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Reaction of *N-tert*-butyl-2-benzothiazolesulphenamide with acetic anhydride in the presence of acids II. Spectral studies

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Abstract

The reaction of *N-tert*-butyl-2-benzothiazolesulphenamide with acetic anhydride catalyzed by acetic acid in a nonpolar solvent has been studied by NMR, GC–MS and EPR techniques. In the catalytic process homolytic decomposition of *N-tert*-butyl-2-benzothiazolesulphenamide prevails over the heterolytic pathway which is typical for uncatalyzed reaction. Besides the typical products formed during the uncatalyzed reaction, in the acid catalyzed process products formed by recombination of radicals were confirmed by ^{13}C NMR and mass spectroscopy. In the formation of TBbisBS by homolytic pathway *N*,*N*′-dialkylhydrazine radicals and $RNH^{\bullet}$ radicals, produced by decomposition of *N*,*N*′-dialkylhydrazine, play probably an important role.

Keywords: *N-tert*-butyl-2-benzothiazolesulphenamides; *Tert*-butylbis(2-benzothiazolyl-sulphen)amide; Acetic anhydride; Acetic acid; NMR; GC–MS; EPR spectra

1. Introduction

In our previous Part I [1] we have described the effect of various technological parameters on the reaction of some derivatives of *N*-alkyl-2-benzothiazolesulphen-amides with acetic anhydride in the excess of a non-polar solvent and in the presence of an acid, which acts as catalyst of the reaction. It was found out that the way of alkylbis(2-benzothiazolylsulphen)amide and alkylacetamide formation is different in the catalyzed and in the uncatalyzed reaction.

The main aim of this paper is to study the pathways of product formation in the acid catalyzed reaction of *N*-alkyl-2-benzothiazolesulphenamides with acetic anhydride by spectral techniques. Since the type of the alkyl group of a sulphenamide strongly influences the rate of formation of the corresponding bissulphenamide derivative, the experiments were performed with the *N-tert*-butyl-2-benzothiazolesulphenamide derivative which reacts at moderate rate.

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2. Experimental

2.1. Materials

N-tert-butyl-2-benzothiazolesulphenamide (TBBS, Monsanto), *tert*-butylbis(2-benzothiazolylsulphen) amide (TBbisBS, Monsanto), 2,2′-dithiobisbenzothiazole (MBTS, Istrochem) and benzothiazole (BT, Aldrich) (Fig. 1) were commercial products. TBBS was purified by crystallization from an ethanol — water solution and TBbisBS from diethyl ether. MBTS was purified by washing with acetone. Benzothiazole was freshly distilled under vacuum. *N-tert*-butylacetamide (TBAA) was prepared from *tert*-butylamine (TBA) and acetic anhydride (Ac_2O). The purity of all materials was checked by HPLC and NMR spectroscopy.

5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO), purchased from Aldrich (USA), was freshly distilled at 75°C and 66 Pa. The colorless liquid was stored at −25°C under argon. Other chemicals were analytical grade purity.

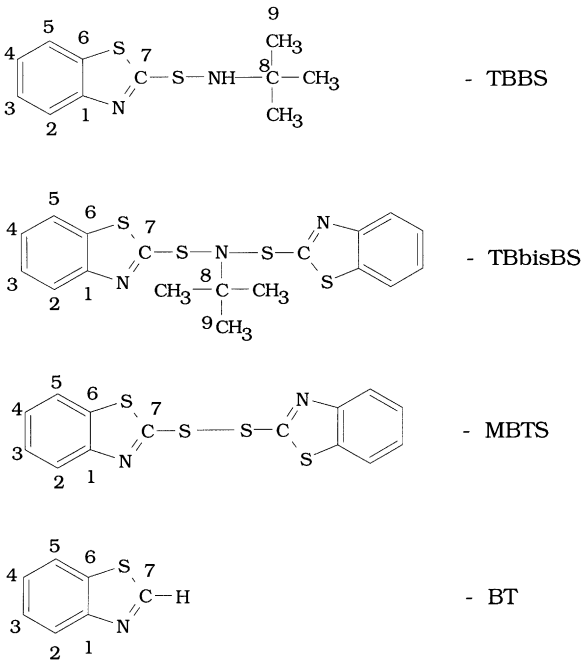


Fig. 1. Derivatives of 2-benzothiazolesulphenamide.

