8. M. M. Bursey and M. K. Hoffman, J. Am. Chem. Soc., 91, 5023 (1969).
9. M. L. Gross and F. W. McLafferty, Chem. Commun., 254 (1968).
10. G. I. Zhungietu, V. A. Budylin, and A. N. Kost, Preparative Chemistry of Indole [in Russian], Shtiintsa, Kishinev (1975).
11. C. M. Atkinson, C. E. Simpson, and A. Taylor, J. Chem. Soc., 167 (1954).
12. B. E. Shaw and D. W. Woolley, J. Am. Chem. Soc., 75, 1877 (1953).

EFFECT OF ARYL SUBSTITUENTS ON THE RATE OF DARK DECOLORIZATION OF PHOTOCHROMIC SPIROCHROMENES OF THE INDOLINE SERIES

M. A. Gal'bershtam, N. M. Przhiyalgovskaya,
N. P. Samoilova, E. V. Braude,
I. B. Lazarenko, and N. N. Suvorov

UDC 541.145:547.752'814.1.07:543.422.6

The introduction of aryl substituents in the 3' and 7 positions of the indoline spirochromene molecule gives rise to a certain amount of slowing down of dark decolorization in toluene and dioxane; similar changes in the 5', 6, and 8 positions do not change the rate appreciably.

It is necessary to know the principles that link the structures of compounds with their photochromic properties for the directed creation of photochromic materials. These principles are presently being studied intensively in the case of a number of indoline spirochromenes, the most promising class of photochromic substances.

We have previously established that the introduction of aryl substituents in the 5' and 6-8 positions of the spirochromene molecule leads to a bathochromic shift of the absorption band of the photomerocyanine to the visible region [1-3], whereas the introduction of aryl substituents in place of methyl substituents in the 3' position does not give rise to substantial spectral changes [4, 5]. It seemed of interest to ascertain how the indicated structural changes would affect such an important characteristic of the photochromic behavior of the spirochromene as the rate constant for dark decolorization. In addition to a direct evaluation of the lifetime of the photocolored form, a study of the kinetics of the dark reaction also makes it possible to evaluate the change in the light sensitivity of the photochromic system [6] and thus to obtain an idea regarding the complex change in the spectral and kinetic parameters of the photochromic material as the structure of the spirochromene changes.

With this in mind, we measured the rate constants and activation parameters of the dark decolorization of photocolored solutions of 15 indoline spirochromenes containing a phenyl or p-methoxyphenyl substituent in various positions. In most of the investigated cases we observed good compliance of the investigated reaction with a first-order kinetic equation: The scatter in the rate constants for individual points of the kinetic curve did not exceed 10% up to practically total completion of the decolorization reaction. Dioxane and toluene, which are usually employed for spectral-kinetic studies of spirochromenes, were used as the solvents.

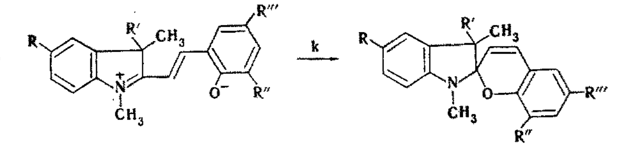
The results are presented in Table 1. The rate constants that we determined for spirochromenes I and XII agreed satisfactorily with the literature data.

A comparison of the rate constants and the activation parameters for spirochromenes I and II and III and IV makes it possible to establish that the introduction of a phenyl substituent in the 6 and 8 positions of the spirochromene molecule does not give rise to appreciable changes in the kinetic behavior of the photochromic

---

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. D. I. Mendeleev Moscow Chemical-Engineering Institute, Moscow 125047. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 79-81, January, 1977. Original article submitted October 24, 1975; revision submitted May 4, 1976.

