THERMOLYSIS OF QUATERNARY SALTS OF 2-METHYLBENZOTHIAZOLE AND THEIR METHYLENE BASES

M. A. Al'perovich, V. G. Khesin,
R. D. Raikhina, and T. D. Medvedeva

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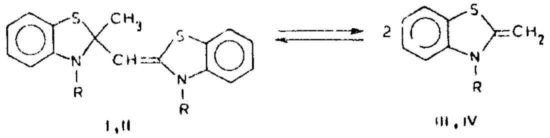
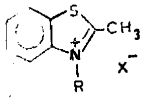
The pathways of the thermal transformations of quaternary salts of 2-methylbenzothiazole and their methylene bases were investigated. The schemes of the thermal fragmentation of these compounds are discussed. The possibility of the formation of methylene bases in the thermolysis of quaternary salts of 2-methylbenzothiazole is demonstrated.

Quaternary salts of 2-methylbenzothiazole are finding wide application in the synthesis of polymethin dyes [1], in connection with which their reactions in solutions have been studied in rather great detail [2-9]. Thus when they are treated with alkalis, triethylamine, and piperidine, they form dimers (I and II) of the methylene bases [3], the structure of which was established by Babichev during a study of various chemical transformations [5] and was subsequently confirmed by Metzger and co-workers [7] by means of NMR spectroscopy. Vorsanger [8], on the basis of mass-spectrometric data, has expressed the assumption that dimer I undergoes dissociation in the gas phase to give monomer III, while Owen [9] has isolated and identified monomers III and IV, which are stable only at low temperatures and are converted rapidly to dimers I and II at room temperature.



I, III R=CH_3; II, IV R=C_2H_5

It seemed of interest to investigate the pathway of the thermal transformations of quaternary salts of 2-methylbenzothiazole and, in particular, to ascertain whether the corresponding methylene bases are formed during their thermolysis, as in the case of the quaternary salts of 2,3,3-trimethylindolenine [10]. We selected I, II, and V as the subjects of our investigation.



V a, b

Va R=CH_3, X=I; Vb-d R=C_2H_5, X=Cl, Br, I

The investigated compounds were heated to 300°C in the vaporization chamber of a gas chromatograph in an inert gas atmosphere. The volatile pyrolysis products were detected after passing through the separating column by means of a flame-ionization detector or by means of a mass spectrometer directly connected to the gas chromatograph; they were also collected in hexane for recording of the UV or NMR spectra.

To identify the volatile thermolysis products we compared their chromatographic characteristics and UV, PMR, and mass spectra (with direct introduction into the ion source of the mass spectrometer) with similar data for the individual substances, the presence of which was assumed in the pyrolyzate.

Data on the compositions and structures of the chromatographically identified compounds with an indication of the relative retention times (α_{rel}) and the relative percentages of

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TABLE 1. Compositions and Structures of the Volatile Products of Pyrolysis of I, II, and V

