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PRODUCTS OF THE REACTION OF THE BASES OF CYANINE DYES WITH SILVER IONS

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The reaction of 2-[3'-(3"-alkyl-2"-benzothiazolylidene)propenyl]benzothiazole, -pyridine, and -quinoline with silver ions in various solvents was studied. In anhydrous methanol, chloroform, and acetonitrile the indicated bases of cyanine dyes reduce silver ions with the liberation of acid in an amount equivalent to the silver metal formed, and the bases are partially converted to the salts. Similar reaction products are obtained by electrolysis of solutions of them in methanol and acetonitrile at the potentials established for them. It was established that the unstable salts of their N-oxides are formed in the presence of water in the reaction of the bases with silver salts; the products of the transformations of the N-oxides were identified.

The dependence of the color of the bases of symmetrical cyanine on their structure was studied in [1]. In the case of bases of unsymmetrical monomethylidynecyanines [2] and in a number of bases of unsymmetrical carbocyanines [3] it has been established that of the two isomeric compounds, the more deeply colored compound is that in which the alkyl group is bonded to the nitrogen atom of the more basic heterocyclic residue. A relationship between the structures of the bases of the cyanines and their pK_a values and dipole moments was revealed in the latter study. It has been shown [4] that bases of carbocyanines with a dihydrobenzo-1,5-thiazepine residue form complexes with silver salts.

In the patent literature it is mentioned that the bases of cyanine dyes, particularly those that contain a nitrile group in the α position of the polymethylidyne chain, are sensitizers of silver halide emulsions (e.g., see [5, 6]). In this connection it seemed of interest to study the reaction of these compounds with silver ions, since it may occur in photographic layers.

In the present research we studied the reaction with silver ions in various solvents of bases of carbocyanines of the general structure

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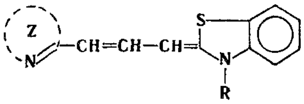

I

where Z is a benzothiazole residue and R = C_2H_5 (Ia), Z is a 2-pyridyl residue and R = C_2H_5 (Ib), and Z is a 2-quinolyl residue* and R = CH_3 (Ic).

The reactions were carried out in the dark. We used methanol, chloroform, acetonitrile, benzene, and acetic acid as the solvents for bases I. Silver nitrate and tosylate were dissolved in methanol or acetonitrile.

The liberation of a finely dispersed precipitate, which was found to be silver metal, and an equivalent amount of free acid was observed in all cases when a twofold excess of a $1 \cdot 10^{-2}$ N solution of silver salt was added to $2 \cdot 10^{-3}$ mole/liter solutions of bases I, regardless of the nature of the solvents used. However, the amount of reduced silver depended to a great extent on the solvents used. Thus when the reaction was carried out in acetonitrile for 1 h, 0.22-0.25 g-atom of silver per mole of base was isolated, as against 0.5-0.6 g-atom of silver per mole of base in the case of a mixture of chloroform with acetonitrile (24:1), 1.0-1.1 g-atom of silver per mole of base in the case of a mixture of chloroform with methanol (24:1), and up to 2.0 g-atoms of silver per mole of base in the case of 95% methanol.

The curves of the spectral absorption of the reaction mixture obtained in the reaction of equivalent amounts of base Ib in chloroform with a solution of silver tosylate in anhydrous acetonitrile in a nitrogen atmosphere, the product of its neutralization with triethylamine, and, for comparison, the starting base and its salt with p-toluenesulfonic acid are presented in Fig. 1. It is apparent that the salt of the starting base is formed in the reaction of carbocyanine base Ib with silver ions in an anhydrous medium due to the acid that is liberated during the reaction. Only one spot, the R_f value of which and the absorption spectrum of the eluate correspond to base Ib, was observed in the chromatography of the neutralized reaction solution. A similar pattern was observed in the case of bases Ia and Ic and also when other anhydrous solvents were used.

