Asian Journal of Chemistry; Vol. 31, No. 4 (2019), 971-976

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21879

Intramolecular Excited-State Proton Transfer in Biologically Active Flavones: A Combined Experimental and Theoretical Study

SANJAY KUMAR, L. SAYA, H.C. TANDON and SHIKHA GULATI*

Department of Chemistry, Sri Venkateswara College (University of Delhi), Delhi-110021, India

*Corresponding author: E-mail: shikha2gulati@gmail.com

Received: 17 December 2018; *Accepted*: 28 January 2019; *Published online*: 27 February 2019; AJC-19314

The absorption and fluorescence characteristics of two biologically active flavone derivatives 6-hydroxy-7,3',4',5'-tetramethoxyflavone (6HTMF) and 7-hydroxy-6,3',4',5'-tetramethoxyflavone (7HTMF) were studied as a function of acidity (pH/H_0) of the solution. Dissociation constants were determined for ground and first excited singlet states and the results were compared with those obtained from Forster-Weller calculations. The acidity constants for these two compounds (6HTMF and 7HTMF) obtained from fluorimetric titrations are in poor agreement with those obtained from Forster-Weller data but are in good agreement with ground state pK_a values indicated the deactivation of excited state (S_1) before the prototropic equilibrium is complete. The broad band emission of both the flavones in acidic aqueous solution suggests their use as tuneable dye lasers. 6-Hydroxy-7,3',4',5'-tetramethoxyflavone undergoes adiabatic photo-dissociation in the singlet excited state indicating the formation of an exciplex or a photo-tautomer. The stability of photo-tautomer was confirmed by calculated value of enthalpy of formation using AM1 method.

Keywords: Flavones, Dissociation constants, Prototropic equilibrium, AM1 method, Phototautomer.

INTRODUCTION

Flavones are well-known for their efficient biological use in medicinal industry as highly potential anticancer, anti-inflammatory and antiallergic agents [1-5]. These properties are attributed to the structure of flavones which is based on their chemical behaviour. On going from ground state to excited state, there is a drastic change in these chemical properties. One such characteristic change on electronic excitation is in fluorescence intensity at different pH values. Solvent and pH dependent fluorescence spectroscopy has proved to be a valuable tool for studying primary photochemical processes, in particular, photo-dissociations and photo-protonations. The fluorescence based methods are also useful in understanding highly selective protein interactions and properties [6-8]. Since many transitions are accompanied by extensive reorganization of the molecular electron density, the acidity or basicity of such molecules may vary significantly in different electronic states. Therefore, the response of an otherwise neutral molecule to an incoming proton may strongly depend on the nature of the particular electronic state the acceptor molecule is in. Just as the absorbance of the acidic and basic forms of an acid-base system provides information concerning the extent of dissociation of the un-excited molecules, so does the fluorescence of the acidic and basic forms of excited molecules. Fluorescence, in comparison to absorbance, is thus a measure by which the change in acidity upon excitation can be detected. After Weber's study on fluorescence intensity variation with pH [9] and Forster's method to calculate pK_a in excited state [10], Weller used the method of fluorimetric titrations [11]. Acidity constant values can, therefore, be calculated using Forster-Weller method by taking fluorescence intensity as a function of pH or Hammett's acidity scale (H_0). An interesting phenomenon is phototautomerism. Following charge transfer excitation, a molecule is protonated at one site and deprotonated at another site to form a tautomer. This often results in unusually large Stokes shift in the fluorescence band.

In continuation of our earlier work on the photophysical properties of certain novel flavone compounds [12-15], we have investigated the effect of pH on absorption and fluorescence spectra of the compounds 6-hydroxy-7,3',4',5'-tetramethoxyflavone (6HTMF) and 7-hydroxy-6,3',4',5'-tetrame-