2.2. NMR spectroscopy

Standard ^{1}H, ^{13}C and ^{13}C-ATP spectra were measured using a Varian VXR-300 spectrometer with an operating frequency of 300 MHz for protons and 75 MHz for carbons. For some samples, additional H,H and one-bond or long H,C correlation NMR experiments were performed. Samples were dissolved in $CDCl_3$ at the concentration 50 mg cm^{-3}.

2.3. EPR spectroscopy

The same reaction conditions as in the chemical experiments were used for EPR measurements. A sample with the reaction components was saturated with argon, put into a capillary tube and then placed into the cavity of a Bruker 200D spectrometer (Germany), equipped with a field frequency lock and coupled to an Aspect 2000 computer. The temperature was kept at 295 or 323 K. The same procedure was repeated adding DMPO as a spin trap to the sample.

2.4. GC–MS

Before analysis, a liquid reaction mixture was neutralized with a 0.5 M aqueous solution of NaOH and extracted into *n*-hexane. The extract was analyzed using GC–MS 25 RFA (Kratos, Manchester). The compounds were separated on a fused-silica capillary column CP-Sil 8 CB (25 m × 0.32 mm i.d., 0.12 μm) with a chemically bonded phase (Chrompack). The initial temperature of the column during the first minute was 40°C and then the linear gradient 8°C min^{-1} was used up to 220°C. The flow-rate of the carrier gas, helium, was 1 cm^3 min^{-1}. The injector temperature was 240°C and 1 μl of the sample was injected using a splitter 50:1. MS, electron impact ionization by the source temperature 220°C, the electron energy 70 eV and the scan speed 0.6 s/decade were used.

2.5. Procedure

The apparatus, experimental procedure and analysis of the reaction products are described in Part I [1]. Some additional samples were prepared to study the formation of the reaction products in the presence of

a spin trap (DMPO) by NMR technique. The experiments were carried out in an intensively stirred 3 cm^3 glass reactor at a temperature of 60°C and a molar ratio of TBBS:Ac_2O:AcOH = 1:0.5:5, similarly as it is described in Part I. However, before the addition of the mixture of acetic anhydride and acetic acid (in the volumetric ratio 1:4), the spin trap was injected into the solution in the molar ratio of TBBS:DMPO = 4:1. At defined time intervals the reactor was quickly cooled to −10°C and the reaction mixture analyzed.

3. Results

3.1. NMR measurements

The reaction of TBBS with Ac_2O in the excess of an *n*-heptane — $CDCl_3$ solution and in the presence of AcOH as catalyst was studied by NMR spectroscopy. Although sulphenamides are common materials their complete NMR spectral data are rare [2]. For the identification and semiquantitative analysis of the main reaction components containing the benzothiazolyl group, the ^{13}C NMR technique was used [3]. Chemical shifts of these compounds obtained experimentally are summarized in Table 1.

In agreement with Ignatov et al. [4] the uncatalyzed reaction of TBBS with acetic anhydride produces TBbisBS, MBTS and TBAA as the main products. When a mixture of acetic acid and acetic anhydride is injected into the solution of TBBS in *n*-heptane, lines characteristic for BT appear in the spectrum (Fig. 2). Similar components were detected in the reaction mixture also in the absence of acetic anhydride, but in the presence of acetic acid. However, under these conditions the amount of formed TBbisBS was significantly lower as a result of its partial transformation to MBTS. This transformation was confirmed by an experiment, where TBbisBS (0.5 mol) dissolved in acetic acid (33.3 mol) at a temperature of 80°C was completely converted to MBTS during 1 h.

Table 1
^{13}C chemical shifts of the identified compounds[a]

C_i/compound[b]	TBBS	TBbisBS	MBTS	BT
C_1	155.0	153.5	154.4	153.0
C_2	121.5	121.2	121.2	121.8
C_3	123.5	124.5	125.3	125.7
C_4	125.8	126.25	126.5	126.3
C_5	120.9	122.2	122.5	123.1
C_6	134.4	135.1	135.8	133.0
C_7	181.6	173.2	167.1	155.1
C_8	55.5	69.1	–	–
C_9	28.7	29.2	–	–

[a] In ppm relative to TMS.
[b] For the numbering of carbons see Fig. 1.

