

PROTONATION ACIDITY CONSTANTS FOR SOME BENZAMIDES IN SULFURIC ACID SOLUTIONS

Goran Stojković,* Emil Popovski and Frosa Anastasova

*Institute of Chemistry, Faculty of Natural Sciences and Mathematics,
Sts. Cyril & Methodius University, P.O. Box 162, MK-1001 Skopje,
Republic of Macedonia*

*e-mail: goranst@junona.pmf.ukim.edu.mk

Abstract: The protonation of some *m*- and *p*-benzamide in sulfuric acid solutions was studied by UV spectroscopy in the 190–350 nm region. Principal component analysis was applied to separate the effect of protonation from the medium effect. The same spectral region was used for calculation of the ionization ratio from coefficients of the first principal component. The dissociation constants as well as the solvent parameters m^* and ϕ were calculated using Excess Acidity Method and Bunnett-Olsen Method. In order to estimate the effect of substitution on the pK_{BH^+} values of the compounds studied, a correlation with Hammett σ_m and σ_p constants was performed.

Keywords: benzamides, protonation, spectrophotometry, Hammett

1. INTRODUCTION

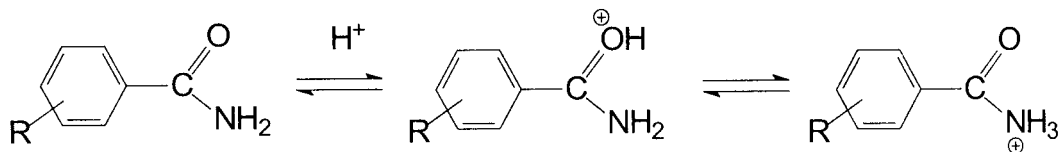
Knowledge of the acidity of weakly basic substrates is of central importance to the study of reaction mechanisms that take place in acidic media. Acidity constants are obtained by analysing the changes of some physical properties of the observed substrates, by varying the acid concentration. The three most commonly studied properties are the UV-VIS, 1H and ^{13}C NMR spectra [1-3], i.e. the observed changes that occur in the characteristics of the spectrum, going from free towards protonated base with increasing the acidity of the solutions.

However, for carbonyl compounds, such as amides, the situation is more complex since the spectra of one or both forms are usually subject to substantial medium effects. Namely, distilled water and 15 mol dm⁻³ H₂SO₄ are completely different media, so it is not surprising that spectral peaks for the same species in these two solvents can occur at rather different wavelengths or different chemical shifts. So far, various methods have been widely employed for compensation of the medium effect, e.g. principal component analysis (PCA) [4], target factor analysis (TFA) [5], characteristic vector analysis (CVA) [1,6] etc.

In this work the protonation of seven benzamides (Scheme 1) in sulphuric acid media was studied. Some of these compounds previously investigated [1, 2, 3, 7]

Thus, one could compare the presently obtained values with those already known and discuss the influence of the substituent's different position in the structure of the studied compounds on the protonation process.

The structures of the studied compounds are presented in the following scheme.



R = H, *m*-Me, *m*-Cl, *m*-NO₂, *p*-Me, *p*-Cl, *p*-NO₂

Scheme 1. Assumed reaction of protonation of benzamides.

2. EXPERIMENTAL

Benzamide (Fluka products), were used without further purification. Substituted benzamides were synthesized and purified according to standard procedures [8]. The purity of the all benzamides was checked by FT-IR spectrometry (Perkin Elmer System 2000 FT-IR). Stock solutions of the compounds were prepared in ethanol (Riedel-de Haën product). Reagent grade sulfuric acid (97% by weight, product of Alkaloid – Skopje) was used. The exact concentration of sulfuric acid was determined by titration against 0.1000 ± 0.005 mol dm⁻³ sodium hydroxide (Titrival, product of Alkaloid – Skopje).

The concentrations of the benzamides for the pK_{BH^+} determination were $2-5 \times 10^{-5}$ mol dm⁻³. The diluted solutions of sulfuric acid were with a concentration range from 0.0 to 15.0 mol dm⁻³, and the same were used as blank.

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, at room temperature (25 ± 1 °C).

To compensate the effect of the medium on the appearance of the spectra, PCA was employed (using procedure developed in Mathcad [9] environment) on preprocessed experimental data (all normalized to unit area under the curves).

