₂ to produce the base peak at m/z 93 (scheme 2).

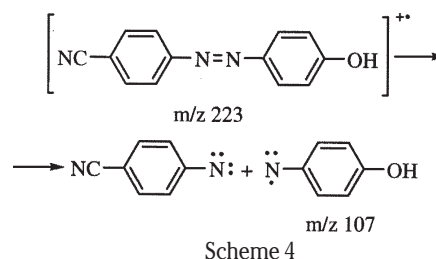


The ion at m/z 93 loses CO and acetylene, leading to the cyclopropenilium ion, m/z 39 (scheme 3):



TGA wt. loss (%)	Temperature range (°C)	DTA peak temperatures (°C)	Peak description
42	150-259	185	Endothermic
58	259-300	271	Exothermic

Another cleavage of the parent ion is at the N=N bond, giving the fragment at m/z 107 (scheme 4):

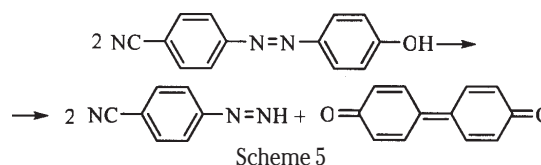


Thermal analyses

The thermoanalytical results obtained from DTA and TG curves of HCA are given in table 2.

The TGA data show that the HCA molecule is thermally decomposed in two main steps. The first step occurs at 150–259°C as a result of 42.0 % practical weight loss. This step may be due to the departure of C₆H₄O part, (calculated wt. loss% = 41.7 %). It is followed by the second practical weight loss of 58%. This loss may be due to the complete decomposition of the remainder benzene ring that occurs at 259–300°C (calculated wt. loss = 58.3 %). This weight loss is associated by one endothermic peak at 185 °C and one exothermic peak at 271°C as given by the heat flow curve.

For the first step, the experimental loss of weight is in good agreement with the theoretical loss of weight, leading to the probable mechanism (scheme 5):



The proposed mechanism is correlated to the elementary analysis of the solid residue, where nitrogen was found.

The apparent activation energy for first step (150–259°C) has been determined using the logarithmic form of the Arrhenius equation.

$$\lg k_g = \lg A - E_a/2.303RT$$

where:

- k_g – weight loss in time at T temperature (K);
- A^g – pre-exponential factor;
- E_a – apparent activation energy;
- R – universal gas constant.

The lg k_g = f (1/T) graphical representation is straight line, with the slope d (lg k_g)/d(1/T) = E_a/2.303R (fig. 2); thus, the value of the apparent activation energy has been determined and was 82.25 kJ/mol.

Analyzing the thermal and electron impact decomposition of 4-hydroxy-4'-cyano-azobenzene, it may be noticed that the two processes can be characterized by the cleavage of the C_{ring B}-N bond. In the MS obtained by EI, the peak at m/z 93 (scheme 2) corresponds to the base ion and it is formed through the cleavage of the C_{ring B}-N bond. Using TA, it can also be deduced that the two fragments formed by heating the dye molecule (scheme 5) are generated by the cleavage of the same bond.

Table 2
THERMOANALYTICAL
RESULTS OF HCA

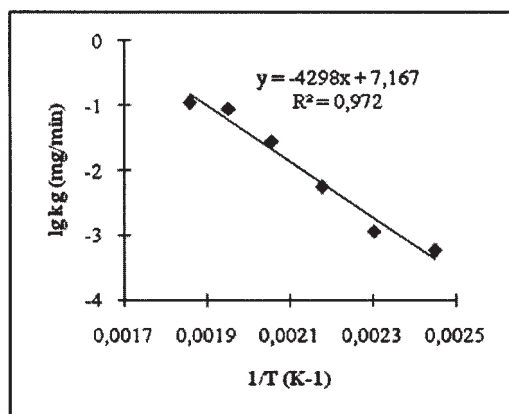


Fig. 2. Arrhenius diagram for the HCA degradation monitored by TG/DTA

Conclusions

This study provides further insights into applicability of experimental thermal analyses and mass spectrometry techniques for HCA. From the application of these two techniques, it can be concluded that:

- the primary fragmentation of HCA by applying both experimental techniques (TA and MS) can be explained through the cleavage of the C_{ring B}-N bond in the dye molecule;

- the fragmentation under electron impact can also take place through the cleavage of the C_{ring A}-N bond or of the N=N bond;

- the thermal degradation occurs in two steps, the process ending at 300 °C.

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