In an effort to investigate the course of the reaction of TBBS with Ac_2O in the presence of AcOH the carbon spectra of the reaction mixtures were measured after the reaction was stopped at a defined time. From the spectra summarised in Fig. 2 it is evident, that BT is a relatively stable reaction product formed already at the initial stage of the reaction. Its concentration is practically constant after 15 min of the reaction. However, the intensity of ^{13}C signals of MBTS present in the reaction mixture during first 15 min of the reaction increases and then decreases almost proportionally with the formation of TBbisBS. This indicates that MBTS is an intermediate product of the reaction.

The changes in the region corresponding to the NMR spectral lines of aliphatic groups are more complex. Only strong signals belonging to the *tert*-butyl group of TBBS and TBbisBS were clearly resolved. The weak signals of methyl groups belonging to the protonated salt of *tert*-butylamine with acetic acid, TBAA and other unknown compounds were not clearly resolved. Therefore, the formation of these compounds was investigated by mass spectrometry.

3.2. Mass spectrometry

The combination of gas chromatography and mass spectrometry was used for the identification of reaction products which contain mainly aliphatic groups. The presence of *tert*-butylamine, BT, TBAA, TBBS, di-*tert*-butyldiazene and *N*-acetyl-*N*-*tert*-butyl-2-benzothiazolesulphenamide in an *n*-hexane solution of the reaction mixture was confirmed on the basis of their mass spectral analysis and data available in the literature [6]. The mass spectra of some other reaction products which were not found in the literature were interpreted as follows.

The first unknown compound present in the reaction mixture has a very simple spectrum (Fig. 3) with a predominant appearance of an ion at *m*/*z* 57, which

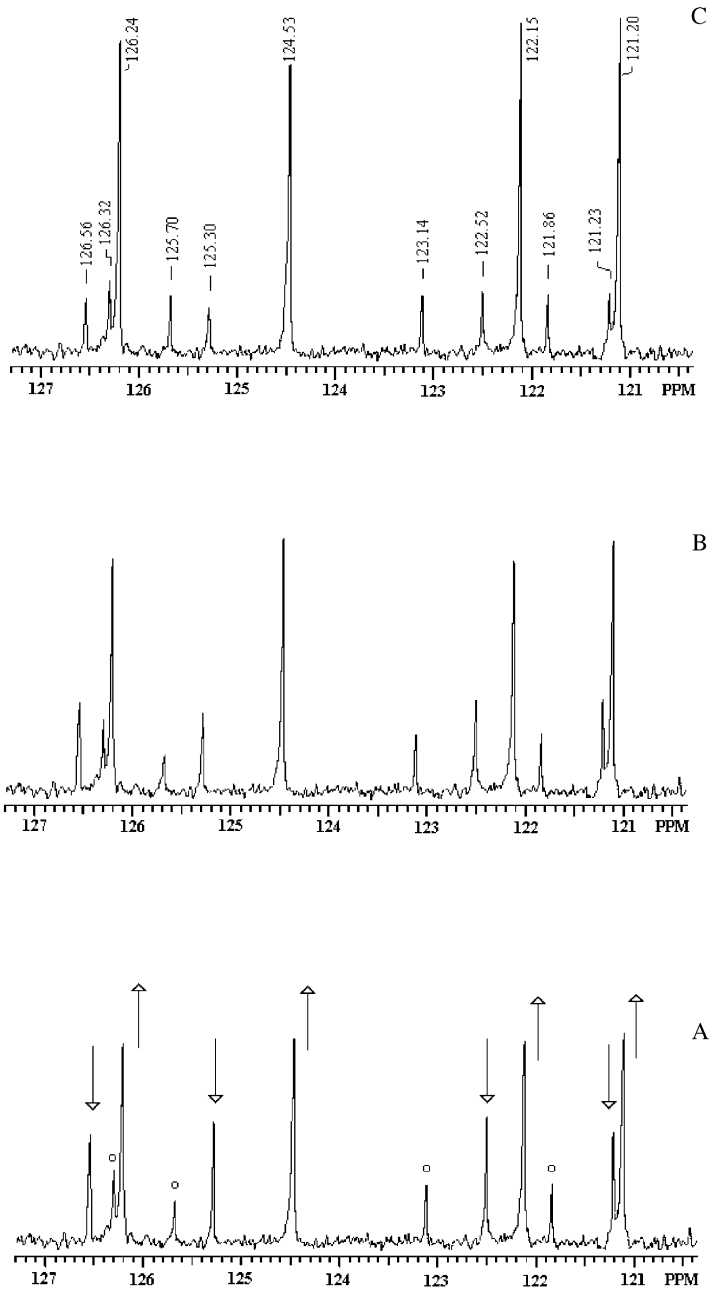


Fig. 2. Part of ^{13}C NMR spectra of the reaction mixture in the presence of acetic acid after: A — 15 min; B — 30 min and C — 60 min of the reaction ((○): BT; (↑): TBbisBS; (↓): MBTS).

