EFFECT OF SUBSTITUENTS IN THE 5 AND 8' POSITIONS ON THE RATE OF DARK DECOLORIZATION OF PHOTOCOLORED SOLUTIONS OF 1,3,3-TRIMETHYLSPIRO[INDOLINE-2,2'-[2H-1]BENZOPYRANS]

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UDC 547.752.754'814.5:541.127'651

It is statistically reliably shown that the kinetics of the dark decolorization of photocolored solutions of indoline spiropyrans in toluene at 10°C is satisfactorily described by a first-order equation. The rate constants for the dark decolorization of 35 indoline spiropyrans with various substituents in the 5 and 8' positions were measured. Treatment of the experimental results by multiparameter correlation methods with allowance for the specific steric effect of substituents in the 8' position did not lead to a satisfactory correlation dependence.

Despite the considerable number of studies devoted to the investigation of the photochromism of spiropyrans, the problem of the quantitative principles that link the photochromic properties of spiropyrans with their structure has not received fully adequate study. Berman and co-workers [1] in 1959 concluded that the effect of substituents in the pyran portion of 1,3,3-trimethylspiro[indoline-2,2'-[2H-1]benzopyrans] on the rate constant of the dark decolorization of photocolored solutions of them in alcohol at 6° correlates well with the Hammett equation. However, in [2] it is noted that similar quantitative principles do not hold in a number of benzothiazoline spiropyrans, although Vanderwyer and co-workers were able to note a purely qualitative link between the electronic effect of substituents and the rates of dark-decolorization reactions.

Continuing our investigation of the principles that link the structure of indoline spiropyrans with their photochromic properties [3, 4], we studied the kinetics of the dark-decolorization reactions of photocolored solutions in toluene of 1,3,3-trimethylspiro[indoline-2,2'-[2H-1]benzopyrans] that contain various substituents in the 5 and 8' positions.* For these investigations we selected 35 spiropyrans, the synthesis of the majority of which has been described in the literature (Table 1). Some of the spiropyrans (Table 2) were obtained for the first time via the standard method – condensation of 5-substituted 1,3,3-trimethyl-2-methyleneindolines with 3,5-disubstituted salicylaldehydes [11].

The literature contains data that indicate both the compliance of the investigated reaction with first-order kinetics [1, 2, 4] and the presence of deviations from this regularity [3, 12, 13]. In this connection, we made a detailed analysis of the kinetic curves obtained for solutions of spiropyrans in toluene at 10°. It was found that the change in the optical density of the photocolored solution satisfactorily follows a first-order kinetic equation, and the values of the confidence intervals for the significance level $p = 0.05$ in the determination of the rate constant of the dark reaction by the method of long intervals [14] did not exceed 10% of the measured values. Repetition of the kinetic experiments also demonstrated good reproducibility of the constants. We compared the reproducibility of the results on passing from point to point within the limits of one kinetic curve with the reproducibility of the results obtained in different kinetic experiments. The calculations were made from the following formulas [15]:

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* See [5] for the preliminary communication.

All-Union Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 653-658, May, 1973. Original article submitted January 6, 1972.

TABLE 1. List of Spiropyrans of Structure A Described in the Literature and Used in This Research

Compound	R	R′	Literature	Compound	R	R′	Literature
I	H	OCH_3	1	XIV	F	$COOC_2H_5$	7
II	H	CH_3	6	XV	Cl	OCH_3	8
III	H	H	1	XVI	Cl	H	9
IV	H	Br	1	XVII	Cl	Br	4
V	H	$COOC_2H_5$	7	XVIIII	Cl	$COOCH_3$	7
VI	H	$CH_2CH{=}CH_2$	1	XIX	Cl	$COOC_2H_5$	7
VII	CH_3	OCH_3	6	XX	Br	Br	4
VIII	CH_3	H	6	XXI	Br	$COOCH_3$	7
IX	CH_3	$COOCH_3$	7	XXII	Br	$COOC_2H_5$	7
X	CH_3	$COOC_2H_5$	7	XXIII	NO_2	OCH_3	5
XI	F	OCH_3	6	XXIV	NO_2	H	10
XII	F	Br	4	XXV	NO_2	$COOCH_3$	7
XIII	F	$COOCH_3$	7	XXVI	NO_2	NO_2	5

