

Determination of the pKa of Benzophenones in Ethanol-Water

G.T. Castro¹, S.E. Blanco¹ and O.S. Giordano²

¹Química-Física, Facultad de Química, Bioquímica y Farmacia. Universidad Nacional de San Luis. Chacabuco y Pedernera, (5700) San Luis, Argentina

²Química Orgánica. Facultad de Química, Bioquímica y Farmacia. Universidad Nacional de San Luis. Chacabuco y Pedernera, (5700) San Luis, Argentina

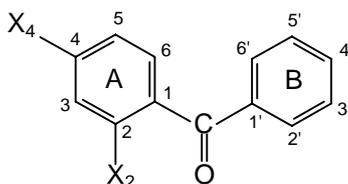
E-mail: sblanco@unsl.edu.ar

Abstract: The pKa of monohydroxylated benzophenones was determined by UV spectroscopy. The values obtained are coherent with the resonant forms and hydrogen bond intramolecular of the analyzed compounds.

Introduction

The pKa of a drug is one of the most important parameters to explain its physicochemical behavior and acid-base properties [1], to program assays of pharmaceutical preformulation [2], etc. In this work, the pKa values of monohydroxylated benzophenones (BP) were determined by UV-visible spectroscopy. These substances exhibit interesting adsorptive properties, they act as ligands in the complexation of metallic ions and, also, they have biochemical applications as antimicrobial agents and in industry as commercial sun blocks [3].

Experimental



The figure shows the basic structure of the analyzed aromatic ketones: **1**: 4(OH)-BP ($X_2=H$, $X_4=OH$); **2**: 2(OH)-BP ($X_2=OH$, $X_4=H$); **3**: 2(OH),4(CH₃O)-BP ($X_2=OH$, $X_4=CH_3O$). For pKa determination, a UV-vis spectroscopic procedure based on the Henderson-Hasselbalch [4] was used. The buffer solutions used were: a) HCl-KCl, pH 1.5; b) NaOH-KCl, pH 12.5; c) KH₂PO₄-Na₂HPO₄ 0.01M for a 7.2-8.0 pH interval; d) Na₂CO₃-NaHCO₃ 0.01M, pH 9.2-10.0. All buffer solutions were prepared with a 20% w/w ethanol-water mixture, keeping the ionic strength constant (0.05) with KCl.

Results and Discussion

The maximum absorption wavelengths record for the acid (λ_a) and ionized (λ_b) forms of the BP were: λ_a (**1**) 294.5nm, λ_b (**1**) 348nm; λ_a (**2**) 334nm, λ_b (**2**) 382nm; λ_a (**3**) 320nm, λ_b (**3**) 372nm. The pKa determined were the following: pKa (**1**)=7.83; pKa (**2**)=9.54 and pKa (**3**)=9.60. The carbonyl group of the benzophenones interacts with the adjacent aromatic rings through the σ and π bonds, favoring the π -electronic delocalization of the molecules. The participation of the C=O group in the conjugate molecular system is reflected in its bonding characteristics and in the influence it exerts on the acid-base properties of the hydroxyl groups. The increase of the pKa values in the order pKa (**1**) < pKa (**2**) < pKa (**3**) is coherent with the resonant forms and intramolecular hydrogen bonds exhibited by BPs **2** and **3**. The pKa of **1** is markedly lower than that of 4(OH)-chalcone, pKa=8.17 [5]. This indicates that the C=O α,β -unsaturated group of the chalcone, increase the π -electronic delocalization of the molecule, decreasing the acidity of the H atom the OH group at position 4.

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References and Notes

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