Thus the carbocyanine bases with structure I, in contrast to dihydrobenzo-1,5-thiazepine derivatives (see [4]), reduce silver ions in anhydrous solutions, an amount of acid equivalent to the silver metal that is formed is liberated, and part of the starting base is converted to a salt.

The possibility and degree of occurrence of the redox reaction between silver ions and the carbocyanine bases will evidently be determined by the ratio of the standard redox potentials (E°_{Ag/Ag^+}) of the Ag/Ag^+ system and the half-wave potentials of oxidation ($E^{ox}_{1/2}$) of the bases in various media. We determined the $E^{ox}_{1/2}$ values of bases I in methanol and acetonitrile.

The standard redox potentials (E°_{Ag/Ag^+} [7] and $E^{ox}_{1/2}$) of bases I are presented in Table 1.

It is apparent from Table 1 that the redox potential of the Ag/Ag^+ system is quite positive in methanol and that rapid oxidation of bases I is therefore possible. In the case of acetonitrile the oxidation potentials of the bases are shifted slightly to the negative side, while the redox potential of the Ag/Ag^+ system decreases sharply. As a consequence of this, a significant decrease in the yield of silver metal is observed in the chemical reaction of silver ions with the carbocyanine bases.

To clear up the problem as to whether the redox reaction of carbocyanine bases I with silver ions is a specific reaction or has overall electrochemical character we made a polarographic study and carried out the preparative electrolysis of methanol and acetonitrile solutions of bases Ia-Ic. The one-electron character of the process in the polarographic oxidation I, which was determined from the Ilkovic equation [8], provides evidence for the formation of a cation radical as an intermediate. The accumulation of acid in the electrochemical cell and the formation of salts of the bases (see [9]), just as in the reaction

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*This compound was kindly supplied to us by Yu. L. Slominskii, to whom we express our gratitude.

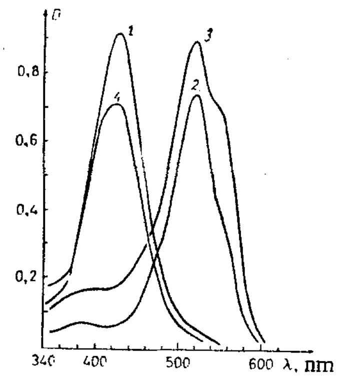


Fig. 1

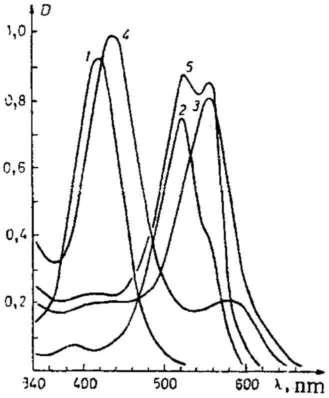


Fig. 2

Fig. 1. Curves of the spectral absorption of $8 \cdot 10^{-5}$ M solutions [$CHCl_3$—CH_3CN (24:1)]: 1) base Ib (l = 0.3 cm); 2) salt of base Ib (l = 0.2 cm); 3) reaction product Ib + AgTs (1:1) (l = 0.3 cm); 4) neutralized reaction product (l = 0.3 cm).

Fig. 2. Curves of the spectral absorption of $8 \cdot 10^{-5}$ M solutions [$CHCl_3$—95% CH_3OH (24:1)]: 1) base Ib (l = 0.3 cm); 2) salt of base Ib (l = 0.2 cm); 3) reaction product Ib + AgTs (1:1) (l = 0.2 cm); 4) neutralized reaction product (l = 0.3 cm); 5) product of oxidation of base Ib with monoperphthalic acid.

TABLE 1. Standard Redox Potentials E^{o}_{Ag/Ag^+} and $E^{ox}_{1/2}$ of Bases I

Base	Methanol			Acetonitrile		
	E^o Ag/Ag⁺, V	$E^{ox}_{1/2}$*, V	ΔE†, V	E^o Ag/Ag⁺, V	$E^{ox}_{1/2}$*, V	ΔE†, V
Ia	+0,764	+0,628	+0,136	+0,230	+0,596	+0,366
Ib		+0,566	+0,198		+0,536	−0,306
Ic		+0,486	+0,278		+0,486	−0,256

*Relative to the hydrogen electrode.