3. RESULTS AND DISCUSSION

The reconstructed UV spectra of methyl- and chloro- substituted benzamide are very similar with the one of the previously studied benzamide [3]. The UV spectra of *p*-methylbenzamide in sulfuric acid solutions (Figure 1) exhibit four bands that outgoing from $\pi \rightarrow \pi^*$ transitions. The bands 1B_a , 1B_b , 1L_a and 1L_b have been assigned and interpreted using the free-electron model [10].

Because of the existing heavy overlap of 1B_a and 1B_b bands, it is very difficult to estimate their exact behavior during the medium acidity alteration. It is very probable that as the concentration of the mineral acid increases, the 1B_a band exhibits hypsochromic and hypochromic effect, i.e. it shifts towards shorter wavelengths and decreases in intensity, while in the 1B_b band hypochromic and bathochromic effects appear.

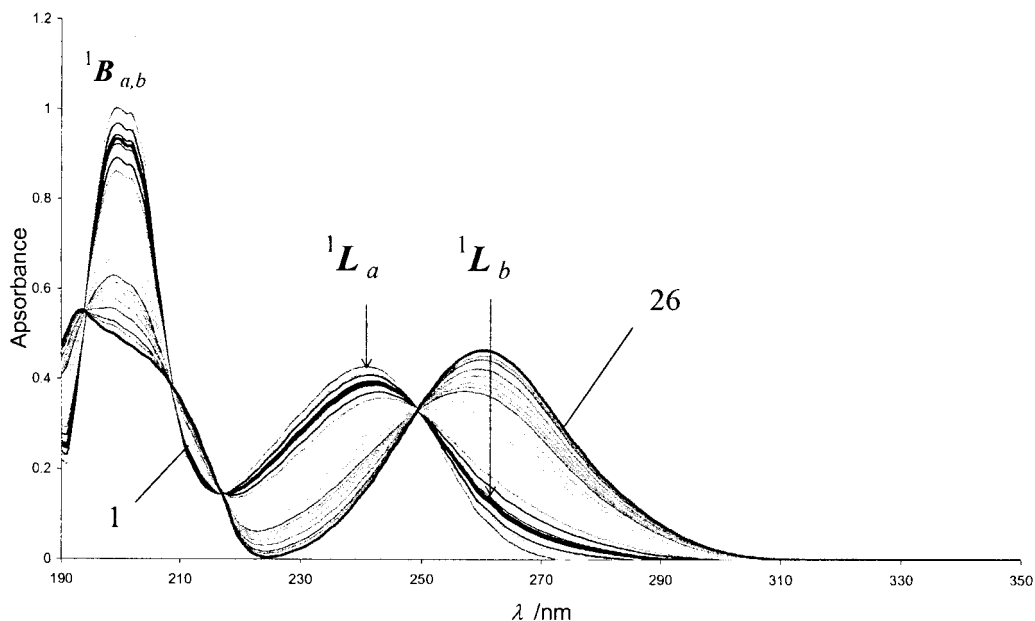


Fig. 1. Changes in the ultraviolet absorption spectra of *p*-methylbenzamide as a function of sulfuric acid concentration from 0.0 (curve 1) to 15.0 mol dm⁻³ (curve 26).

In the same time, the ¹L_a band shifts toward longer wavelengths (bathochromic effect). The absorption band ¹L_b appears as a shoulder at approximately 260 nm which can not be seen clearly, because it is submerged (hidden) under the high-intensity ¹L_a band.

The reconstructed spectra using the first principal components (PC) intersect at four isosbestic point. This gives additional support that, indeed, the first PC describes the behaviour of the system due to the protonation that occurs in acidic media.

Determination of pK_{BH+}

In order to determine the strength of the studied weak bases, the thermodynamic pK_{BH+} values were calculated using two different methods [11]: Excess Acidity Method (EAM) (eq. 1) and Bunnett and Olsen method (eq. 2):

$$(1) \quad \log I - \log \{c_{H^+}\} = m^* X + pK_{BH^+}$$

$$(2) \quad \log I + H_0 = \phi (H_0 + \log \{c_{H^+}\}) + pK_{BH^+}$$

where $\{c_{H^+}\} = c_{H^+} / \text{mol dm}^{-3}$, H_0 is Hamett's acidity function and X is excess acidity function. Values of $\log \{c_{H^+}\}$ and X are available for aqueous H₂SO₄ [12]. The data for H_0 are calculated using equations: $-H_0 = X + \log \{c_{H^+}\}$ [13].

