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UV STUDY OF THE PROTONATION OF BENZAMIDE AND N-PHENYL BENZAMIDE IN SULFURIC ACID MEDIA

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Introduction

The base strength of a weak Bronsted base, such as the compounds that are subject of our interest, could be determined from the changes in the ultraviolet spectrum of the compound when dissolved in aqueous sulfuric acid by increasing acid concentration. The protonation processes of benzamide (eq. 1) and other amides were studied in sulfuric acid media by the methods of ultraviolet, ^{1}H and ^{13}C NMR spectroscopy.[1-4]

$$B + H^+ \rightleftharpoons BH^+ \quad (1)$$

where BH^+ the is protonated base.

The measurement of pK_{BH+} values is sometimes complicated by the fact that the spectroscopic methods used are subject to medium effects. Water and 80 % (wt) H_2SO_4 are very different media, and it is not very surprising that spectral peaks for the same species in the two media can occur at different wavelengths or different chemical shifts. Various methods for the compensation of medium effect have been employed: principal component analysis (PCA),[5] characteristic vector analysis (CVA),[1,7] target factor analysis (TFA).[6]

A different equations have been used for determination of the pK_{BH}^+ values: equations proposed by Yates and McClelland[8] (eq. 2), its modification (eq. 3), Bunnett and Olsen[9] (eq. 4) and the excess acidity method (EAM)[10] (eq. 5).

$$\log I = m(-H_0) + pK_{BH}^+ \quad (2)$$

$$\log I = m'(-H_A) + pK_{BH}^+ \quad (3)$$

$$\log I + H_0 = \Phi (H_0 + \log c_H^+) + pK_{BH}^+ \quad (4)$$

$$\log I - \log c_H^+ = m^* X + pK_{BH}^+ \quad (5)$$

where H_0 is Hamett's acidity function; H_A its corrected value for amides, X is excess acidity function.

Ionization ratios was calculated according to the following equation:

$$I = c_{BH}^+ / c_B = (A_B - A)/(A - A_{BH}^+) \quad (6)$$

where A_B and A_{BH}^+ are absorbances of free base and protonated base respectively.

The same ionization ratios could also be obtained directly from the coefficients of the first characteristic vectors (CVA).[1,7]

Experimental

Materials. Benzamide and N-phenylbenzamide (or benzanilide), Fluka products, were used without further purification. Stock solutions of benzamide and benzanilide were prepared in deionised water and ethanol (Riedel-de Haën product), respectively. Reagent grade sulfuric acid (product of Alkaloid – Skopje) was used.

* Editorial note: Recognized by Greece as FYROM

Concentrations of the substances for the pK_{BH^+} determination were ~$2 \cdot 10^{-5}$ mol dm^{-3} in diluted solutions of sulfuric acid with concentration range from 0.5 to 12 mol dm^{-3}. The same acid solutions were used as blank.

Measurements. The UV spectra were recorded, immediately after preparing the solutions, on a Varian Cary 50 Spectrophotometer in 1 cm quartz cell, in the range from 190 to 350 nm, with resolution of 1 nm.

Results and Discussion

In the UV spectrum of benzamide in water, two bands can be notified, denoted as $1L_a$ (λ_{max} =196 nm) and $1L_b$ (λ_{max} = 227 nm).[11] With increasing the concentrations of the mineral acid, the intensities of the $1L_a$ band decrease (Tab. 1). Concerning the $1L_b$ band, besides this, a chemical shift to higher wavelengths appears, thus the maximum at 247 nm can be observed in the case of highest acid concentration of 11 mol dm^{-3}.

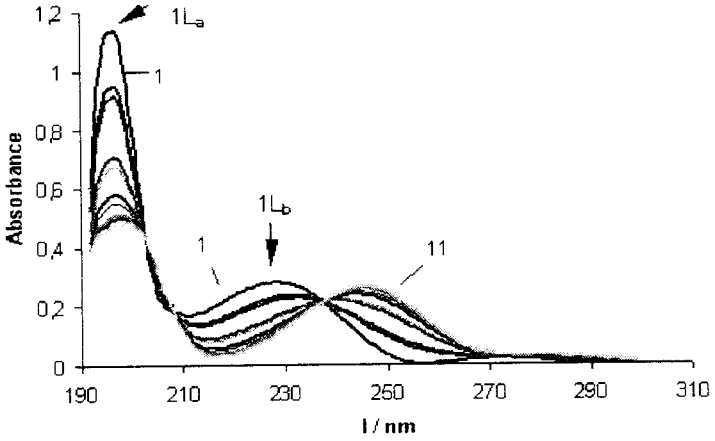

Figure 1. Reconstituted UV spectra of benzamide (2.45·10-5 mol dm^{-3}) as function of sulfuric acid concentration from 0 (curve 1) to 11 mol dm^{-3} (curve 11).

In the reconstituted spectra of benzamide (Fig. 1), using CVA,[1,7] few isosbestic points (at 202, 208,237 nm), can be observed. The presence if isosbestic points, indicates that there are at least two different absorptive species in the system.[1] Also, the isosbestic point gives us confidence in the validity of the analytical procedure.