$$\bar{k}_j=\frac{1}{m}\sum_{i=1}^{m}k_{ij};\ s_j^2=\frac{1}{m-1}\sum_{i=1}^{m}(k_{ij}-\bar{k}_j)^2;\ s_0^2=\frac{1}{L}\sum_{i=1}^{L}s_j^2;$$

$$\bar{\bar{k}}=\frac{1}{L}\sum_{j=1}^{L}\bar{k}_j;\ s_L^2=\frac{m}{L-1}\sum_{j=1}^{L}(\bar{k}_j-\bar{\bar{k}})^2,$$

where m is the number of points on the individual kinetic curve, L is the number of kinetic curves measured for the same spiropyran, k_{ij} is the rate constant calculated for the i-th point of the j-th kinetic curve, $\bar{k}_j$ is the arithmetic mean rate constant for the j-th kinetic curve, $\bar{\bar{k}}$ is the average value of the rate constant for the spiropyran calculated from the total set of experimental data, s_j^2 is the dispersion that characterizes the scatter in the k values within the limits of the j-th kinetic curve, s_0^2 is the dispersion that characterizes the scatter on passing from point to point within the limits of one curve for the entire system as a whole, and s_L^2 is the dispersion that characterizes the scatter on passing from curve to curve.

We used the Fischer criterion – $s_L^2/s_0^2 \geq F$ – to compare the scatter associated with transition from point to point of one kinetic curve with the scatter caused by transition from curve to curve. The results for a confidence probability of 95% are presented in Table 3. It follows from the data that inequality $s_L^2/s_0^2 > F$ is valid in the majority of cases. This means that the scatter in the experimental data caused by passing from curve to curve is more substantial than that in passing from point to point within the limits of one curve. Thus the $\bar{k}_j$ values can be considered to be random and one can determine $\bar{\bar{k}}$ and the confidence interval from the formula

$$k=\bar{k}\pm\frac{t_\alpha\sigma}{\sqrt{L}},$$

where t_α is the Student criterion determined for $f = L-1$ degrees of freedom, and σ is the mean-square deviation of the $\bar{k}_j$ values.

In the case of spiropyran XXVIII, we studied the effect of the degree of purity of spiropyran and the duration of storage of the prepared solutions in the dark and in scattered light and also the effect of repeated

TABLE 2. 5-R-8'-R'-1,3,3-Trimethyl-6'-nitrospiro[indoline-2,2'-[2H-1]benzopyrans]

Compound	R	R′	mp, °C	Empirical formula	Found, %			Calculated, %		
					C	H	N	C	H	N
XXVII	H	$COOCH_3$	174—175	$C_{21}H_{20}N_2O_5$	66,6	5,2	7,5	66,3	5,3	7,4
XXVIII	CH_3	CH_3	166,5—167	$C_{21}H_{22}N_2O_3$	72,1	6,4	8,1	72,0	6,3	8,0
XXIX	F	CH_3	115—116	$C_{20}H_{19}FN_2O_3$	67,5	5,4	8,0	67,8	5,4	7,9
XXX	Cl	CH_3	149—149,5	$C_{20}H_{19}ClN_2O_3$	64,7	5,1	7,6	64,8	5,2	7,6
XXXI	Cl	Cl	258	$C_{19}H_{16}Cl_2N_2O_3$	58,3	4,3	7,0	58,4	4,1	7,2
XXXII	I	H	180,5—181	$C_{19}H_{17}IN_2O_3$	51,2	3,7	6,1	50,9	3,8	6,2
XXXIII	$COOCH_3$	OCH_3	200,5—201	$C_{22}H_{22}N_2O_6$	64,6	5,6	7,1	64,4	5,4	6,8
XXXIV	$COOCH_3$	H	178—178,5	$C_{21}H_{20}N_2O_5$	66,4	5,3	7,1	66,3	5,3	7,4
XXXV	$COOCH_3$	NO_2	251—252	$C_{21}H_{19}N_3O_7$	59,3	4,4	9,7	59,3	4,5	9,9

TABLE 3. Analysis of the Reproducibility of the Experimental Data

Compound	$k_j \cdot 10^2$, sec^{-1}	$s_j \cdot 10^2$, sec^{-1}	s_L^2/s_0^2	f_1*	f_2†	F	Observance of the condition $s_L^2/s_0^2 > F$
IV	0,589 0,538 0,728 0,611 0,556	0,0887 0,0571 0,1290 0,0680 0,0543	18,99	4	115	2,45	+
XII	1,32 1,01 1,09 1,14 1,07	0,193 0,160 0,134 0,201 0,194	10,94	4	115	2,45	+
XVII	1,58 1,64 1,58 1,75	0,399 0,394 0,384 0,198	1,24	3	92	2,70	−
XX	2,41 2,39 2,15 2,02 1,92	0,258 0,643 0,354 0,629 0,308	5,19	4	115	2,45	+

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*f_1 = L − 1 is the number of degrees of freedom for dispersion s_L^2.

