

SPECTROPHOTOMETRIC DETERMINATION OF THE ACID DISSOCIATION CONSTANTS OF SOME 1,5 - DIPHENYLFORMAZAN DERIVATIVES

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ABSTRACT

The acid dissociation constants of some 1 - (o - carboxyphenyl 3 - acetyl - 5 - aryl) formazans are determined in 40 % (v/v) ethanolic buffer solutions spectrophotometrically. The spectral changes with variation of pH were discussed in relation to the different ionic species existing in solution. The pKa values were discussed in terms of molecular structure and substituent effect.

INTRODUCTION

Several reports on the use of formazans as analytical reagents for the determination of various metal ions have appeared (Hooper, 1969).

The ionization constants of some benzimidazolyl formazans were determined spectrophotometrically (Mulkina, 1969).

Solvent effects on the absorption spectra of some diphenyl and triphenyl formazans in ultraviolet and visible regions were studied (Petrovanu, 1982).

Avramenko, (1975) studied the tautomerism and tautomers of some triaryl formazans spectrophotometrically.

The present article includes a spectrophotometric study of some diphenyl formazans in alcoholic-aqueous buffer solutions. The pK values of the COOH as well as the OH and AsO(OH)₂ groups are determined.

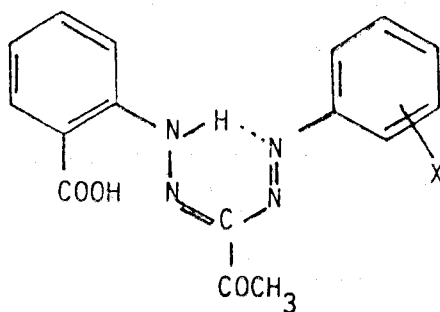
EXPERIMENTAL

i) Preparation of 3 - (o-carboxyphenylhydrazone) -2,4-pentanedione

Hydrazone was prepared by coupling of o-carboxybenzene diazonium chloride with acetylacetone in a ratio of 1:1 in weakly alkaline medium of sodium acetate. The yellow product was kept in a refrigerator overnight, then acidified with 1:1 HCl, filtered, washed with water and recrystallized from ethanol to give yellow needles of m.p. 228°C (Mulkina, 1969).

ii) Preparation of formazans:

Assymmetric formazans were prepared by coupling of the corresponding benzene diazonium chloride with the above prepared hydrazone in a ratio of 1:1 in alkaline medium of sodium hydroxide. The produced formazan was kept in a refrigerator overnight then acidified with 1:1 HCl, filtered, washed with water and recrystallized from methanol-water (50 % v/v) to constant melting point. All the resulting formazans are dark red crystals. They have the following structural formula:



1- (o-carboxyphenyl), 3-acetyl, 5-aryl formazans where X = H (I), o-NO₂ (II), p-NO₂ (III), o-CH₃ (IV), p-CH₃ (V), o-OH (VI), m-OH (VII), p-OH (VIII), m-COOH (IX), p-COOH (X), p-OCH₃ (XI), p-Cl (XII), p-Br (XIII), p-I (XIV) and o-AsO (OH)₂ (XV).

The water used was always twice distilled. The chemicals were all of the highest purity available. 10⁻³M formazan solutions were prepared by dissolving the accurately weighed amount in the appropriate volume of absolute ethanol. Modified Britton and Robinson

universal buffers (Britton, 1952) were used to control the ionic strength and pH of the solutions. Solutions for spectral measurements were obtained by diluting known volumes of the stock solution of the formazan with the buffer solutions. The absorption spectra were run at room temperature using Shimadzu 240 UV recording spectrophotometer.

The pH was always checked immediately after each set of measurements.