Compound	Name	α_{rel}	Relative percentage, %						m/z values (relative intensities, %) for the principal ion peaks in the mass spectra
			I	II	V, $R=C_2H_5$			V, $R=CH_3$	
					$\overline{X}=Cl$	$\overline{X}=Br$	$\overline{X}=I$	$\overline{X}=I$	
VI	Benzothiazole	0,89	<0,1	<0,1	<1	<0,1	<0,1	<0,1	135 (100), 108 (40), 82 (11), 69 (25), 63 (13)
VII	2-Methylbenzothiazole	1,00	16	11	82	96	99	99	149 (100), 148 (49), 108 (67), 82 (27), 69 (55), 63 (29)
VIII	N-Methyl-o-aminothiophenol	1,04	2						139 (100), 124 (62), 109 (33), 77 (30)
IX	N-Ethyl-o-aminothiophenol	1,12		1	<0,1				153 (100), 138 (92), 136 (27), 125 (27), 124 (30), 94 (88)
X	o-Methylmercapto-N-methylaniline	1,28	17					<0,1	153 (75), 138 (38), 137 (7), 136 (16), 109 (12), 93 (100)
XI	o-Ethylmercapto-N-ethylaniline	1,31		12	1,8	<1	<0,1		181 (100), 166 (79), 152 (54), 137 (45), 136 (57), 119 (38)
XII	2,3-Dimethylbenzothiazoline	1,35	9					<0,1	165 (37), 150 (100), 109 (47), 151 (9), 75 (9)
XIII	2,2,3-Trimethylbenzothiazoline	1,37	5					<0,1	179 (26), 165 (13), 164 (100), 149 (16)
XIV	3-Methyl-3-ethylbenzothiazoline	1,37		10	2,5	<1	<0,1		179 (29), 165 (17), 164 (100), 136 (61), 109 (29), 65 (20)
XV	2,2-Dimethyl-3-ethylbenzothiazoline	1,46		3	1	<0,1	<0,1		193 (51), 179 (46), 178 (100), 150 (65), 136 (44), 109 (47)
XVI	2-Methyl-2,3-diethylbenzothiazoline	1,50		2					179 (46), 178 (73), 177 (100), 149 (18)
III	2-Methylene-3-methylbenzothiazoline	1,51	49					<0,1	163 (100), 162 (41), 148 (53), 121 (27), 104 (17)
IV	2-Methylene-3-methylbenzothiazoline	1,56		56	9,5	<1	<0,1		178 (13), 177 (98), 176 (20), 150 (20), 149 (100), 148 (30)
XVII	3-Methyl-2-ethylidenebenzothiazoline	1,63	2						177 (67), 176 (65), 62 (100), 149 (14), 108 (11)
XVIII	3-Ethyl-2-ethylidenebenzothiazoline	1,66		2	<1				191 (48), 176 (74), 162 (100), 161 (44), 109 (17)
XIX	3-Ethyl-2-propylidenebenzothiazoline	1,76		3	<1	<1	<0,1		205 (67), 191 (16), 190 (100), 177 (13), 162 (38), 149 (27)

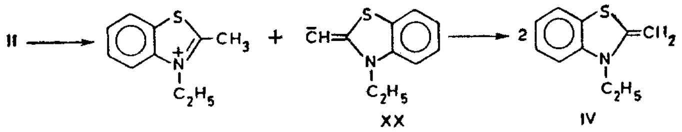
each of them in the mixture, disregarding the other volatile pyrolysis products (alkyl halides, hydrocarbons, etc.), are presented in Table 1.

The m/z values and relative intensities (in percent) of the principal ions in the mass spectra of each of the indicated products of pyrolysis of I, II, and Va-d are also presented in Table 1. It should be noted that in the pyrolysis of the investigated compounds, another series of individual compounds is formed in addition to the substances and hydrocarbons presented in Table 1; however, we were unable to correctly assign their chromatographic peaks in view of the absence of model compounds. The total amount of these substances is very small (no more than 5%).

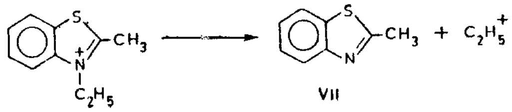
It is apparent from Table 1 that in the thermolysis of the dimers (I and II) of the methylene bases, in addition to dissociation to monomers III and IV, one observes the formation of a series of other compounds that constitute evidence for several pathways for the thermal destruction of these substances.

