Benzothiazole compounds XXV. Kinetic study of the reaction of 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts with water

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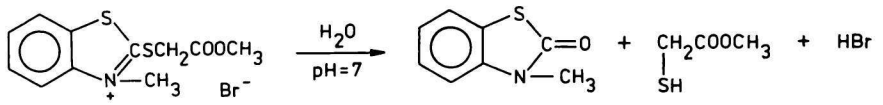
The stability of 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts in aqueous medium has been studied. The rate of hydrolysis was significantly dependent on the substituent in the position 3 as well as on the alkoxy group and pH of the medium. In the reaction medium 3-alkyl-2-benzothiazolinone was proved by spectral methods and esters of thioglycolic acid by gas chromatography.

Изучена устойчивость солей 2-алкоксикарбонилметилтио-3-алкилбензотиазолия в водной среде. Скорость гидролиза в значительной степени зависела от заместителя в положении 3, а также от алкокси-группы и pH среды. В реакционной среде наличие 3-алкил-2-бензотиазола было подтверждено спектральными методами, а наличие эфиров тиогликолевой кислоты посредством газовой хроматографии.

In the previous work [1] it was found that 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium bromides exhibited growth-stimulating and/or growth-inhibiting activity on plant root system. Since in practical application of these compounds it is necessary to take into account their interaction with water, we decided to study the kinetics of this reaction. Prior to the kinetic study itself, the course of this reaction was followed by analysis of the reaction products. When 2-methoxycarbonylmethylthio-3-methylbenzothiazolium bromide was treated with water 3-methyl-2-benzothiazolinone [2] was isolated. Its structure was proved by IR spectra $\tilde{\nu}/cm^{-1}$: 2980 $\nu_{as}(CH_3)$, 2930 $\nu_s(CH_3)$, 1680 $\nu(C{=}O)$, 1650 $\nu(C{=}C)$, 1470 $\delta_{as}(CH_3)$. In the solution methyl thioglycolate was proved by gas chromatography (internal standard). The reaction proceeded according to Scheme 1. The results of kinetic study



Scheme 1

are presented in Table 1. It is evident that the reaction rate was mostly influenced by the substituent R^1. The reaction rate was monitored by UV spectroscopy as a concentration decrease of the starting compound. The rate constants with the derivatives where $R^1 = CH_3$ and $R = CH_3$, C_2H_5, C_3H_7, i-C_3H_7 were higher than twofold values of rate constants when $R^1 \neq CH_3$ (The numerical values of $10^4 \cdot k$ stand in parentheses behind the symbols of compounds: *I* (19.4), *V* (20.8), *IX* (19.2), *XIII* (16.3)). It is of interest that the reaction rate was observed to be dependent also on the nature of the alkyl group, *e.g.* compounds *I* (19.4), *II* (8.1), *III* (7.4), and *IV* (6.6). It can be explained by the different steric demands of the alkoxy group substituents and, hence, different hindering of the reaction centre from the attachment of a water molecule.

Comparison of rate constants obtained with the compounds where $R^1 = CH_3$ and $R = CH_3$, C_2H_5, C_3H_7, i-C_3H_7 revealed that the rate constant for the derivative where $R^1 = CH_3$ and $R = C_2H_5$ (*V* (20.8)) was higher than that for the derivative where $R = R^1 = CH_3$ (*I* (19.4)). Also in other groups when $R^1 = C_2H_5$, C_3H_7, C_4H_9 it could be observed that the rate constants did not change regularly on changing R but in those cases when the substituent R contained by one carbon atom more than R^1 their values were higher than in cases when $R^1 = R$ (*X* (8.4), *XII* (6.4)). At present, we cannot explain this anomaly on the basis of the results obtained.

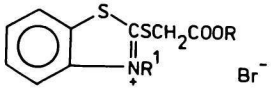
In the case when R^1 changed in the order C_2H_5, C_3H_7, C_4H_9 and R in the order CH_3, C_2H_5, C_3H_7, i-C_3H_7, the differences in rate constants were less significant (the group of compounds *II* (8.1), *III* (7.4), *IV* (6.6); the group of compounds *VI* (7.7), *VII* (8.4), *VIII* (6.7); the group of compounds *X* (8.4), *XI* (6.2), *XII* (6.4), and the group of compounds *XIV* (6.0), *XV* (5.9), *XVI* (5.9)). The measured values also revealed that with the increasing number of carbons in R and R^1 (compounds *I* (19.4), *VI* (7.7), *XI* (6.2), *XV* (5.9)) the rate constant decreased in the order CH_3, C_2H_5, C_3H_7, i-C_3H_7. In the group where R = i-C_3H_7 and $R^1 = C_2H_5$, C_3H_7, C_4H_9 the rate constant practically did not change (compounds *XIV* (6.0), *XV* (5.9), *XVI* (5.9)) and thus was independent of R^1.

On the basis of these facts and comparability of induction effects of the alkyl groups it can be assumed that the rate constants of the reactions studied changed in dependence on R and R^1 due to steric arrangement of side chains of the thiazole ring.