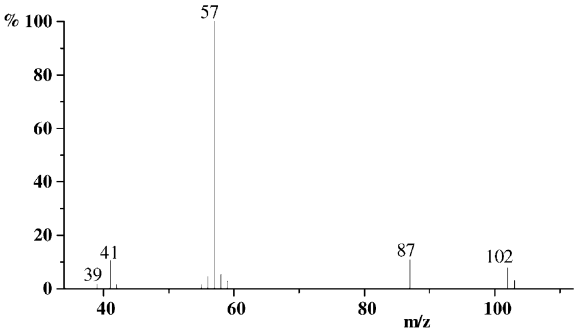


Fig. 3. Mass spectrum of the compound interpreted as *N*-methyl-*N′-tert*-butylhydrazine.

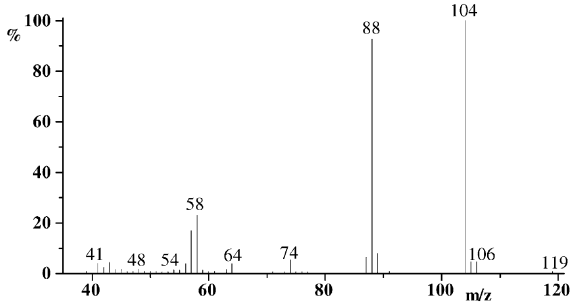
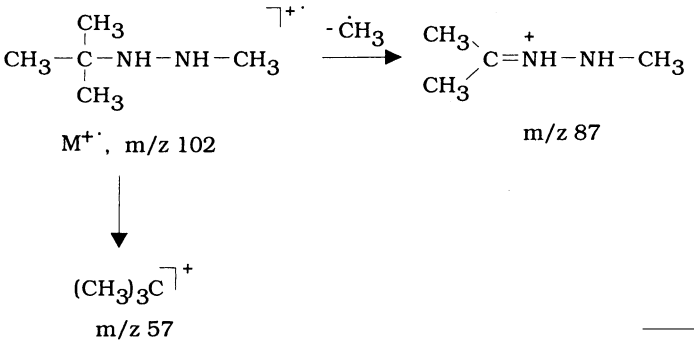


Fig. 4. Mass spectrum of the compound interpreted as *N-tert*-butylaminothioamine.

is probably $(CH_3)_3C^+$. The molecular ion at *m/z* 102 shows an intensive isotopic contribution $(M + 1)^+$. It can be formed by the addition of a proton to the lone electron pair of nitrogen atoms in the molecular ion. The fragmentation pathway of this compound, which is probably *N*-methyl-*N′-tert*-butylhydrazine, may be illustrated as follows:



The base peak at *m/z* 104 in the mass spectrum of the next unknown compound (Fig. 4) has probably the structure $[(CH_3)_3C–NHS]^{\bullet+}$. When this intermediate product losses two methyl groups and is rearranged the fragment ion $CH_2 = CHNHS^{\bullet+}$ corresponding to *m/z* 74 is formed. The presence of the *tert*-butyl group is confirmed by the presence of the fragment ions in the spectrum at *m/z* 57 and *m/z* 58. We suppose that the loss of a proton from the molecular ion at *m/z* 120 results the formation of a slight peak observed at *m/z* 119. In the field of fragments with lower masses, the ion at *m/z* 64 corresponds to $(H_2N–S–NH_2)^{\bullet+}$. The fragment at *m/z* 88 does not contain a sulfur atom. Its formation can be explained by a straight expulsion of a sulfur atom from the molecular ion. On the basis of these facts we suggest that the studied compound is $(CH_3)_3C–NH–S–NH_2$.

