Oxidation of α-hydroxypyridine. To a solution of 2.6 mM of substance in 10 ml of water acidified with a drop of conc $H_2SO_4$ was added 0.02 mole of 79% hydrogen peroxide and a solution of 0.36 mM of $FeSO_4 \cdot 7H_2O$ in 2 ml of water. The mixture, which had become dark, was shaken in a sealed vessel for about 1 hr, after which it had become lighter, and then the water was evaporated off in vacuum, and the residue was sublimed. After resublimation in vacuum, mp of the $C_2H_2O_4$ 194° C.

The $^{18}O$ label was introduced into the water, the hydrogen peroxide, or the α-hydroxypyridine. The latter was prepared by the diazotization of α-aminopyridine with subsequent decomposition of the diazonium salt in $H_2{}^{18}O$. α-Hydroxypyridine with mp 105–106° C was obtained. The isotopic analysis of the α-hydroxypyridine, oxalic acid, $H_2{}^{18}O$, and $H_2{}^{18}O_2$ was carried out by known methods [5]. The accuracy of the analysis, including the errors in isolating the samples, was 5%. The isotopic results obtained are given as atomic excess percentages over the natural content of the isotope.

## REFERENCES

1. E. J. Behrman and R. J. Stamer, J. Biol. Chem., 228, 923, 1957.
2. A. L. Hunt, D. E. Hughes, and J. M. Lowenstein, Biochem. J., 69, 170, 1958.
3. L. Ingraham, Biochemical Mechanisms [Russian translation], Moscow, 103, 1964.
4. M. Anbar, J. Am. Chem., Soc., 83, 2031, 1961.
5. D. Rittenberg and L. Ponticorvo, Intern. J. Appl. Radiat. and Isotopes, 1, 208, 1950.

5 April 1967

Pisarzhevskii Institute of
Physical Chemistry AS
UkrSSR

---

LETTERS TO THE EDITOR

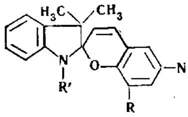
## KINETIC CONFIRMATION OF THE PRESENCE OF ISOMERS OF THE COLORED FORM OF 2H-BENZOPYRAN-2-SPIRO-2'-INDOLINES

M. A. Gal'bershtam and N. A. Donskaya

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, p. 757, 1969

UDC 547.754'814:541.127'651

It has been reported [1] that the kinetics of the dark decoloration of the photochromic spiropyrans is described by a first-order equation. We have studied the kinetics of the dark decoloration of the spiropyrans I–III in 95% ethanol at 20° C by the method of Berman [1] et al.



I R = H, R' = $CH_3$; mp 179–180,5°; [2] $\lambda_{max}$ 540 nm
II R = $OCH_3$, R' = $CH_3$; mp 152,5–153,5°; [1] $\lambda_{max}$ 560 nm
III R = Br, R' = $C_6H_5$; mp 165,5–166° [3] $\lambda_{max}$ 580 nm

It was found that the dependence of the logarithm of the optical density on the time deviates considerably from linearity in the initial section but is linear in the final section. By treating the curves obtained according to Brown and Fletcher's method [5], we have established that the process studied can be described by two parallel first-order reactions of dark decoloration. For the spiropyran I, $K_1 = (3.8 \pm 0.3) \cdot 10^{-3}$ sec$^{-1}$, $K_2 = (1.80 \pm 0.05) \cdot 10^{-4}$ sec$^{-1}$; for II, $K_1 = (6.1 \pm 0.2) \cdot 10^{-3}$ sec$^{-1}$, $K_2 = (1.4 \pm 0.2) \cdot 10^{-3}$ sec$^{-1}$; and for III, $K_1 = (1.5 \pm 0.5) \cdot 10^{-2}$ sec$^{-1}$, $K_2 = (2.6 \pm 0.2) \cdot 10^{-3}$ sec$^{-1}$.

Apparently, in the irradiation of solutions of the spiropyrans with UV light at room temperature, just as is the case at low temperatures [5–7], a mixture of at least two isomers with a colored merocyanin structure is formed which take part in the dark decoloration reaction at different rates.

### REFERENCES

1. E. Berman, R. E. Fox, and F. D. Thomson, J. Am. Chem. Soc., **81**, 5605, 1959.
2. C. F. Koelsch and W. R. Workman, J. Am. Chem. Soc., **74**, 6288, 1952.
3. D. A. Drankina, V. G. Brudz, V. A. Inshakova, and I. P. Plitina, Methods of Preparing Chemical Reagents and Materials [in Russian], **15**, p. 154, 1967.
4. H. C. Brown and K. S. Fletcher, J. Am. Chem. Soc., **71**, 1845, 1949.
5. J. Hirshberg and E. Fisher, J. Chem. Soc., 297, 1954.
6. P. Douzou, Compt. rend., **256**, 1769, 1963.
7. R. Heligman-Rim, J. Hirshberg, and E. Fisher, J. Phys. Chem., 66, 2465, 2470, 1962.

2 April 1968

All-Union Scientific-Research Institute of Organic Intermediates and Dyes, Moscow