†f_2 = (m − 1) L is the number of degrees of freedom for dispersion s_0^2.

cycles of photocolorization and subsequent dark decolorization on the reproducibility of the rate constant of dark decolorization. The results are presented in Table 4. As seen from the data, neither a difference in the degree of purity of the starting spiropyran nor prolonged storage in the dark or in scattered light substantially affects the rate constant. However, the rate constant of the dark reaction increases appreciably after irradiation of the solution with UV light during a repeated colorization–decolorization cycle; this is apparently associated with the catalytic effect of specific impurities formed as a result of photodecomposition processes. Considering these facts, we used brief illumination of the solution with a low-intensity UV light source to form the photocolored solutions and took a fresh portion of solution for each measurement. The rate constants of the dark reactions that we obtained for 35 studied spiropyrans are presented in Table 5 along with the confidence intervals. As seen from Table 5, the nature of the substituents may substantially affect the magnitude of the constants.

We attempted to describe the relationship between the structure of the investigated spiropyrans and the rate constants for their dark reactions by a correlation equation of the form [16]

$$\lg k = \lg k_0 + \rho_1 \sigma_1 + \rho_2 \sigma_2.$$

TABLE 4. Effect of Various Factors on the Reproducibility of the Rate Constant of the Dark Reaction of Spiropyran XXVIII

mp of the sample, °C	$c \cdot 10^5$, M	Experimental conditions	$k \cdot 10^2$, sec^{-1}
164—165,7	2,84	Spiropyran purified by one recrystallization from acetone–water	1,15
165—166	4,83	Spiropyran purified by two recrystallizations from acetone–water	1,10
166,5—167	5,68	Spiropyran purified by repeated recrystallizations from it has a constant melting point	1,14
165—166	4,83	Solution held in scattered light for 1 month	1,08
166,5—167	5,68	Solution held in the dark for 1 month	1,10
166,5—167	5,68	Successive cycles (from 1 to 8) of photocolorization and dark decolorization	0,99; 1,16; 1,21; 1,28; 1,43; 1,49; 1,60; 1,71

TABLE 5. Rate Constants and Confidence Intervals of the Dark Decolorization of Spiropyrans in Toluene at 10°

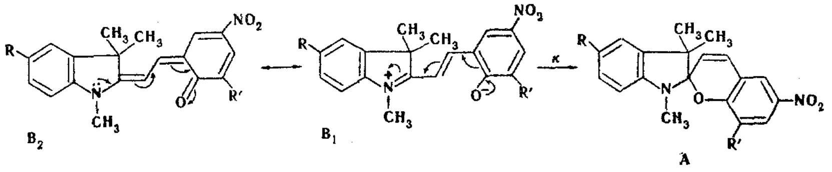
Compound	$k \cdot 10^2$, sec^{-1}	Compound	$k \cdot 10^2$, sec^{-1}
I	0,704±0,064	XIX	2,32±0,18
II	0,554±0,092	XX	2,18±0,27
III	1,680±0,240	XXI	2,07±0,57
IV	0,604±0,093	XXII	2,69±1,17
V	0,670±0,047	XXIII	14,40±1,73
VI	0,832±0,051	XXIV	14,40±1,77
VII	2,88±1,45	XXV	3,71±0,53
VIII	2,14±0,171	XXVI	1,78±0,14
IX	0,256±0,019	XXVII	0,701±0,038
X	0,396±0,101	XXVIII	0,99±0,026
XI	1,02±0,094	XXIX	0,599±0,098
XII	1,12±0,05	XXX	0,618±0,056
XIII	0,901±0,061	XXXI	2,51±0,15
XIV	1,56±0,23	XXXII	1,36±0,19
XV	1,55±0,097	XXXIII	3,72±0,290
XVI	1,50±0,102	XXXIV	1,28±0,047
XVII	1,64±0,130	XXXV	0,18±0,03
XVIII	1,95±0,37		

