NEW METHOD FOR THE DETERMINATION OF THE EXTINCTION COEFFICIENT OF THE PHOTOCOLORED FORM OF SPIROPYRANS

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The greatest difficulties in the study of the parameters of the phototransformations of spiropyrans involve the accurate measurement of the extinction coefficient (ε_B) of the photocolored form because of the complexities of an accurate determination of the concentration of photocolored molecules. Previously proposed methods [1-3] are not always applicable and do not make it possible to obtain values with an accuracy greater than 15%. The ability of the photocolored form of spiropyran B to bond with protons to form yellow saltlike structure C considerably more rapidly than the analogous reaction of the starting colorless form A ($K_1 \gg K_2$) is the basis of the method which we propose; this process occurs considerably more rapidly than the dark reaction ($K_1 \gg K_3$) [1-4]. If a neutral solution of a spiropyran is irradiated with UV light until a photosteady state is attained with an optical density of D^B_{st} and a drop of a solution of gaseous hydrogen chloride in the same solvent (the HCl : spiropyran molar ratio should be ~2 : 1) is added to it at the instant the illumination is stopped, the blue color of the solution instantaneously changes to the yellow color of form C ($\lambda_{max} \approx 420$ nm, optical density D^C_{st}), and the color then disappears rapidly as a result of the dark transformation C → A. Using the data that $K_1 \gg K_2$ and $K_1 \gg K_3$, one can assume that form B is converted entirely to form C. Then, $\varepsilon_B = \varepsilon_C D^B_{st}/D^C_{st}$. The ε_C value can be determined by shifting the A ⇌ C equilibrium completely to the right due to a substantial increase in the concentration of hydrogen ions by prolonged bubbling of gaseous HCl through the spiropyran solution. The D^B_{st} and D^C_{st} values were measured with an apparatus with perpendicular activating and probe beams and with a cuvette equipped with a stirrer by first establishing the D^B_{st} value and then resetting the monochromator at the wavelength of the light absorption maximum of form C, after which a drop of HCl solution was added and the D^C_{st} value was determined. The proposed method makes it possible to obtain reproducible ε_B values with a scatter which does not exceed 5%. The results we obtained for several spiropyrans [5] are presented in Table 1.

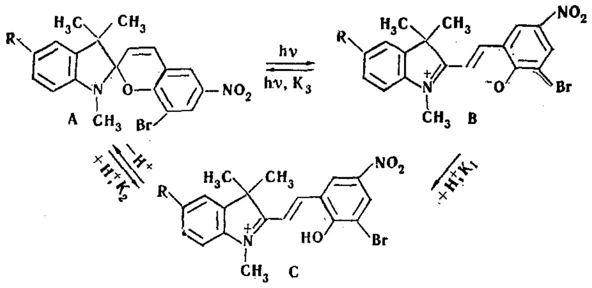

TABLE 1. Extinction Coefficients Calculated for Spiropyrans of General Formula A

R	λ^B_{max}, nm	$\varepsilon_B \cdot 10^{-4}$
H	610	3,13
F	595	5,80
Cl	616	3,51
Br	595	5,68

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