It is interesting that when dimer II is introduced directly in the ionization chamber of the mass spectrometer at 80°C and ionizing-electron energies of 15, 20, and 70 eV, the first ion recorded in the mass spectrum with m/z 177 corresponds to the mass of monomer IV, which confirms the data in [8]. The dissociative ionization of the molecular ion (M^+) leads to a set of fragment ions, of which only the ion with m/z 149, the peak of which is the maximum peak in the spectrum, corresponds to the molecular mass of 2-methylbenzothiazole (VII). Peaks of ions with m/z values corresponding to the molecular masses of VI, IX, XI, XIV-XVI, XVIII, and XIX are absent in the mass spectra in the case of direct introduction of dimer II. This constitutes evidence that the indicated compounds are formed by heating II under more severe conditions than those that develop in the chamber of the mass spectrometer (80°C at a residual pressure of $13.3 \cdot 10^{-7}$ Pa).

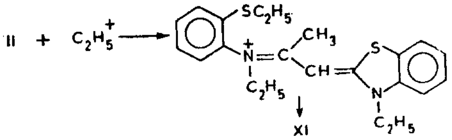
We examined the scheme of the thermal fragmentation of the dimers of the methylene bases in the case of II. It may be assumed that the first step in the process is thermal dissociation of dimer II to give the benzothiazolium cation and the carbanion (XX) of the methylene base (see [8]):



If the carbanion accepts a proton from the benzothiazolium cation, two molecules of monomeric methylene base IV are formed. Judging from the relative percentage of base IV in the pyrolyzate, this process is the most probable one. However, when the temperature is raised, the benzothiazolium cation may undergo dealkylation:

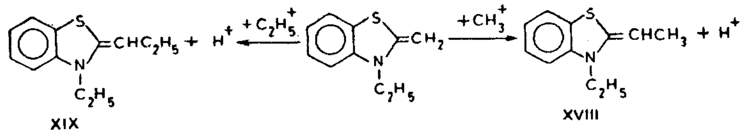


The ethyl cation reacts with dimer II to give a product of opening of one of the thiazole rings (see [5]):



the pyrolysis of which may lead to XI.

N-Ethyl-o-aminothiophenol (IX) may be produced similarly if one assumes that opening of the thiazole ring in dimer II occurs under the influence of a proton, which may be generated by the ethyl cation. The formation of XVIII-XIX probably takes place via the scheme:



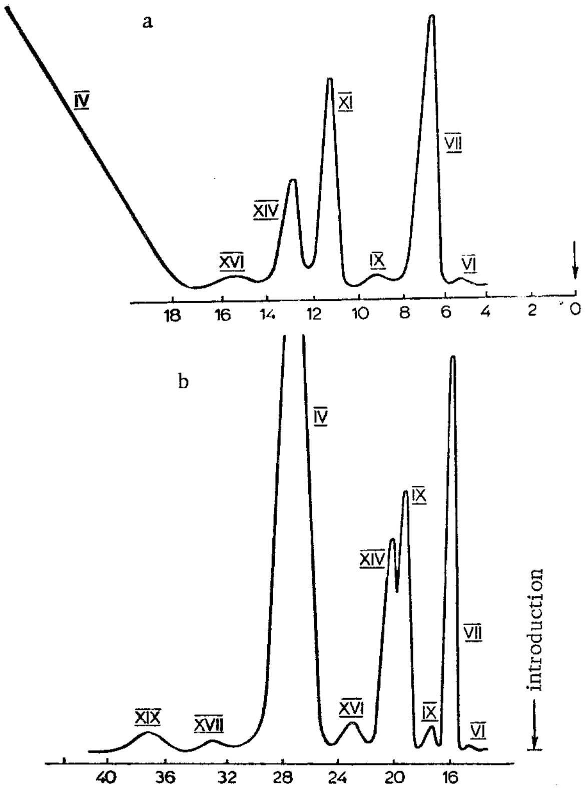
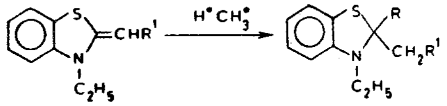


Fig. 1. Chromatograms of the volatile products of pyrolysis of dimer II: a) under isothermal conditions (120°C); b) with temperature programming (80-220°C).

