EXISTENCE OF A PHOTODECOLORIZATION REACTION OF THE COLORED FORM OF SPIROPYRANS UNDER THE INFLUENCE OF INITIATING UV IRRADIATION

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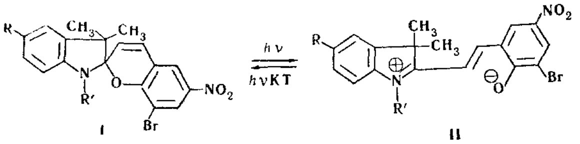
The kinetics of photochromic transformations of spiropyrans of the indole series with various substituents in the 1 and 5 positions were studied. The existence of a photodecolorization reaction under the influence of activating UV light was proved, and the effect of substituents on the quantum yields of the photocoloration and photodecolorization reactions was studied.

It is known that transformations illustrated by the following scheme are the basis for the photochromism of indoline spiropyrans:



I

II

A number of authors [1-3] have assumed the existence of photodecolorization under the influence of initiating UV light during the photochromic transformations of spiropyrans. This problem was studied in particularly great detail in [3], where the presence of the proposed reaction was confirmed on the basis of a kinetic investigation. However, in connection with the fact that Besnard used a number of essential assumptions (the change in the intensity of the activating irradiation with the length of the layer and during the photochemical reaction was not taken into account), it is difficult to evaluate the reliability of the evidence obtained.

We have studied the kinetics of the photochromic transformations of 1-(p-tolyl)-3,3,5-trimethyl-6'-nitro-8'-bromospiro(indoline-2,2'-[2H]chromene) in toluene at 10°C under the influence of UV radiation (λ_1 366 nm). For a photochromic system in which irreversible photodecomposition processes are absent, the rate of change of the optical density obeys the following equation [4]:

$$\frac{dD}{dt}=\frac{J_0 l(1-10^{-D'})}{VD'}[D'_o\Phi\varepsilon_B-D(\Phi\varepsilon'_A-\Phi'\varepsilon'_B)]-KD. \tag{1}$$

We determined several of the parameters of this equation [the rate constant of the dark reaction (K), the optical density and coefficient of extinction for λ_1 of the colorless solution (D'_0 and ε'_A), the coefficients of extinction of the colored form at wavelengths corresponding to the light absorption maximum for λ_2 = 625 nm and λ_1 (ε_B and ε'_B, respectively), the intensity of the activating radiation (J_0), and the length and volume of the cuvette (l and V)] by an independent path [5]. The experimental dependence of the optical density on time at wavelengths λ_2 [$D = f(t)$] was approximated by a function of the form $D = [at/(bt+1)] + [ct/(dt+1)]$, while the a, b, c, and d constants were determined from the condition of a minimum of the sum of the squares of the deviation of the experimental D values from the calculated values. The $dD/dt = f(t)$ curve was constructed from the a-d constants obtained. The experimentally obtained dependences of

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TABLE 1. Characteristics of the Spiropyrans (I)