RESULTS AND DISCUSSION

The absorption spectra of $2-4 \times 10^{-5}$ M of the formazan derivatives under investigation in (40 % v/v) ethyl alcohol-water mixtures of varying pH values are represented in Fig. (1). The spectra in acidic solutions of pH 2-3 are characterised by a broad band absorbing maximally within the wavelength range 440-360 nm. This band is attributed to $\pi - \pi^*$ electronic transition within the azo linkage (Issa, 1973) influenced by charge migration through the whole molecule. The absorbance of the whole band decreases with increasing pH values up to pH 7.0. It is of interest to mention that such changes in absorption spectra are due to changes of absorbing species i.e. perturbation of the π -system of the molecule. This can be understood by assuming the existence of the Zwitter ion in solution through the transfer of the proton of the carboxylic group to one of the nitrogen atoms of the formazan. The pK values of the compounds under investigation range from 3.2 to 4.6 which can be assigned to the COOH group. For compounds IX and X containing two COOH groups, the changes in spectra within the pH range 3-7 reflects the ionization of the two COOH groups where the absorbance decreases with the increase of pH up to 4.0 then increases up to pH 7.0. Above pH 7.0 the absorption spectra show no variation with change of pH for all compounds except VI, VII, VIII and XV that is compounds containing OH or AsO(OH)₂ groups, indicating complete transfer to the anionic species. i.e. complete ionization of COOH groups and no further changes take place in the molecule.

For compounds containing OH or AsO(OH)₂ groups (VI, VII, VIII and XV) the spectra above pH 7 display two overlapping bands, the first at 365 nm while the second appearing "as a shoulder" at the longer wavelength at 390 nm. A vast variation of absorbance is observed after pH 10 where the first band decreases and the shoulder is

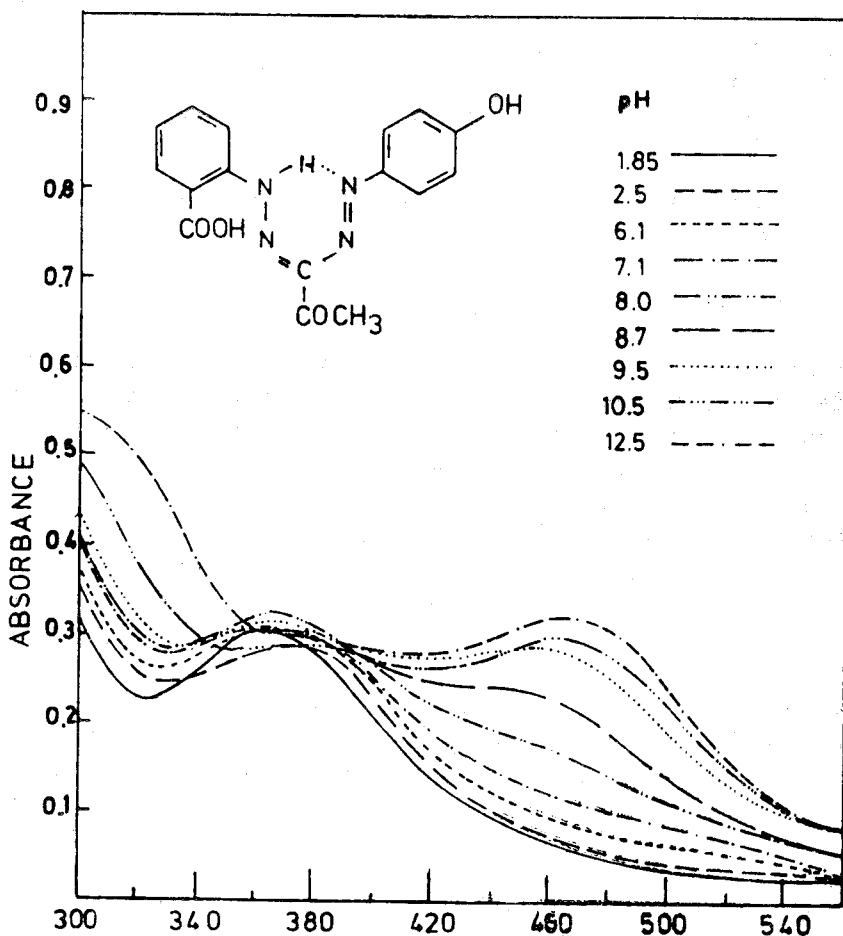
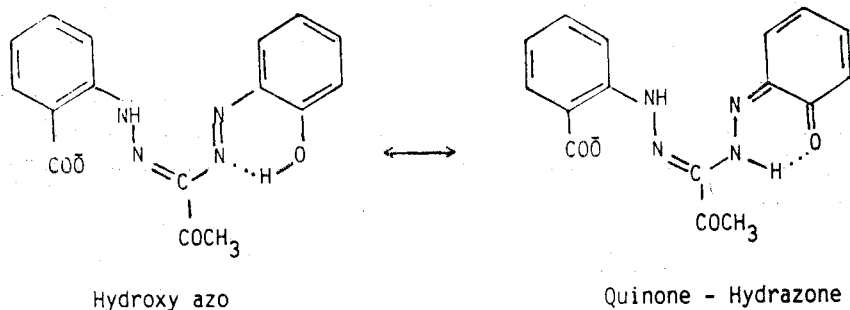