Table 1. Wavelengths with molar absorbtivities of benzamide and N-phenylbenzamide.

compound	form	$\bar{\varepsilon}$ / μmol^{-1} dm^3 cm^{-1}				
		196 nm	227 nm	247 nm	258 nm	277 nm
benzamide	B	46367	11428	2857	-	-
	BH^+	18653	3632	10816	-	-
N-phenyl benzamide	B	51914	11026	-	11893	9086
	BH^+	28024	4594	-	12863	14395

The UV spectrum of N-phenylbenzamide is very similar to the one obtained for benzamide, in the region from 190 to 210 nm. It is interesting to discuss the change in the 227 nm band (it can be slightly notified in water solution of the compound), which with the increasing of the acid concentration obtains a minimum (Fig. 2). The protonated specie shows a band with maximum at 277 nm, resulting to chemical shift of the band at 258 nm (^1L_b), incoming from the unprotonated base (Fig. 2). This was followed by the appearance of the isosbestic point at 260 nm.

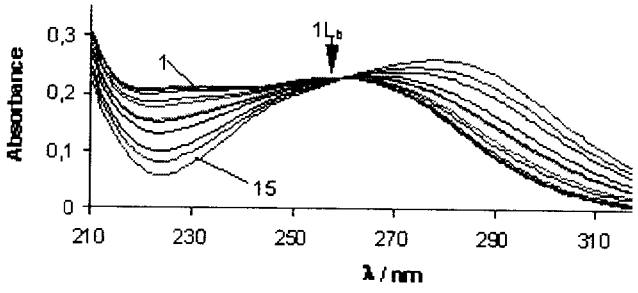

Figure 2. Reconstituted UV spectra of N-phenylbenzamide ($1.96 \cdot 10^{-5}$ mol dm^{-3}) as function of sulfuric acid concentration from 0 (curve 1) to 15 mol dm^{-3} (curve 15).

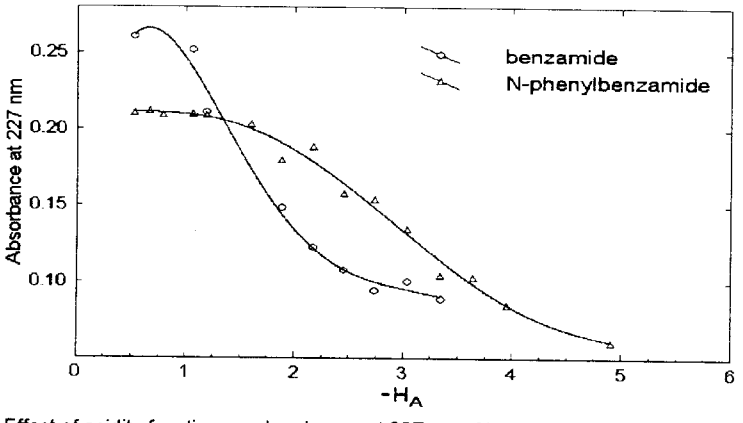

Figure 3. Effect of acidity function on absorbance at 227 nm of benzamide and N-phenylbenzamide.

Plots of the absorbances at 227 nm vs. H_A for benzamide (N-phenylbenzamide) gives a nonlinear curve (Fig. 3), indicating the degrease of the concentration of the unprotonated base in the region of acidity from -0.5 to -3.5 H_A (-0.5 to -5 H_A, respectively). This spectra region was used for calculating the pK_{BH}^+ values (Tab. 2) through the ionization ratio, from reconstituted UV spectra and coefficients of the first characteristic vectors using equation (6).

Table 2. pK_{BH}^+ calculated from the characteristic vector c_1.

	pK_{BH}^+ (eq.2)	m	pK_{BH}^+ (eq.3)	m'	pK_{BH}^+ (eq.4)	Φ	pK_{BH}^+ (eq.5)	m*
benzamide	−1.04 ±0.12 [a] (0.9623)[b]	0.53 ±0.04 [a]	−1.54 ±0.12 (0.9762)	0.91 ±0.05	−1.42 ±0.10 (0.9558)	0.50 ±0.04	−1.45 ±0.08 (0.9755)	0.52± 0.03
N-phenyl benzamide	−2.21 ±0.14 (0.9441)	0.52 ±0.04	−2.78 ±0.16 (0.9256)	0.93 ±0.04	−2.38 ±0.10 (0.9489)	0.58 ±0.04	−2.42 ±0.11 (0.9161)	0.44 ±0.04

a – standard error; b - square of correlation coefficient (r^2)

Conclusions

The Hammett's postulate (the slopes of the plots log *I* *vs.* *H* should be equal to 1) is valid only for H_A (amide's function). The pK_{BH}^+ values (using eq. 3,4,5) for benzamide are in good agreement with the literature data.[1,3,6] Because of the charge delocalization in the molecule, N-phenylbenza-

mide is weaker base than benzamide. Further, the calculated values for m' and m* are close to those characteristic for amides, indicating that the protonation site in the molecule is O-atom.

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