The ρ_1 and ρ_2 constants in this equation reflect the electronic effects of substituents in the 5 and 8' positions on the reaction centers of the spiropyran molecule. The σ_n values were used as the substituent σ constants. The rate constants of the decolorization of spiropyrans IV–VI and VIII–XXVII were used for the calculation. The following correlation-equation parameters were obtained by means of a Razdan-2 computer: $\log k_0 = -1.850$, and $\rho_1 = 1.00$, and $\rho_2 = -0.56$; multiple correlation coefficient $R = 0.85$, and standard deviation $S = 0.22$. Allowance for the specific steric effect of substituents in the 8' position by the method in [17] and introduction of cross term $\rho_{12}\sigma_1\sigma_2$ into the equation did not substantially improve the correlation. The use of σ^+ and σ^- values as the constants of the substituents in the 5 and 8' positions, respectively, also did not improve the correlation.

We also verified the presence of a partial correlation between the rate constants and the substituent σ constants in series of spiropyrans in which only one substituent was changed. The computed results are presented in Table 6. In this table, the spiropyrans are grouped in such a way that the substituent in the 8' position is changed in series 1–5, while the substituent in the 5 position is changed in series 6–11. As seen from the data, a satisfactory correlation is observed in only four cases out of 11. Thus neither calculation by the two-parameter correlation method nor determination of the correlation dependences in series with one changed substituent makes it possible to conclude that there is a satisfactory correlation between the substituent constants and the rate constants of the dark-decolorization reactions of photocolored solutions of the spiropyrans under the selected conditions. We note only that there is a tendency for electron-acceptor substituents in the 5 position to accelerate and for electron-donor substituents to retard the rate of dark decolorization. Substituents in the 8' position have the opposite effect. Our data are in agreement with the results obtained by Vanderwyer and co-workers [2] and are in conformity with concepts according to which the rate of dark decolorization is higher, the greater the magnitude of the charges on the reaction centers: positive on the carbon atom in the 2 position and negative on the oxygen atom linked to the aromatic ring.

TABLE 6. Correlation in Series with One Changed Substituent

Series	Compounds	r	$\lg k_0$	ρ
1	I, II, III, IV, V, XXVII	0,08	−2,11	−0,05
2	VII, VIII, IX, X, XXVIII	0,91	−1,93	−1,32
3	XI, XII, XIII, XIV, XXIX	0,57	−2,03	0,27
4	XV, XVI, XVII, XVIII, XIX, XXX, XXXI	0,23	−1,98	0,27
5	XXIII, XXIV, XXV, XXVI	0,97	−0,99	−0,94
6	I, VII, XI, XV, XXIII, XXXIII	0,77	−1,87	1,06
7	II, XXVIII, XXIX, XXX	0,76	−2,13	−0,73
8	III, VIII, XVI, XXIV, XXXII, XXXIV	0,62	−1,84	0,75
9	IV, XII, XVII, XX	0,96	−2,18	2,02
10	V, X, XIV, XIX, XXII	0,97	−2,06	2,05
11	IX, XIII, XVIII, XXI, XXV, XXVII	0,88	−2,18	1,22



The absence of a correlation may be associated with the fact that the effect of substituents is transmitted not only to the closest but apparently also to the more far-removed reaction center and also with the greater complexity of those elementary steps that determine the overall rate of the dark-decolorization process.

EXPERIMENTAL

To synthesize the spiropyrans, we used 5-methyl-, 5-fluoro-, and 5-chloro-1,3,3-trimethyl-2-methyleneindolines [6] and also the previously undescribed 5-iodo- and 5-carbomethoxy-1,3,3-trimethyl-2-methyleneindolines. The 5-iodo-substituted compound was obtained via the Fischer reaction from p-iodophenylhydrazine [18] and methyl isopropyl ketone, with subsequent methylation of the resulting 2,3,3-trimethyl-5-iodoindolenine by the action of methyl iodide and treatment of the methiodide with alkali solution. 5-Carbomethoxy-1,3,3-trimethyl-2-methyleneindoline was similarly obtained from p-carbomethoxyphenylhydrazine [19]. Condensation of the indicated methyleneindolines with 3-methyl-5-nitro- [6], 3-methoxy-5-nitro- [20], 3-chloro-5-nitro- [21], 5-nitro- [22], and 3,5-dinitrosalicylaldehydes [23] gave the corresponding spiropyrans.

The kinetics of the dark decolorization were studied spectrophotometrically [1] at 10 ± 0.1°. Absolute toluene, purified by the method in [24], was used as the solvent.

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