

Benzothiazole compounds

XXX. Hydrolysis of 2-styrylbenzothiazolium salts substituted at the position 3

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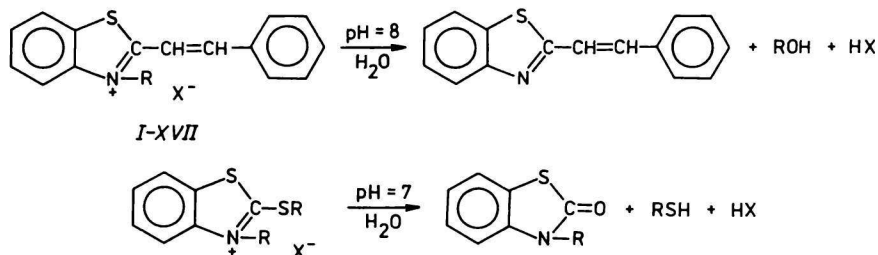
Stability of 2-styryl-3-alkoxycarbonylmethylbenzothiazolium bromides, 2-styryl-3-benzylbenzothiazolium bromide, perchlorate, tetrafluoroborate, nitrate, 2-styryl-3-allylbenzothiazolium bromide, and 2-styryl-3-propargylbenzothiazolium bromide in water was studied. At pH = 8 hydrolysis takes place and 2-styrylbenzothiazole, esters of α -hydroxyacetic acid, benzyl alcohol, allyl alcohol, and propargyl alcohol are formed. The rate constants of hydrolysis of the individual derivatives were determined.

Изучалась устойчивость бромидов 2-стирил-3-алкоксикарбонилметилбензотиазолия, бромида, хлорита, борофторида и нитрата 2-стирил-3-бензилбензотиазолия, бромида 2-стирил-3-аллилбензотиазолия и бромида 2-стирил-3-пропаргилбензотиазолия в водной среде. При pH = 8 происходит гидролиз, приводящий к образованию 2-стирилбензотиазола, эфиров α -гидроксиуксусной кислоты, бензилового спирта, аллилового спирта и пропаргилового спирта. Определены константы скорости гидролиза каждого производного.

Compounds possessing thiazole or benzothiazole skeleton in their molecules are attractive from the theoretical point of view as well as from the point of view of their practical applications [1]. Recently we prepared 2-styryl- and 2-alkylthiobenzothiazolium salts substituted at the position 3 [2, 3]. The different growth-regulation activities of these two classes of compounds prompted us to examine their stability in water. The rate constants of hydrolysis of 2-alkylthio-3-R-benzothiazolium salts exhibit no linear dependence on bulkiness of a substituent at the positions 2 and 3 or on inductive effects of these substituents.

2-Styryl-3-R-benzothiazolium salts derivatives are stable in water and in methanol at pH < 7 and UV spectra of such solutions do not show appreciable change during 24 h. In the range of pH \approx 8 one can observe, by UV spectra, rapid enough decomposition of the starting salt and formation of 2-styrylbenzothiazole, whereas 3-R-2-benzothiazolone was isolated after hydrolysis of 2-alkylthio-3-R-benzothiazolium salts (Scheme 1). In case of derivatives *II* and

XIV the reaction mixture was analyzed by gas chromatography, IR and ^1H NMR spectra. As chief components were determined methyl α -hydroxyacetate and benzyl alcohol. The ring opening described for thiamine [4], was not observed under given conditions.



Scheme 1

The rate constants of hydrolysis of salts under study are substituent R as well as anion X dependent (Table 1). In general, reaction rates of hydrolysis of compounds *I*—*VIII* increase with increased number of alkyl carbon atoms of the ester group. Such a trend is probably due to a diminished association of molecules caused by enlargement of the alkyl group in the ester moiety. Changes of rate constants for the derivatives substituted at the position 3 by ethoxycarbonylmethyl (*III*), propoxycarbonylmethyl (*IV*), isopropoxycarbonylmethyl (*V*), and butoxycarbonylmethyl (*VI*) are inferior and, in fact, the hydrolysis of *IV* is slower than that of *III* or *V*. Also the hydrolysis of compound *I* is relatively slow in comparison with the rest of derivatives taking into account an increment of one carbon atom unit of alkyl of the ester group to the reaction rate. In this case the rate of hydrolysis is affected by intermolecular interactions which are characteristic of aliphatic carboxylic acids. In a similar way one can explain the slow reaction of *IV*, by assumption of an intermolecular interaction between the oxygen of carbonyl group and the methyl hydrogen of propoxy group (“propyl effect”) [5]. Comparison of rates of hydrolysis of compounds *XII* and *XIV* reveals agreement of the rates with the inductive effects of allyl ($\sigma^* = 0.180$) and benzyl ($\sigma^* = 0.215$) groups.