The ionization ratios were determined directly from the coefficients of the first PC [1,3] i.e. weighting coefficients c_1 :

$$(3) \quad I = c_{BH^+}/c_B = (c_{1B} - c_1)/(c_1 - c_{1BH^+})$$

The coefficients of the first PC are plotted (Fig. 2) as a function of $c(\text{H}_2\text{SO}_4)$, for illustrative purposes.

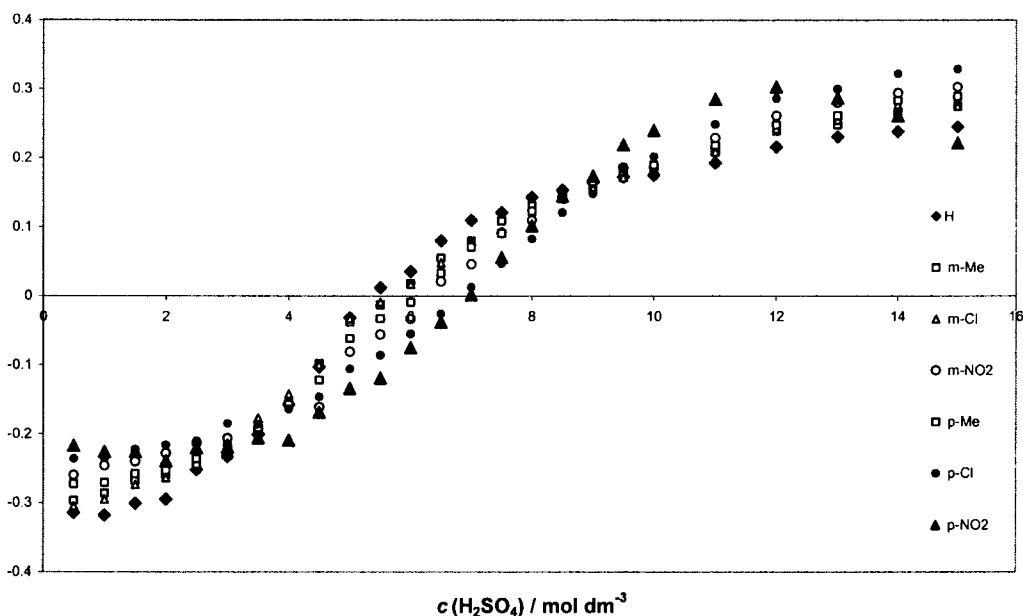


Fig. 2. Coefficients of the first principal components of seven benzamides as a function of sulfuric acid concentration from 0.5 to 15.0 mol dm⁻³.

Protonation reaction would give a sigmoidal curve, changing from a constant concentration of the unprotonated base to a constant concentration of the conjugated acid. A process such as described in Scheme 1 would likely produce two superimposed sigmoid curves, reaching a constant value at high acidity. However, the existence of only one step of the sigmoidal curve suggests that only one process in Scheme 1 occurs.

The values of the thermodynamic dissociation constants of the protonated benzamides, calculated from the reconstructed spectra, at 95 % confidence level, using coefficients of the first principal components, are given in Tab. 1.

Tab. 1. The values of the thermodynamic dissociation constant of the protonated benzamides, calculated from the reconstructed spectra in the region 190-350 nm, using the first weighting coefficients

substituent	Excess Acidity Method		Bunnett and Olsen	
	- pK _{BH+} (eq.1)	m*	- pK _{BH+} (eq.2)	ϕ
H	1.43 ± 0.07 ^a 0.9575 ^b (n=18)	0.36 ± 0.03 ^a	1.42 ± 0.08 0.9834 (n=16)	0.64 ± 0.03
m-Me	1.28 ± 0.02 0.9964 (n=14)	0.27 ± 0.01	1.24 ± 0.02 0.9995 (n=14)	0.75 ± 0.01
p-Me	1.24 ± 0.01 0.9982 (n=12)	0.25 ± 0.01	1.29 ± 0.03 0.9991 (n=14)	0.73 ± 0.01
m-Cl	1.79 ± 0.03 0.9938 (n=21)	0.38 ± 0.01	1.76 ± 0.03 0.9973 (n=23)	0.64 ± 0.01
p-Cl	1.51 ± 0.03 0.9914 (n=14)	0.31 ± 0.01	1.58 ± 0.05 0.9953 (n=18)	0.68 ± 0.02
m-NO ₂	2.00 ± 0.02 0.9977 (n=20)	0.41 ± 0.01	1.95 ± 0.02 0.9979 (n=21)	0.62 ± 0.01
p- NO ₂	2.43 ± 0.04 0.9934 (n=16)	0.61 ± 0.02	2.38 ± 0.05 0.9824 (n=16)	0.42 ± 0.02

a - standard error, b - correlation coefficient (r)