†ΔE = $E^{o}_{Ag/Ag^+} - E^{ox}_{1/2}$ relative to the hydrogen electrode.

of I with Ag^+, were observed in the electrolysis of I at potentials corresponding to the one-electron oxidation.

Proceeding from the data presented above, one may assume the following mechanism for the reaction of bases I (DH) with silver ion in nonaqueous solvents S:

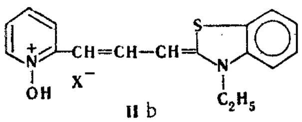
$$
\begin{array}{rcl}
Ag^+ + S & \rightleftharpoons & Ag^+S \\
OH + Ag^+S & \longrightarrow & DH^{\cdot +} + Ag + S \\
DH^{\cdot +} & \longrightarrow & D^{\cdot} + H^+ \\
D^{\cdot} + S & \longrightarrow & DH + S^{\cdot} \\
DH + H^+ & \longrightarrow & DH_2^+ \\
\hline
DH + Ag^+ + S & \longrightarrow & DH_2^+ + Ag + S^{\cdot}
\end{array}
$$

Complexes of the silver ions with the solvent (Ag^+S) oxidize base DH, during which silver metal is liberated, and the cation radical of the base ($DH^{\cdot +}$) is formed; the latter eliminates a proton to give neutral radical $D^{\cdot}$. Radical $D^{\cdot}$ detaches a hydrogen atom from solvent S, thereby regenerating starting base DH. The latter forms simple salt DH_2^+ with the protons that have accumulated in the system.

The reaction of the bases of carbocyanine dyes with structure I with silver salts proceeds in a different manner when water is present.

Thus the principal product when a solution of silver tosylate in methanol that contains an amount of water equivalent to the amount of base is added to a chloroform solution of base Ib in a nitrogen atmosphere is not the salt of base Ib but rather IIb, which absorbs in the longer-wave part of the spectrum. The absorption maximum of the product of neutralization of this compound with triethylamine also lies in the longer-wave region as compared with base Ib (Fig. 2). Compound IIb is extremely unstable both in the salt form and in the free base form, and it has not yet been possible to isolate it in the individual state. One's attention is directed to the fact that the absorption maximum of product IIb is close to the absorption maximum of 1-methoxy-3'-ethylpyrido(2)thiacarbocyanine (III) [10] (550 and 548 nm, respectively in chloroform, and 544 and 542 nm in methanol). In addition, the same compounds that are formed as a result of thermal and hydrolytic transformations of dye III — 3,3'-diethylthiacarbocyanine (IV), 1,3'-diethylpyrido(2)thiacarbocyanine (V), 3,3'-diethyl-10-pyridyl(2")thiadicarbocyanine (VI), 1,3'-diethyl-10-benzothiazolyl(2")pyrido(2)-thiadicarbocyanine (VII), base Ib, the isomeric (with respect to the latter) base with an ethyl group attached to the nitrogen atom of the pyridine ring (VIII), and 2-formylmethylene-3-ethylbenzothiazoline (IX) — were isolated by chromatography of the reaction mixture after reaction for several hours (see [11]).

Since it is known that the corresponding N-oxides of the amines are formed in the oxidation of primary, secondary, and tertiary amines in aqueous media in the presence of the dye methylene blue [12], it is assumed that IIb is a salt of the N-oxide of base Ib:



IIb

The N-oxides of bases of cyanine dyes have not been described in the literature. Only Ib and IV-IX were isolated in attempts to obtain IIb by condensation of α-picoline N-oxide with 2-formylmethylene-3-ethylbenzothiazoline by refluxing in pyridine in the presence of potassium hydroxide (see [13]) or in benzene with the addition of piperidine and acetic acid (see [14]) and also with 2-β-chlorovinyl-3-ethylbenzothiazolium chloride at room temperature in chloroform (see [15]).