It is known that the alkyl substituent adds to the methylene group in the reaction of alkylating agents with monomeric methylene bases such as 1,3,3-trimethyl-2-methyleneindoline and 3-methyl-2-ethylidenebenzothiazoline [5]. Similar reactions have not yet been described for monomeric 3-methyl-2-methylbenzothiazoline (III) and 3-ethyl-2-methylbenzothiazoline (IV). The possibility that XVIII and XIX may also be formed in the reaction of carbanion XX with alkyl cations is also not excluded.

Compounds XIV-XVI can be obtained in radical reactions:

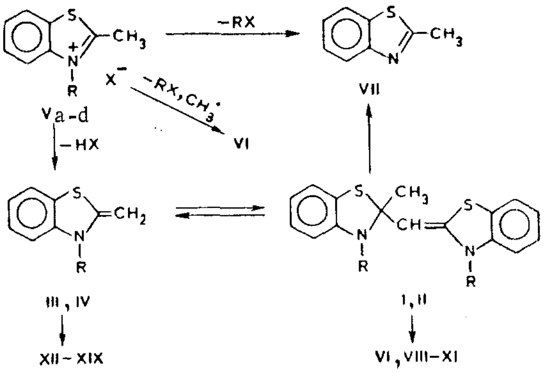


XIV R=R'=H; XV R=CH_3, R'=H; XVI R=R'=CH_3

The possibility of radical reactions is confirmed by the presence of ethane and traces of butane among the volatile products along with ethylene; the yield of ethane is three times the yield of ethylene.

One's attention is directed to the fact that the form of the chromatographic peak of 3-ethyl-2-methylenebenzothiazoline (IV) depends markedly on the temperature of the chromatographic column (Fig. 1). Thus, whereas it has the normal configuration when the temperature of the thermostat of the chromatograph is 180°C, when the temperature is lowered, the peak of thiazoline IV begins to broaden and at 120°C takes on the form of a sloping straight line. This phenomenon can be explained by the fact that monomeric methylene base IV exists in the chromatographic column in equilibrium with dimer II; the position of the equilibrium is determined by the temperature. The possibility of the decomposition of dimer II as it moves through the column also leads to anomalous character of its chromatographic signal. Similar thermal fragmentation principles were also obtained in the case of the 2-methylene-3-methylbenzothiazoline dimer (I). The thermal destruction of 2,3-dimethyl- and 2-methyl-3-ethylbenzothiazolium halides V leads primarily to the formation of 2-methylbenzothiazole (VII) and alkyl halides. In addition, we observed the same compounds as those observed in the pyrolysis of I and II, although in considerably smaller amounts. This constitutes evidence that methylene bases I and II are formed in the pyrolysis of quaternary salts V. On passing from the chloride to the bromide and iodide their relative percentages decrease markedly (see Table 1). In analogy with [10], this can be explained by the fact that in the intimate ion pairs of quaternary salts V the degree of transfer of the negative charge from the anion to the cation increases successively in the order $\overline{Cl} < \overline{Br} < \overline{I}$. In this connection, the proton of the methyl group in the 2 position is eliminated more readily during pyrolysis in the case of the chloride but with greater difficulty on passing to the bromide and iodide.

Thus the thermal destruction of quaternary salts Va-d ($X = \overline{Cl}, \overline{Br}, \overline{I}$) proceeds via the scheme



The thermal destruction of 2-methyl-3-ethylbenzothiazolium perchlorate (Ve, $X = \overline{ClO_4}$, $R = C_2H_5$) proceeds specifically, and the relative amount of the benzothiazole in the volatile products increases markedly (by a factor of 100) as compared with Vd ($X = \overline{I}$, $R = C_2H_5$), and methane and ethyl chloride are formed. This fact is evidently explained by homolytic cleavage of the ClO_4 ion and subsequent radical splitting out of a methyl group from the 2 position of the benzothiazole ring.