Differences in obtained values of rate constants do not account only for electronic effects of substituents and conformational changes in molecules (*e.g.* bulkiness of a substituent) as explained in literature [6] for a cleavage of some quaternary benzothiazolium, benzoxazolium, and thiazolium salts in the presence of $(\text{C}_6\text{H}_5)_3\text{P}$ in dimethyl sulfoxide. Such an interpretation is in accord with neither λ_{max} and $\log\{\varepsilon\}$ in UV spectra (Table 1) nor $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ in IR spectra of the derivatives under study [2]. In addition to the above-mentioned effects, the reaction rate is presumably affected also by an ability of the individual derivatives to form aggregates. Such an ability depends on R in

Table 1

Rate constants of hydrolysis and UV spectral data of 2-styryl-3-R-benzothiazolium salts

Compound	R	X ⁻	10 ⁴ <i>k</i> s ⁻¹	λ _{max} /nm	log (ε/(m ² mol ⁻¹))
<i>I</i>	CH ₂ CO ₂ H	Br	1.76 ± 0.1	368	4.37
<i>II</i>	CH ₂ CO ₂ CH ₃	Br	6.26 ± 0.4	375	4.56
<i>III</i>	CH ₂ CO ₂ C ₂ H ₅	Br	12.98 ± 0.7	373	4.57
<i>IV</i>	CH ₂ CO ₂ C ₃ H _{7-i}	Br	10.46 ± 0.3	365	4.52
<i>V</i>	CH ₂ CO ₂ C ₃ H _{7-i}	Br	12.97 ± 0.3	375	4.47
<i>VI</i>	CH ₂ CO ₂ C ₄ H ₉	Br	11.30 ± 0.4	382	4.47
<i>VII</i>	CH ₂ CO ₂ C ₅ H ₁₁	Br	15.82 ± 0.3	381	4.44
<i>VIII</i>	CH ₂ CO ₂ C ₇ H ₁₅	Br	30.72 ± 1.2	370	4.55
<i>IX</i>	CH ₂ CO ₂ CH ₂ C ₆ H ₅	Br	1.37 ± 0.1	370	4.36
<i>X</i>	CH ₂ CO ₂ CH=CH ₂	Br	1.84 ± 0.1	368	4.45
<i>XI</i>	CH ₂ CO ₂ CH ₂ CH=CH ₂	Br	12.47 ± 0.9	373	4.46
<i>XII</i>	CH ₂ CH=CH ₂	Br	2.03 ± 0.2	368	4.48
<i>XIII</i>	CH ₂ CH≡CH	Br	2.76 ± 0.2	375	4.47
<i>XIV</i>	CH ₂ C ₆ H ₅	Br	5.52 ± 0.3	370	4.55
<i>XV</i>	CH ₂ C ₆ H ₅	BF ₄	5.90 ± 0.2	375	4.53
<i>XVI</i>	CH ₂ C ₆ H ₅	ClO ₄	7.94 ± 0.3	375	4.58
<i>XVII</i>	CH ₂ C ₆ H ₅	NO ₃	3.11 ± 0.4	375	4.62

the same way as it is in the case of some dyes containing the benzothiazole skeleton [7].

Van der Waals forces are accountable for an association of molecules in a reaction medium. Stability of associated species (influenced by a substitution at the position 3 of the benzothiazolium salts) is responsible for relatively large changes of entropy and consequently, for the rate of hydrolysis. Also the effect of an anion on the rate of the examined reaction is not negligible. The explanation probably lies in different polarizabilities of anions or in their differing oxido-reduction properties.

Experimental

2-Styryl-3-R-benzothiazolium salts were prepared by the method described in our previous paper [2]. The rates of reactions were determined in water at $\theta = (50 \pm 0.1)^\circ\text{C}$, $c = 10^{-4} \text{ mol dm}^{-3}$, $\text{pH} = 8$, and $\lambda_{\text{max}} = 370 \text{ nm}$. Solutions were maintained at $\text{pH} = 8$ by a Britton—Robinson buffer the pH of which was checked by MV 870 pH -meter (Präcitronic, GDR). The temperature was measured by a thermometer with a diode sensor immersed directly in a cell [8]. The decrease of amount of starting compounds was monitored by a Perkin—Elmer 450 instrument equipped with a device for re-recording

of spectra and with a punch unit, Perkin—Elmer 2G (GDR). The detailed description of the apparatus was given earlier [9]. The rate constants were calculated by Guggenheim's method under conditions of pseudo-first-order of a reaction, using a calculator EMG 666. Gas chromatography analysis was performed on a Chrom 4 instrument with a column (150 cm × 0.3 cm) packed with 3 % Carbowax 20M and 4 % KOH on Chromosorb W, using nitrogen as a carrier gas at a pressure of 0.04 MPa and at a column temperature of 150—200 °C.

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