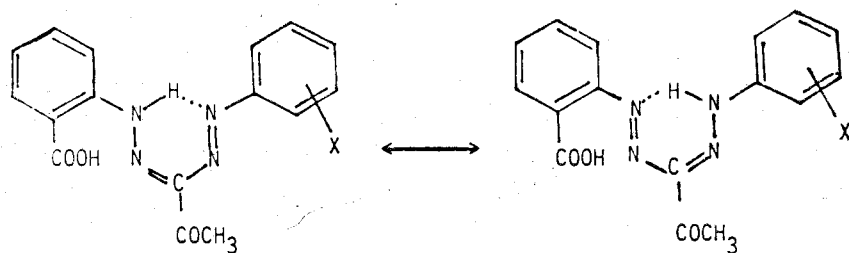
Fig. 1. Absorption spectra of 4×10^{-5} M of p-OH (VIII) derivative in 40 % ethanolic buffer solutions of varying pH values.

shifted towards longer wavelength, acquiring a limiting absorbance value at pH 11.5–12.5. This can be attributed to the ionization of OH group. The existence of two overlapping bands in (VI) containing o-OH group may be due to the participation of the o-hydroxy azo-quinone hydrazone tautomerism (Etaiw, 1978) thus:



For *o*-arsonic derivative (XV) the successive increase of pH values of the medium is accompanied by a slight decrease in absorbance until pH 9.5 where it attains a constant minimum value. This decrease in absorbance is due to the ionization of the first proton of the arsonil group. On further increase of pH the absorbance increases again where it tends to attain a limiting value at pH 12.0 and the maximum absorbance is shifted to shorter wavelength, this increase is due to the ionization of the second proton of the arsonil group.

The ionization of the NH group is very difficult. The expected pKa value being higher than 14 (Gill, 1977). This may be attributed to the contribution of the NH group in the formation of a hydrogen chelate ring with the participation of the azo-hydrazone tautomerism (Avramenko, 1974) thus:



The absorbance-pH curves at wavelengths around the maximum indicate one step ionization of the proton of the COOH group for all compounds except VI, VII, VIII, IX, X and XV, i.e. compounds that exhibit two ionization steps (in the case of VI, VII and VIII which reflects the ionization of the COOH and phenolic OH groups and in case of IX and X the two ionizations of the two COOH groups) In case of *o*-arsonil compound XV the absorbance-pH curve is characterized

by three steps, indicating the ionization of COOH and the two OH's of the AsO(OH)₂ group.

The pK values of carboxylic, phenolic and arsonic groups were calculated applying the half height method (Issa, 1971) and the limiting logarithmic method either mathematically by direct application in the equation:

$$\text{pH} = \text{pKa} + \log \frac{A - A_{\min}}{A_1 - A} - \log f$$

or graphically by the plot of $\log \frac{A - A_{\min}}{A_1 - A}$ versus pH where a straight line is obtained intersecting with the X-axis at pH equal to the pKa value. The results are depicted in table (1).

In a previous investigation (Issa, 1983), it was pointed out that, the ionization of acidic groups which are not directly attached to the π -resonating system in the molecule do not affect the absorption spectra. However, the ionization of groups which are participating in the π -system will cause spectral changes, where the unsubstituted diphenyl formazan show no spectral variation with change of pH of the medium indicating that only one species exist in such solutions and the ionization of NH group is very difficult as mentioned previously.