Another unknown reaction product is probably $(CH_3)_3C–NH–S–CH_3$. It has a very similar spectrum as the previous compound (Fig. 5). The molecular

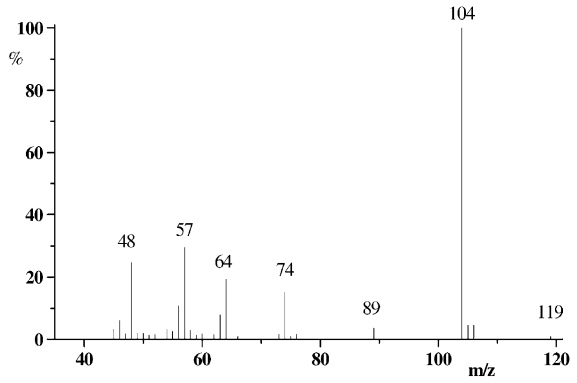


Fig. 5. Mass spectrum of the unknown compound interpreted as *N-tert*-butylmethane-sulphenamide.

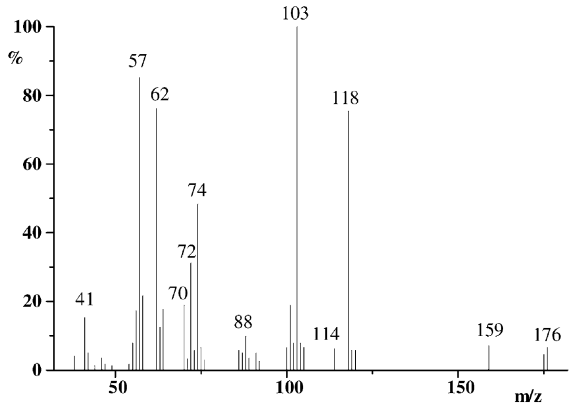


Fig. 6. Mass spectrum of the unknown compound interpreted as *N*,*N*-bis(*tert*-butyl)-aminothioamine.

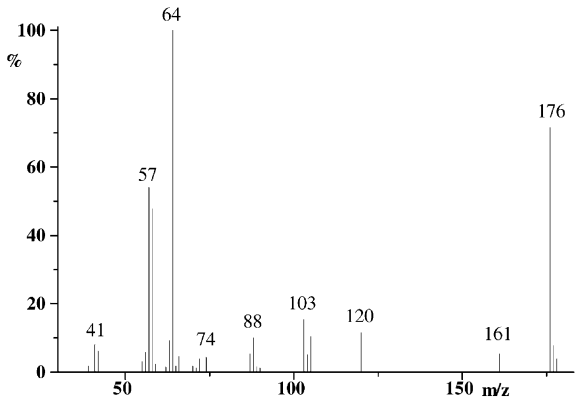
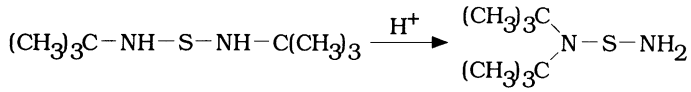


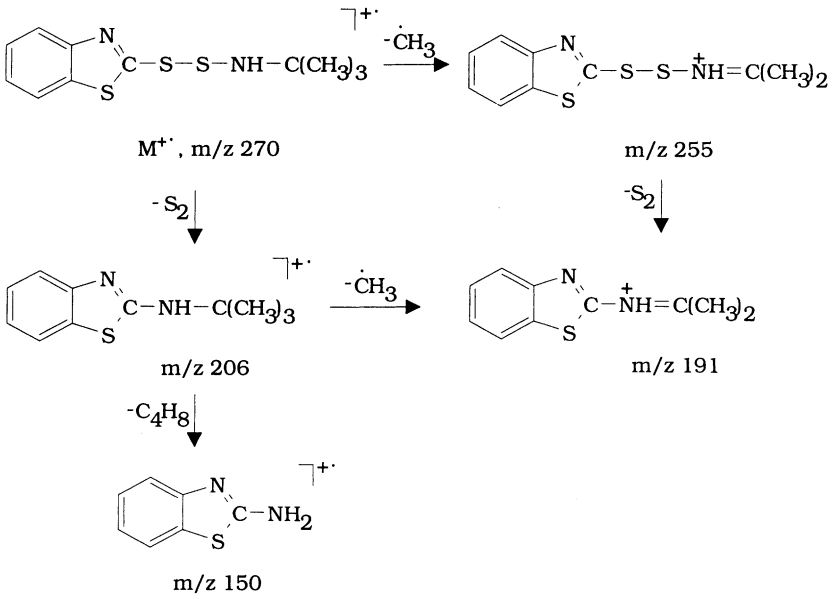
Fig. 7. Mass spectrum of synthesized *N*,*N*′-bis(*tert*-butylamino)-sulphide.