By comparison the calculated pK_{BH+} values using equations proposed by the Excess Acidity Method and Bunnett and Olsen method it could be concluded that they do not differ significantly.

The values for solvation parameter m* are close to those characteristic for amides [2,3], indicating that the most probable protonation site in the molecule is the oxygen atom. Furthermore, the obtained ϕ (≈1-m) values presented in Tab. 1 are positive, as expected for oxygen Brønsted bases.

The substituent effect on protonation process is expressed by plotting pK₀ -pK values against Hammett σ_m and σ_p constants (Fig. 3) Values of Hammett constants are provided from literature data [14].

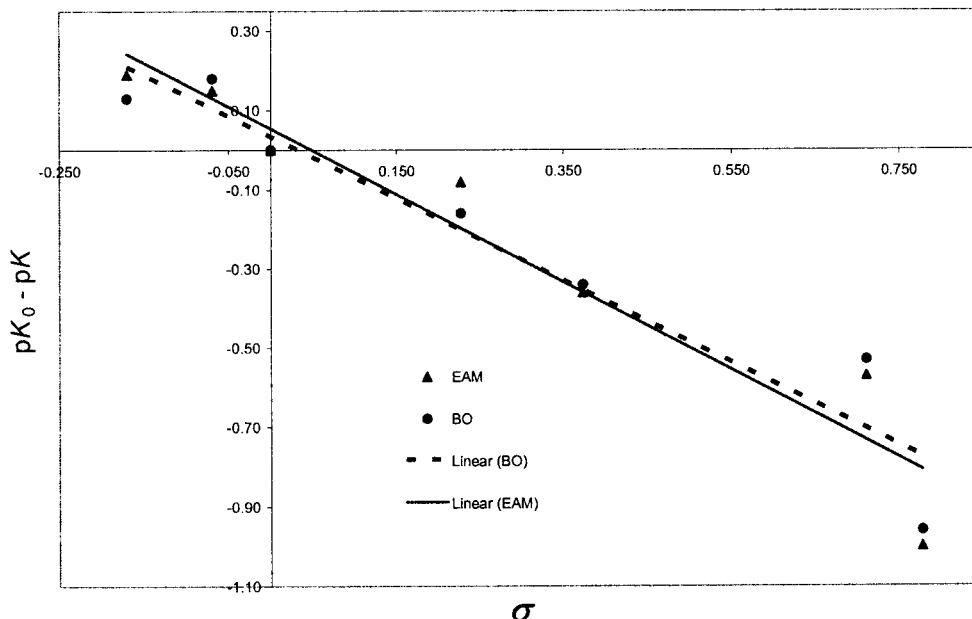


Fig. 3. Plot of $pK_0 - pK$ vs Hammett σ_m and σ_p constants.

The corresponding Hammett equation ($pK_0 - pK = \rho\sigma$) obtained in this case is:

$$pK_0 - pK = -1.03 \cdot \sigma \quad (\text{Excess Acidity Method})$$

with $r=0.9561$, $s=0.11$ and $n=7$

$$pK_0 - pK = -0.99 \cdot \sigma \quad (\text{Bunnett and Olsen method})$$

with $r=0.9904$, $s=0.10$ and $n=7$.

4. CONCLUSIONS

Principal Component Analysis is employed with intention to separate the protonation of benzamides from medium effects in the spectral region 190–350 nm. The same spectral region was used for calculation of the ionization ratio from coefficients of the first principal component.

The values of pK_{BH^+} for studied benzamides calculated using equations proposed the Excess Acidity Method and Bunnett and Olsen method do not differ significantly.

The obtained high values of the correlation coefficients using the Hammett equation with σ_m and σ_p constants proves that the pK_{BH^+} values of the studied compounds is the function on the chemical properties and position of the substituent in the benzamide molecule.

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