However for the compounds under investigation, though the ionizable proton of the COOH or AsO(OH)₂ group is not directly attached to the resonating system yet the ionization of such proton imparts spectral changes. The change in absorption can only be attributed to changes in the absorbing species present in solution. The only possibility for this is the existence of an acid-base equilibrium. This can only be accounted for by assuming the formation of Zwitter ion in solution.

Considering the data given in table (1) the following points can be deduced:

- (a) In general the pK values of the COOH groups decrease by the increase of the electron donating character of the substituent on the other phenyl ring. However, a trial to correlate the pKa value with Hammett substituent constant (σ) was not satisfactory, this may be taken as evidence for non coplanarity

Table I. λ_{\max} and mean pK values of Diphenyl Formazan Derivatives.

Comp.	x	Acid.	λ_{\max} nm		pK	
			Neut.	Alk.	pK ₂	pK ₂
I	H	362	365	365	3.60	—
II	o-NO ₂	360	360	365	3.65	—
III	p-NO ₂	365	370.380 ^{sh}	370.380 ^{sh}	3.60	—
IV	o-CH ₃	365	362.380 ^{sh}	362.380 ^{sh}	3.43	—
V	p-CH ₃	365.390 ^{sh}	360.390 ^{sh}	360.390 ^{sh}	4.45	—
VI	o-OH	365	365	370.335 ^{sh}	4.15	11.75 ^a
VII	m-OH	378	380.390 ^{sh}	380.390 ^{sh}	3.30	8.00 ^a
VIII	p-OH	370	460.370	470.380	2.30	7.80 ^a
IX	m-COOH	370	360	360	3.65	5.75
X	p-COOH	355	360	360	2.50	5.45
XI	p-OCH ₃	365	365	370	4.64	—
XII	p-Cl	440.360	440.360	440.365	4.25	—
XIII	p-Br	440.360	440.360	445.365	3.25	—
XIV	p-I	360	365	365	4.20	—
XV	AsO(OH) ₂	365	365.390 ^{sh}	460.365.390 ^{sh}	4.10	9.20 ^b 11.0 ^b

pK₁ : Ionization constant of the first COOH group.

pK₂ : Ionization constant of the second COOH group.

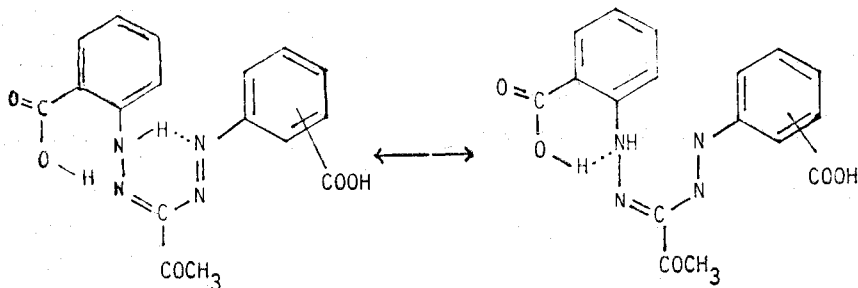
pK₂(d) : Ionization constant of the phenolic OH group.

pK₂(b) : Ionization constant of the first and second proton of arsonic AsO(OH)₂ group.

sh : Shoulder.

of the 1 and 5 phenyl rings of the formazan molecule also the molecule may acquire a trans configuration, this minimizing the substituent effect.

- (b) The compounds IX and X containing two COOH groups, the proton of the COOH group on the substituted phenyl ring (on m- or p-position) is firstly ionized before that of the proton of the other phenyl ring (o-position) which may be involved in the hydrogen bond formation as follows:



- (c) The change of the position of the OH-group to the o-position (XV) leads to an increase of the pK value by 3.75 and 3.95 pK units with respect to m- and p-derivatives. Such increase is equivalent to 5.15 and 5.43 K cal / mole which lies within the range of hydrogen bond formation energy.
- (d) For the arsono compound (XV), the As atom may act as electron conductor or bridge to the π -system thus leading to the existence of Zwitter ion in solution which in turns leads to the participation of the ionizable center with the π -system. The pK values were 9.2 and 11.0 for the first and second proton of the arsonic group such values are comparable to those of arsonic acid (Weast, 1970).

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