TABLE 1. Kinetic Parameters of the Dark Decolorization of Spirochromenes



Compound	R	R′	R″	R‴	Solvent	k, sec$^{-1}\cdot 10^2$, at a temp. of, °C				Activation parameters	
						10[a] or 12[b]	20	30	40	$\Delta H^{\neq}$, kcal/mole	$\Delta S^{\neq}$, cal·mole^{-1}·deg^{-1}
I	H	CH_3	H	NO_2	Toluene	1,80[c]	3,09[d]	8,24	18,0	13,2	−20,0
					Dioxane	1,10	2,97[e]	9,67	33,8	20,7	5,5
II	H	CH_3	C_6H_5	NO_2	Toluene	1,53	3,17	7,15	16,1	13,2	−20,2
					Dioxane	1,17	3,73	10,5	22,1	17,7	−4,8
III	H	CH_3	NO_2	H	Toluene	2,33	3,89	7.63	24,5	12,9	−20,8
					Dioxane	1,64	3,49	8,70	14,9	13,4	−19,2
IV	H	CH_3	NO_2	C_6H_5	Toluene	2,15	4,14	7,51	20,5	12,3	−23.0
					Dioxane	2.36	4,58	12,9	26,8	14,9	−13.4
V	H	C_6H_5	H	NO_2	Toluene	0,49	1,00	2,79	7,18	15,2	−15.2
					Dioxane	0,82	1,89	3,46	7,38	12,7	−22,9
VI	H	C_6H_5	OCH_3	NO_2	Toluene	0,33	1,19	3,71	11,6	20,1	1,2
					Dioxane	0,34	0,75	2,80	5,48	17,4	−8,4
VII	H	C_6H_5	Br	NO_2	Toluene	0,71	1,83	4,96	13,0	16,4	−10,2
					Dioxane	0,67	1,35	4,62	9,31	16,4	−10.6
VIII	H	4-CH_3O—C_6H_4	H	NO_2	Toluene	0,75	2,18	5,45	16,3	17,2	−7,4
					Dioxane	0.99	1,70	6,43	12,7	16,2	−10.7
IX	H	4-CH_3O—C_6H_4	OCH_3	NO_2	Toluene	0,38	1,23	3,96	12,2	19,7	−0,2
					Dioxane	0,37	0,69	2,01	6,12	17,1	−9,5
X	H	4-CH_3O—C_6H_4	Br	NO_2	Toluene	0,95	3,00	8,87	24,4	15,8	−2,4
					Dioxane	0,50	1,40	4,71	10,3	18,5	−3,6
XI	C_6H_5	CH_3	H	NO_2	Toluene	1,56	3,25	9,88	16,5	13,8	−17,8
					Dioxane	1,01	2,40	7,14	26,9	19,7	1.9
XII	C_6H_5	CH_3	OCH_3	NO_2	Toluene	0,63	1,52[f]	5,00	12,4	17,1	−7,8
					Dioxane	0,45	1,15	3,78	8,88	18,2	−4,8
XIII	C_6H_5	CH_3	Br	NO_2	Toluene	0,60	2,07	6,46	16,7	18.9	−1,5
					Dioxane	0,38	0,63	2,05	7,21	18,1	−6.2
XIV	4-CH_3O—C_6H_4	CH_3	H	NO_2	Toluene	2,19	5,75	12,0	29,2	14.2	−6,6
					Dioxane	0,96	2,11	9,32	25,7	20,5	4.5
XV	4-CH_3O—C_6H_4	CH_3	Br	NO_2	Toluene	0,47	1,63	5,80	16.2	20,0	11.1
					Dioxane	0,18	0.39	1.03	3,32	17,5	−9,5
XVI	4-CH_3O—C_6H_4	CH_3	OCH_3	NO_2	Toluene	0,79	1,65	4,78	12,7	16,4	−10.6
					Dioxane	0,85	1,38	5,50	16,2	18,6	−3,1
XVII	H	CH_3	7-C_6H_5	NO_2	Toluene	0,74	2,32	7,13	16.1	17,6	−5,7
					Dioxane	0,31	0,93	3,51	9,61	21.0	4.2

[a] In toluene.

[b] In dioxane.

[c] According to the data in [8], $1.68 \cdot 10^{-2}$ sec^{-1}.

[d] According to the data in [9], $3.0 \cdot 10^{-2}$ sec^{-1}.

[e] According to the data in [10], $3.9 \cdot 10^{-2}$ sec^{-1}.