ion corresponding to *m*/*z* 119 indicates the presence of one nitrogen atom in this compound. From the abundance of isotopes accompanying the fragment at *m*/*z* 104 follows that it contains a sulfur atom. The ion at *m*/*z* 48 can be $(CH_3–SH)^{\bullet+}$. A consecutive loss of $CH_3^{\bullet}$ radicals from the molecular ion yields the fragments at *m*/*z* 104, 89 and 74. The cleavage of the C–N bond leads to formation of the *tert*-butyl ion $(CH_3)_3C^+$ at *m*/*z* 57.

The molecular ion of another studied compound appears at *m*/*z* 176 (Fig. 6). The fragment at *m*/*z* 57 indicates the presence of the ion $(CH_3)_3C^+$. In the fragments at *m*/*z* 103 and *m*/*z* 118 one sulfur atom is observed. The loss of the *tert*-butyl group from the ion at *m*/*z* 175 and the molecule of *iso*-butene (C_4H_8) explains the formation of the ions at *m*/*z* 118 and *m*/*z* 62, respectively. The composition of the main fragments suggests, that the molecular ion of the investigated compound at *m*/*z* 176 contains two nitrogen atoms, one sulfur atom and two *tert*-butyl groups. This compound is created by recombination of two non-aromatic radicals formed by the decomposition of TBBS, probably $(CH_3)_3CNH^{\bullet}$ and $^{\bullet}SNHC(CH_3)_3$. This assumption was confirmed by mass spectrometric analysis of the synthesized [7] *N*,*N*′-bis(*tert*-butylamino)sulphide ($(CH_3)_3C–NH–S–NH–C(CH_3)_3$) (Fig. 7). Since the observed spectra of the two mentioned compounds are different (Figs. 6 and 7), the stability of *N*,*N*′-bis(*tert*-butylamino)-sulphide was studied under the reaction conditions in the absence of TBBS. It was found that in the presence of acetic acid, *N*,*N*′-bis(*tert*-butylamino)sulphide very rapidly rearranges to *N*,*N*-bis(*tert*-butyl)aminothioamine. The mass spectrum of the formed compound is the same as the spectrum of the investigated compound, present in the reaction mixture (Fig. 6). From these measurements it is evident, that the unknown compound is a structural isomer of the prepared *N*,*N*′-bis(*tert*-butylamino)sulphide:



Another compound formed as a by-product during the acid catalyzed reaction of sulphenamides with acetic anhydride is *N*-*tert*-butyl-2-benzothiazoledisulphenamide. The molecular ion of this compound is observed at *m*/*z* 270 and the base peak at *m*/*z* 57 (Fig. 8). Loss of the $^{\bullet}CH_3$ group gives an intensive fragment at *m*/*z* 255. Formation of fragments at *m*/*z* 191 and 206 can be explained by a straight expulsion of S_2 from the molecular ion and from the fragment at *m*/*z* 255.



The fragment corresponding to *m/z* 150 is formed by loss of C_4H_8 from the fragment at *m/z* 206. The fragment at *m/z* 134 is created from benzothiazole nucleous. The other significant ions present in the spectrum of *N-tert*-butyl-2-benzothiazoledisulphenamide belong to the fragmentation of benzothiazole radical and are present also in the spectrum of TBBS.

3.3. EPR measurements

The EPR spectra registered during the reaction of TBBS with acetic anhydride and acetic acid in *n*-heptane as a solvent are summarised in Fig. 9a. Generally, the concentration of radicals is very low, but already at ambient temperature a radical centred at $g = 2.0010$ is present. With increasing temperature to 323 K the concentration of radicals significantly increases after 60 s and then gradually drops after few minutes. The high *g*-value is characteristic for sulphur centred radicals which have a very limited stability. Their stationary concentration is low and from their hyperfine structure no further information can be obtained.