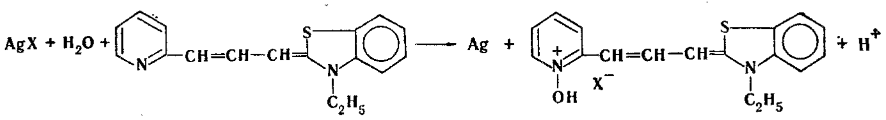
The appearance of a band with λ_{max} = 550 nm, which corresponds to IIb (Fig. 2), was noted in the absorption spectrum of the reaction mixture in the oxidation of base Ib with monoperphthalic acid, which is used for the preparation of the unstable N-oxides of heterocyclic bases (see [16, 17]), in absolute ether at 5°C after 4 h. The same compounds (IV-IX) were isolated along with starting base Ib by chromatography after neutralization and treatment of the reaction mixture with potassium iodide solution.

To obtain dye III, reaction product IIb in the free base form was alkylated at room temperature in anhydrous nitromethane with methyl 2,4,6-trinitrobenzenesulfonate (see [18]); however, in this case only Ib and IV-IX, the formation of which was also observed, as indicated above, in the destruction of dye III, were also isolated.

Compounds IV-IX were also obtained in the electrochemical oxidation of base Ib in methanol in the presence of water at the corresponding $E^{ox}_{1/2}$ potential.

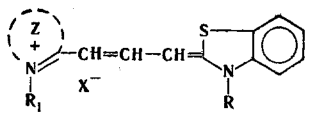
Thus, although the N-oxide of base Ib was not obtained in individual form in any of the experiments, in all cases in which its formation was likely the same transformation products that are formed from 1-methoxy-3'-ethylpyrido(2)thiacarbocyanine (III) were produced.

On the basis of the data presented above, it may be assumed that the salt of the N-oxide (IIb) of Ib is formed in the reaction of base Ib with silver ions in the presence of water:



Similar compounds (IIa and IIc) are also obtained under the conditions described above from thiacarbocyanine (Ia) and quino(2)thiacarbocyanine (Ic) bases. Complex mixtures of substances that include the starting bases and carbocyanine and 10-hetaryl-substituted di-

TABLE 2. Spectral Characteristics of



Z	R	Absorption maxima, nm				
		starting bases I	R_1			
			O⁻	OH	H	Alk
Benzothiazolyl	C_2H_5	455	460	552	554	570
2-Pyridyl	C_2H_5	420	440	550	520	544
2-Quinolyl	CH_3	452	472	602	562	590

carbocyanine dyes are also formed in the decomposition of IIa and IIc. Thus 3,3'-diethyl-10-benzothiazolyl(2")thiadicarbocyanine, which has an absorption maximum in ethanol at 633 nm (631 nm [19]), is isolated in the case of base Ia.

The absorption maxima of bases I, their salts with p-toluenesulfonic acid, N-oxides II and their salts, as well as iodides IV and V, and 1,3'-dimethylquino(2)thiacarbocyanine iodide (X), in a mixture of chloroform and methanol (24:1) are presented in Table 2.

It is apparent from Table 2 that a bathochromic shift of the absorption maxima due to the development of a partial positive charge on the nitrogen atom is observed on passing from the bases to the N-oxides; this shift is substantially higher in the case of pyridine and quinoline derivatives than in the case of the symmetrical thiacarbocyanine derivative, in agreement with the $E_{1/2}^{ox}$ values. A comparison of the absorption maxima of the salts of the bases, their N-oxides, and the corresponding N-alkyl derivatives makes it possible to conclude that there is a decrease in the relative basicity of the heteroresidue when the alkyl group attached to the nitrogen atom is replaced by an electron-donor oxy group. In the case of derivatives of unsymmetrical carbocyanines this leads to a more uniform distribution of the electron density in the polymethylidyne chromophore than in N-alkyl-substituted dyes and, as a consequence, to a bathochromic shift of the absorption maxima. However, in the case of the salt of the N-oxide of the symmetrical carbocyanine base the decrease in the basicity of one of the heteroresidues naturally gives rise to a hypsochromic shift of the absorption maximum.

