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Fluorescent photoproducts of phenothiazine derivatives: a possible application of oxygen sensing based on photodegradation

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Abstract – The phenothiazine derivatives trifluoperazine (TFP) and fluphenazine (FPZ) have been irradiated with UV light under anaerobic and aerobic conditions in order to study their fluorescent photoproducts. The group of phenothiazines with CF_3 in 2-position of the heterocycle (TFP and FPZ) develops high intensity fluorescent photoproducts peaked at 410 nm only in the presence of O_2. The excitation spectra of the fluorescent photoproducts and their LDI mass spectra suggest formation of phenothiazine sulfoxide species. The oxygen dependent response to irradiation suggests that TFP and FPZ are good candidates for oxygen sensing.

Phenothiazine derivatives have been the focus of several biological, physical-chemical, photophysical and photochemical studies due to their pharmaceutical properties and applications. The chemical structure of these drugs involves a tertiary amino group and heteroaromatic rings (Fig. 1). The chemical structure, nature of the solvent, pH, excitation energy and environmental conditions of these drugs seem to make difference in the photodegradation process and photoproduct formation [1]. Structural effects in proteins due to photolabeling reactions has been observed [2].

In this work, UV-visible absorption, LDI-TOF mass spectrometry, steady-state and time-resolved fluorescence were used to characterize photoproducts of irradiated phenothiazines. Phenothiazine solutions were irradiated with the Xenon excitation lamp of the steady-state fluorimeter at 310 nm. The power of the light was measured at the sample position (0,23 mW). Spectroscopic parameters of absorption, fluorescence and mass spectrometry of the intact phenothiazines and their photoproducts formed under increasing irradiation times were obtained and analyzed to correlate the data with their molecular structure.

TFP and FPZ presented similar fluorescent photoproducts with emission peak at 410 nm. Figure 2 shows the fluorescence emission under aerobic and anaerobic conditions. It demonstrates that the fluorescent photoproduct yield is much greater in presence of O_2. The fluorescence excitation spectrum (Fig. 3) presents peaks at 276 nm, 304 nm and 352 nm, characteristic of TFP and FPZ sulfoxide derivatives absorption spectra [3], suggesting that the fluorescent photoproducts are the sulfoxide derivatives. Measurements of time resolved fluorescence were also performed to obtain the fluorescence decay curves of irradiated samples. The lifetimes of the fluorescent photoproducts are 2,3 ns at pH 7.0 and 1,9 ns at pH 3.0. Briefly, TFP and FPZ presented fluorescent photoproducts that are created mainly in the presence of oxygen. Optical sensors have been developed as an alternative to electrodes for O_2 sensing. The O_2 dependence of photoproduct formation, the relatively high fluorescence quantum yield, and the emission maximum at 410 nm are sufficient reasons to suggest the use of phenotiazine photoproducts fluorescence as an O_2 indicator. The operating principle would be the photodegradation of phenothiazines, which produces an O_2 concentration-dependent fluorescence emission.

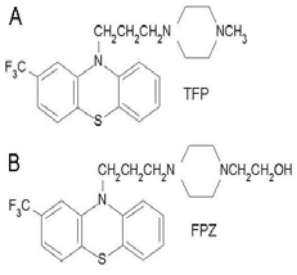

Figure 1: Molecular structure (**A**) Trifluoperazine (TFP) (**B**) Fluphenazine (FPZ).

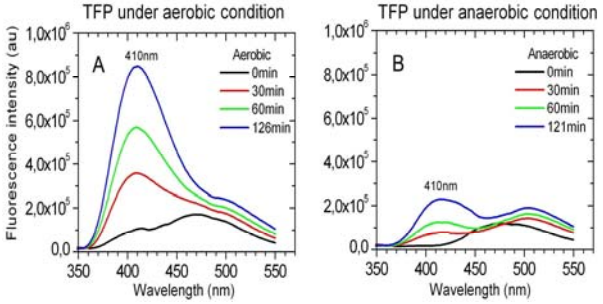

Figure 2: Fluorescence spectra of TFP (20 μM) in phosphate buffer (pH 7.4) for different irradiation times (at 310 nm) with air (**A**) and without air (**B**).

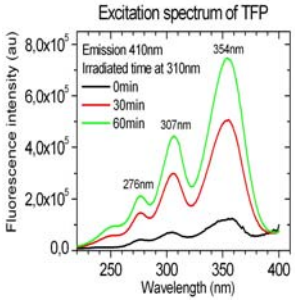

Figure 3: Excitation spectrum of TFP (20 μM) in buffer phosphate (pH 7.4)

References

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