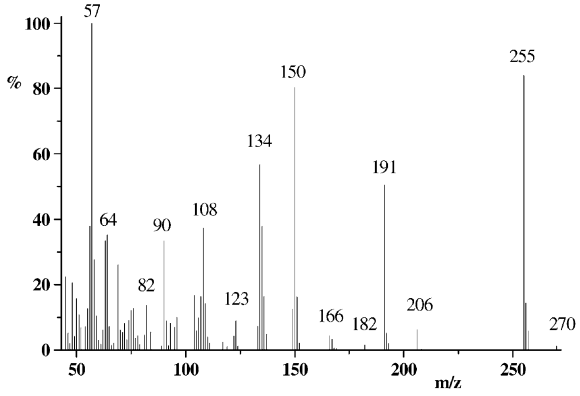
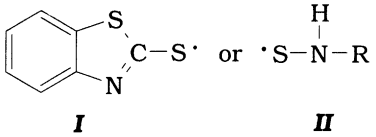


Fig. 8. Mass spectrum of the compound interpreted as *N-tert*-butyl-2-benzothiazole-disulhpenamide.

A more detailed information about the radicals was obtained using a DMPO spin trap. The same experiments done in the presence of 0.01 M DMPO leads to EPR spectra shown in Fig. 9b. The *g*-value 2.0057, splitting constants $a_{N(NO)} = 1.43$ mT and $a_H = 1.62$ mT correspond to the sulfur-centered radicals very well.

By decomposition of TBBS two types of sulfur centered radicals may be formed:



I **II**

From the available experimental data an unambiguous assignment of the EPR spectra to radical I or II is

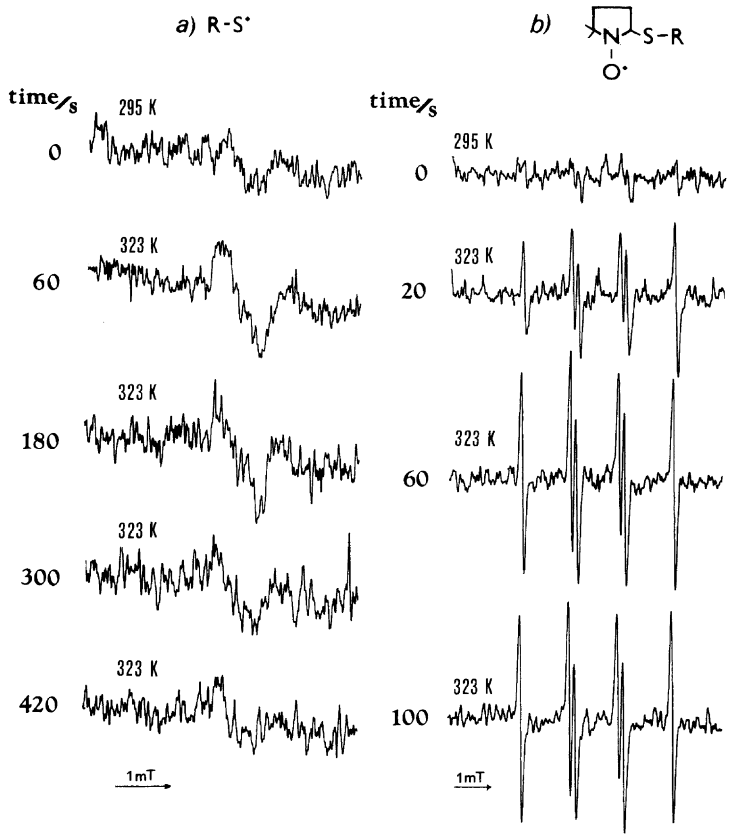


Fig. 9. Time dependence of EPR spectra observed at 323 K during the reaction of TBBS with acetic anhydride and acetic acid in *n*-heptane as a solvent: (a) without and (b) in the presence of a spin trap.

not possible. An additional information about radical I was obtained from photochemically initiated decomposition of MBT and MBTS which preferably generates this type of radicals [8]. However, slightly different values of the splitting constants of the obtained products implies that during the reaction probably radicals II are formed.

The NMR analysis of reaction mixtures prepared at 60°C in the absence and presence of a spin trap (molar ratio of TBBS:DMPO = 4:1) but under reaction conditions has shown that in the presence of DMPO, expressively less MBTS and TBbisBS are formed. The conversion of TBBS was lower but Ac_2O was totally consumed. In the spectra of these reaction mixtures additional lines were observed in the region corresponding to the aromatic groups. Probably these correspond to the products of the reaction of DMPO with radicals containing an aromatic nucleus. The decrease of BT is negligible.