Considerable decrease in the rate constant value was observed when benzyl group was present in the position 3. For example, in the case of the compound

Table 1

Rate constants for S_N reactions of 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium bromides with water



Compound	R	R^1	$\frac{\lambda_{max}}{nm}$	$\log(\varepsilon(\lambda_{max})/(m^2\ mol^{-1}))$	$10^4\ k/s^{-1}$
I	CH_3	CH_3	305	3.25	19.4 ± 0.1
II	CH_3	C_2H_5	305	3.21	8.1 ± 0.3
III	CH_3	C_3H_7	303	3.28	7.4 ± 0.2
IV	CH_3	C_4H_9	307	3.24	6.6 ± 0.1
V	C_2H_5	CH_3	305	3.23	20.8 ± 0.1
VI	C_2H_5	C_2H_5	307	3.28	7.7 ± 0.1
VII	C_2H_5	C_3H_7	307	3.29	8.4 ± 0.2
VIII	C_2H_5	C_4H_9	308	3.36	6.7 ± 80.2
IX	C_3H_7	CH_3	307	3.30	19.2 ± 0.1
X	C_3H_7	C_2H_5	306	3.29	8.4 ± 0.1
XI	C_3H_7	C_3H_7	307	3.27	6.7 ± 0.2
XII	C_4H_9	C_3H_7	307	3.30	6.4 ± 0.1
XIII	i-C_3H_7	CH_3	306	3.24	16.3 ± 0.2
XIV	i-C_3H_7	C_2H_5	305	3.25	6.0 ± 0.1
XV	i-C_3H_7	C_3H_7	307	3.29	5.9 ± 0.1
XVI	i-C_3H_7	C_4H_9	307	3.30	5.9 ± 0.2
XVII	$CH_2CH{=}CH_2$	CH_3	306	3.27	11.4 ± 0.3
XVIII	CH_3	$CH_2CH{=}CH_2$	307	3.30	18.5 ± 0.2
XIX	$CH_2C_6H_5$	CH_3	305	3.26	3.7 ± 0.1
XX	CH_3	$CH_2C_6H_5$	310	3.28	0.8 ± 0.1
XXI	CH_3	$CH_2C_6H_5$	310	3.28	1.6 ± 0.1
XXII	CH_3	$CH_2C_6H_5$	310	3.27	2.2 ± 0.1
XXIII	CH_3	$CH_2C_6H_5$	311	3.25	3.1 ± 0.1

With *XXI* the reaction rate measured at pH = 7.2, with *XXII* at pH = 7.4, and with *XXIII* at pH = 7.9.

where $R = CH_3$ and $R^1 = CH_2C_6H_5$ (*XX* (0.8)) the decrease was more than 20-fold when compared to the derivative where $R = R^1 = CH_3$ (*I* (19.4)). When the alkyls were reversed, *i.e.* $R = CH_2C_6H_5$ and $R^1 = CH_3$, this difference was 5 times smaller and when $R = CH_2CH{=}CH_2$ and $R^1 = CH_3$ (*XVII* (11.4)) it was 2 times smaller. The rate constant obtained in the case when $R = CH_3$ and $R^1 = CH_2CH{=}CH_2$ (*XVIII* (18.5)) was comparable to that obtained with the derivative where $R = R^1 = CH_3$. It means that the substituents in the position 3 influenced the stability of the derivatives more significantly than the substituents R. Though the size of substituents influences the reaction rate, it seems that interactions of the anion with several cations play also a significant role. This assumption is supported by the results in [2] where the authors found that the positive ion is delocalized on the whole thiazole ring. The X-ray structure of 3-benzylbenzothiazolium bromide [3] points also to certain interactions of the anion with the benzyl group. These interactions probably play a significant role also in liquid phase and determine the sterical arrangement of the substituents on the thiazole ring considerably.

The relationship of log $\{k\}$ on pH of the medium is illustrated in Fig. 1. The reaction rate at pH = 8 approaches the limit value, at lower pH decreases rapidly.

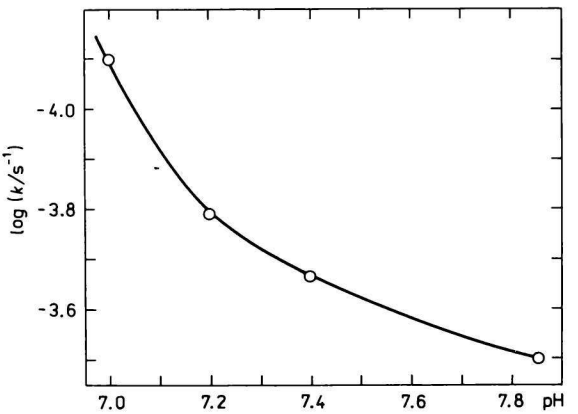


Fig. 1. Dependence of log $\{k\}$ on pH of the reaction medium.

In application of the compounds studied, 3-alkyl-2-benzothiazolinones are formed at different rates. Since they are also growth regulators [4], two biologically active compounds should be taken into account. The nucleophilic substitution reaction in biological material will proceed at lower rates with regard to lower temperature (the experiments were performed at 50 °C) and moreover, it might be hindered by increasing concentration of HBr. The decomposition rate constants were measured at pH = 7.

Experimental

The derivatives of benzothiazolium salts (*I—XXIII*) were prepared according to [1]. The measuring set consisted of the recording Perkin—Elmer 450 spectrophotometer with a device for repeated spectrum recording and perforating punch for Perkin—Elmer-2G (GDR) tape. The measurement was fully automatic with digital control [5]. The reaction rate was monitored as a concentration decrease of the starting compound in aqueous medium at $\lambda_{max}(\approx 300$ nm), pH = 7, and $\theta = (50 \pm 0.1)$ °C. The pH of the reaction medium was stabilized with the Britton—Robinson universal buffer solution and measured with a digital MV 870 (Präcitronic, GDR) pH-meter. The temperature was measured by an electronic thermometer with a diode sensor directly in the measuring cell [6]. The rate constants were calculated by the *Guggenheim* method [7] at the conditions of a pseudo--first-order reaction using an EMG 660 calculator. Gas chromatography was performed with a Chrom 4 apparatus using a column (150 cm × 0.3 cm) of 3 % Carbowax 20M + 4 % KOH on Chromosorb W; carrier gas nitrogen, inlet pressure 0.04 MPa, column temperature 150—200 °C.

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