[f] According to the data in [10], $1.3 \cdot 10^{-2}$ sec^{-1}.

system (at the same time, there is an appreciable bathochromic shift in the long-wave absorption band of the photomerocyanine [1]); the introduction of a phenyl substituent in the 7 position (XVII as compared with I) gives rise to a certain amount of slowing down of the dark reaction; we note that this is accompanied only by slight spectral changes [2]. A comparison of the data for spirochromenes I and XI and I and XIV makes it possible to conclude that the introduction of an aryl substituent in the 5' position of the spirochromene molecule does not lead to a substantial change in the rate of the dark reaction.

The introduction of a bromine atom (spirochromenes V and VII, VIII and X, XI and XIII, and XIV and XV) in the 8 position of the molecule does not slow down the reaction nor lead to a certain amount of slowing down of the decolorization rate; a methoxy group has a similar effect (spirochromenes V and VI, VIII and IX, XI and XII, and XIV and XV). The kinetic parameters of the spriochromenes change in an unexpected manner when aryl substituents are introduced in place of the methyl group in the 3' position. Proceeding from the assumption that the rate of dark decolorization of spirochromenes is controlled primarily by the electronic effects of the substituents [7], one might have expected that this sort of structural change, which does not involve the chromophoric chain of the merocyanine, should not have a substantial effect on the rate of dark decolorization. However, as seen from a comparison of the kinetic parameters of spirochromenes I and V and I and VIII, replacement of the methyl group by an aryl group in the 3' position leads to slowing down of the dark reaction; this is evidently a consequence of steric hindrance in the step involving trans–cis isomerization of the merocyanine, which precedes cyclization. We note that, with respect to their spectral characteristics, photomerocyanines V and VIII do not differ from their methyl analog I [4, 5].

The kinetic data obtained in this study constitute evidence for the low sensitivity of the rate constant of dark decolorization of photomerocyanines in nonpolar or slightly polar media to structural changes in the molecule. This low sensitivity and the associated absence of a correlation between the rate of the dark reaction in toluene and the electronic effect of the substituents have already been noted [8, 10] for spirochromenes of the indoline series.

Thus the introduction of aryl substituents in the indoline spirochromene molecule makes it possible, within certain limits, to modify the spectral characteristics of the merocyanine form while leaving the kinetic characteristics relatively unchanged. This conclusion can be used for the development of photochromic compositions with predesignated properties.

EXPERIMENTAL

The measurement of the kinetics of the dark decolorization reaction and the subsequent statistical treatment of the results were accomplished as described in [8]. The reliability interval of the rate constant for 90% confidence probability in most cases was 2-3% of the measured value and amounted to 10% of the measured value only in the case of the fastest processes ($\tau_{1/2} \approx 3$ sec).

The dioxane was purified by the method in [13], and the toluene was purified by the method in [14].

The synthesis of the compounds was described in [1-5]. Each kinetic experiment was repeated no less than five times in order to increase the statistical reliability of the results.

LITERATURE CITED

1. E. V. Braude and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., No. 7, 943 (1974).
2. E. V. Braude and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., No. 2, 200 (1976).
3. M. A. Gal'bershtam, N. M. Przhiyalgovskaya, I. B. Lazarenko, V. S. Kononova, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 4, 497 (1976).
4. M. A. Gal'bershtam and N. P. Samoilova, Khim. Geterotsikl. Soedin., No. 9, 1209 (1973).
5. M. A. Gal'bershtam and N. P. Samoilova, Khim. Geterotsikl. Soedin., No. 8, 1041 (1974).
6. M. A. Gal'bershtam and M. B. Gordin, Photochem. Photobiol., 17, 103 (1973).
7. R. Bertelson, in: Photochromism, Tech. Chem., edited by G. H. Brown, Vol. 3, Wiley Interscience (1971).
8. V. I. Pantsyrnyi, M. A. Gal'bershtam, and N. A. Donskaya, Khim. Geterotsikl. Soedin., No. 5, 653 (1973).
9. R. Gautron, Theses Sciences, Strasbourg (1967).
10. R. Gautron, Bull. Soc. Chim. France, 3190 (1968).
11. J. C. Metras, M. Mosse, and C. Wippler, J. Chim. Phys., 62, 659 (1965).
12. O. Chaude, Cahieres Phys. (France), 52, 39 (1954).
13. A. Rieche, Angew. Chem., 44, 896 (1931).
14. I. H. Mathews, J. Am. Chem. Soc., 48, 562 (1926).