EXPERIMENTAL

Compounds I and II were synthesized by the method in [6], and VIII and X were synthesized by the method in [4]. Compounds IX and XI were similarly obtained. Compounds XII, XIII, and XVII were synthesized by the method in [7]. Compounds XIV-XVI, XVIII, and XIX were similarly obtained. Chromatography was carried out with a Chrom 3-IKZ chromatograph with a pyrolytic adapter and a flame-ionization detector. The pyrolysis temperature was 300°C.

The following conditions were used for analysis of the hydrocarbon fraction of the pyrolyzate: the column (l = 3 m, d = 0.3 cm) was filled with Porapak "Q" (60-80 mesh), the thermostat temperature was 40°C, and the carrier-gas (nitrogen) flow rate was 20 ml/min.

The following conditions were used for the analysis of the high-boiling fraction of the pyrolyzate: The column (l = 2 m, d = 0.3 cm) was packed with Cellite-545 (50-60 mesh) as the solid support, the stationary phases were Apiezon L (15% of the mass of the packing) (1) and polyethylene glycol 20M (15% of the mass of the packing) (2), the thermostat temperature was 130°C, and the carrier-gas (nitrogen) flow rate was 20 ml/min. The individual compounds were accumulated with a Chrom 3-IKZ chromatograph by means of a preparative adapter. The mass spectra were measured with a Varian MAT-311A spectrometer with direct introduction of the samples into the ion source at ionizing voltages of 70 and 20 eV. The chromatographic mass spectra were measured with an MAT-311A spectrometer with a Varian Aerograph-3700 chromatograph, a 0.25-mm long capillary column; the phase was OV-101, the injector temperature was 300°C, the column temperature was 80-220°C, the heating rate was 10°C/min, the carrier-gas (helium) flow rate was 2 ml/min, the ionizing-electron energy was 70 eV, and the temperature of the source was 150°C. The UV spectra of solutions of the compounds in hexane were measured with a Hitachi EPS-3T spectrometer. The PMR spectra of solutions of the compounds in carbon tetrachloride were recorded with an XL-100 spectrometer.

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INVESTIGATION OF THE PATHWAYS OF THERMAL FRAGMENTATION OF THIACARBOCYANINE DYES

V. G. Khesin, M. A. Al'perovich,
and P. I. Abramenko

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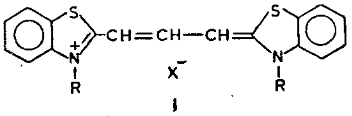
The pathways of the thermal transformations of thiacarbocyanines with various alkyl groups attached to the ring nitrogen atoms of the heteroresidues, of 3,3'-diethylthiacarbocyanine with various anions, and its anhydro base were investigated. The results of the studies are compared with the results of quantum-chemical calculations of the labilities of the bonds in these compounds by the Pariser—Parr—Pople method.

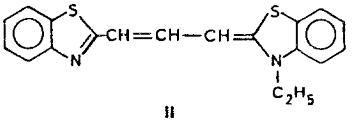
It is known [1, 2] that at high temperatures carbocyanine dyes undergo dealkylation to give anhydro bases. It has also been shown [3] that the corresponding symmetrical dyes are formed in the pyrolysis of unsymmetrical carbocyanines, whereas 2-methylbenzothiazole is detected among the volatile products of the pyrolysis of 3,3'-diethylthiacarbocyanine iodide (I, R = C_2H_5, $\bar{X}$ = $\bar{I}$).



I

It should be noted that the gas—liquid chromatogram of I contains, in addition to a peak of 2-methylbenzothiazole, peaks of other compounds; however, the latter were not identified [3].

In the present research we continued our study of the pathways of the thermal transformations of thiacarbocyanine dyes. It seemed of interest to ascertain whether thermal dealkylation at 300°C and atmospheric pressure is the primary act in the fragmentation, as under mass-spectrometric conditions [2], or whether processes involving cleavage of the C—C bonds of the polymethine chain compete with this reaction.



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