EXPERIMENTAL

2-[3'-(3"-Ethyl-2"-benzothiazolylidene)propenyl]benzothiazole (Ia). This compound was obtained by the method in [1] and had mp 138-140°C.

2-[3'-(3"-Ethyl-2"-benzothiazolylidene)propenyl]pyridine (Ib). A 1.31-g (3 mmole) sample of dye V was heated in a nitrogen atmosphere with 40 ml of diethylaniline at 230°C for 1 h, after which the diethylaniline was removed by steam distillation, and base Ib was extracted from the residue with benzene and purified by chromatography on Al_2O_3 and crystallization to give 0.66 g (78%) of a product with mp 115-116°C (from hexane) and R_f 0.55 [Woelm silica gel, elution with benzene–methanol (6:1)]. Absorption spectrum in ethanol, λ_{max}, (log ε): 418 nm (4.56). Found: C 72.52; H 5.47; N 9.79%. $C_{17}H_{16}N_2S$. Calculated: C 72.75; H 5.72; N 9.99%. The picrate of Ib had mp 176-177°C (from ethanol). Found: C 54.15; H 3.84; N 13.82%. $C_{17}H_{16}N_2S \cdot C_6H_3N_3O_7$. Calculated: C 54.22; H 3.78; N 13.76%.

Solutions ($2 \cdot 10^{-3}$ M) of bases Ia-c were mixed with $1 \cdot 10^{-2}$ N solutions of the silver salts in the appropriate solvents after prior removal of the oxygen from both solutions by bubbling nitrogen through them. After 1 h at room temperature, the solutions were separated from the precipitates by centrifugation, and the precipitate was dissolved in nitric acid. The silver metal was determined by titration with a $1 \cdot 10^{-2}$ N solution of potassium iodide in the presence of $Ba(NO_3)_2$ with an OP-504 potentiometer. The acid was determined by titration of the centrifugate with a $1 \cdot 10^{-2}$ N solution of sodium hydroxide with a pH-340 potentiometer.

The electronic spectra were recorded with a Hitachi EPS-3T spectrophotometer.

Preparative chromatography was accomplished on KSK silica gel (50-80 μm) in 2 by 20 cm columns by means of solvents with increasing polarities. Thin-layer chromatography (TLC) on

Woelm silica gel in benzene—methanol (6:1) and chloroform—methanol (4:1) solvent systems and on activity II/III aluminum oxide in benzene—methanol (19:1) and hexane—chloroform—methanol (3:6:1) solvent systems was used to monitor the course of the reactions and the degree of separation.

The $E_{1/2}^{ox}$ values were measured with an LP-60 polarograph with rotating glass—graphite or platinum-disk electrodes (w = 1600 rpm, S = 9.42 mm^2) and a saturated calomel reference electrode. Methanol containing 0.1 N LiCl and acetonitrile containing 0.1 N $NaClO_4$ were used as the media for the measurements. The concentration of the bases in the polarographic solutions ranged from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mole/liter.

The preparative accumulation of the products of oxidation of the bases was carried out with a P-5848 potentiostat with the aid of an electrochemical cell with separated (by means of a porous diaphragm) anode and cathode compartments. The cell was equipped with a platinum-gauze anode (S = 240 mm^2) and a smooth cathode (S = 200 mm^2). The reference electrode was a saturated silver chloride electrode. The electrolysis time was 6 h, and samples were selected for spectrophotometric and chromatographic monitoring after 0.25, 0.5, 1, 2, 4, and 6 h.

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