R	R′	mp	Empirical formula	Found, %			Calc., %			Yield, %	$K \cdot 10^2$, $\sec^{-1}$	Φ	Φ′	λ_2	$\varepsilon'_a \cdot 10^{-4}$ **	$\varepsilon'_A \cdot 10^{-3}$ **	$\varepsilon'_B \cdot 10^{-4}$ **
				C	H	N	C	H	N								
H	CH_3	236,5—237*	—	—	—	—	—	—	—	—	0,574	0,11	0,040	610	3,13	3,21	3,39
CH_3	4-CH_3C_6H	186—187	$C_{26}H_{23}BrN_2O_3$	63,6	4,7	5,4	63,5	4,7	5,7	38,4	1,100	0,19	0,34	625	4,45	3,46	1,39
F	CH_3	258—259	$C_{19}H_{16}BrFN_2O_3$	54,9	3,9	6,7	54,4	3,8	6,7	40,7	1,12	0,27	0,052	595	5,80	7,75	1,63
H	C_6H_5	165—166*	—	—	—	—	—	—	—	—	1,34	0,29	0,83	600	4,10	3,33	0,78
Cl	CH_3	244—245	$C_{19}H_{16}BrClN_2O_3$	52,5	4,0	6,2	52,4	3,7	6,4	45,3	1,63	0,31	0,11	616	3,51	5,75	1,79
Br	CH_3	253—254	$C_{19}H_{16}Br_2N_2O_3$	47,6	3,6	5,9	47,5	3,3	5,8	36,5	2,18	0,32	0,22	595	5,68	8,31	2,37
F	4-FC_6H_4	193—194	$C_{24}H_{17}BrF_2N_2O_3$	58,6	3,6	5,5	56,6	3,5	5,6	43,3	3,40	0,33	0,58	612	6,23	2,51	2,15

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*These compounds were given to us by D. A. Drapkina, for which we thank her. The synthesis and constants of these compounds are described in [6, 8].

**λ_1 366 nm.

the optical density on time for λ_1 [$D' = f(t)$], as well as the $D = f(t)$ and $dD/dt = f(t)$ dependences provide a possibility for determining the quantum yields of the forward and reverse photoreactions (Φ and Φ′) when Eq. (1) is used. Using a Razdan-2 computer, we performed the described calculations for several series of experiments with different spiropyran concentrations and activating radiation intensities. The Φ and Φ′ values thus obtained were reproduced with an accuracy of ±15% and ±45%, respectively. An attempt to calculate the Φ quantum yield under the condition Φ′ = 0 leads to substantial deterioration of the mathematical description of the process and to inconstancy of the Φ value in different experiments. The results convincingly prove the existence of photodecolorization under the influence of UV radiation.

Using a similar method, we also studied the kinetics of photocoloration and photodecolorization of a number of spiropyrans with the general formula I. We demonstrated (Table 1) that the quantum yield for photocoloration varies symbatically with the rate constant of the dark decolorization. Thus changes in the structure of the spiropyrans that lead to slowing down of the rate of dark decolorization simultaneously decrease the quantum yields of photocoloration. Each of these two effects separately changes the magnitude of the optical density in the photosteady state in the opposite direction, and their simultaneous change partially compensates for one another. In the case of the quantum yields of the reverse photoreactions, one observes a sharp difference between the spiropyrans with methyl substituents attached to nitrogen, for which Φ′ < Φ, and phenyl substituents attached to nitrogen, for which Φ′ > Φ. It is possible that in this series of spiropyrans the starting colorless forms have a monotypic orientation of the excited electronic levels; at the same time, the orientation of the electronic levels of the colored forms is substantially different, and the presence of different substituents in the indoline portion of the molecule can, in principle, lead to more profound changes in the relative orientation of these levels.

EXPERIMENTAL

The spiropyrans were synthesized by the method described in [6]. The properties of the compounds obtained are presented in Table 1.

Kinetic Apparatus. The curves of the change in the optical density of the spiropyran solutions during photocoloration and during dark decolorization were measured by means of a kinetic apparatus with perpendicularly situated probe and activating beams and fitted with rectangular cuvettes with a stirrer. The photometric accuracy of the apparatus was no less than 99%.

Activating Radiation. The monochromaticity of the UV radiation beam with a wavelength of 366 nm was ensured by a combination of UFS-6 and BS-7 glass filters. A PRK-4 mercury lamp was used as the source. The quantum intensity of the radiation that impinged on the reaction cuvette, which was determined by means of a ferrioxalate actinometer, was 9.77 10^{-9} einstein/sec.

Solvent. Toluene purified by the method in [7] was used as the solvent. The concentrations of the spiropyran solutions were 10^{-6} to 10^{-4} M; the optical density in the photosteady state did not exceed 1.0.

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