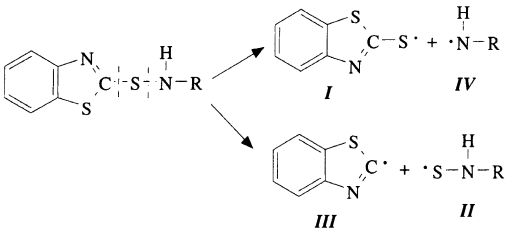
The presence of the spin trap during the reaction influences also the formation of *tert*-butylacetamide. The reaction in the presence of this spin trap leads nearly to an equimolar molar ratio of TBAA:TBbisBS, but in the absence of DMPO the amount of formed TBAA is significantly lower. It means that the presence of the spin trap results the formation of a similar molar ratio of TBAA:TBbisBS as the absence of acetic acid at the beginning of the reaction.

4. Discussion

In the previous Part I [1] was shown that the reaction of alkylBS with Ac_2O in a non-polar solvent

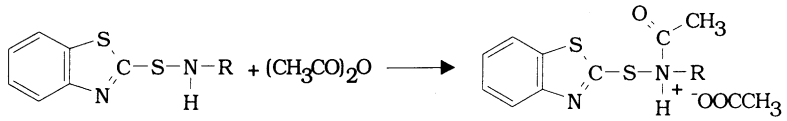
is strongly influenced by the presence of an acid acting as catalyst of the reaction. The way of formation of alkylbisBS and alkylacetamide is different in catalysed and uncatalysed processes.

In agreement with Ignatov et al. [4] in the uncatalysed process an acylated or protonated complex of alkylBS with decreased electron density on the sulfur atom reacts with the nucleophilic nitrogen atom of another molecule of alkylBS to form alkylbisBS and alkylAA in an equimolar ratio (reactions 1 and 2):

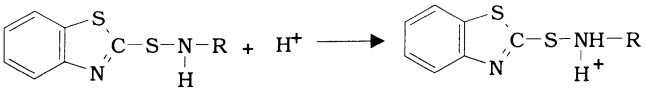


(4)

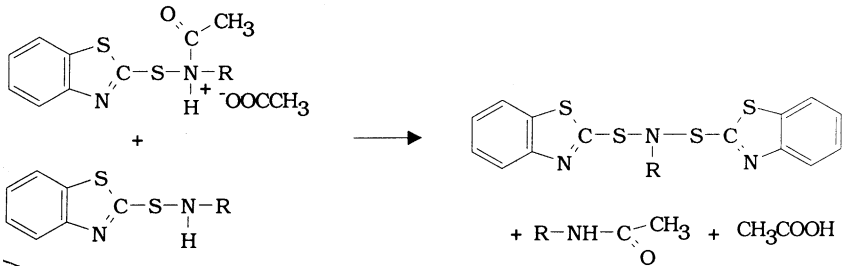
(5)



(1)



(2)

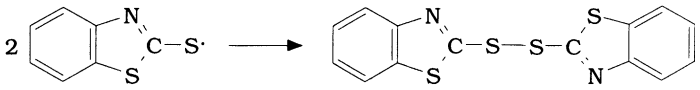


(3)

The protonated salt of *N*-acetyl-*N*-alkyl-2-benzothia zolesulphenamide, compound A, is formed also with acetic anhydride in the presence of acetic acid and in a non-polar solvent. This supports the formation of its neutralized derivative *N*-acetyl-*N*-*tert*-butyl-2-benzothiazolesulphenamide confirmed by the GC–MS method. In the presence of acids *N*-alkyl-2-benzothiazolesulphenamide is converted to its protonated salt, compound B. However, besides a heterolytic pathway of reaction of the protonated compounds A and B, also a homolytic reaction proceeds. In the first step of the homolytic reaction a competitive cleavage of C–S and S–N bonds yields four types of radicals:

The existence of radical II was registered by EPR (Fig. 9) and the formation of all four radicals was confirmed by two indirect observations: (i) experiments with the spin trap have shown that the rate of formation of recombination products is suppressed; (ii) products formed by recombination of the mentioned radicals were determined in the reaction mixture.

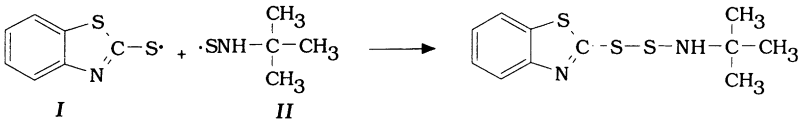
Recombination of radicals I leads to the formation of MBTS [9]:



It was observed experimentally that in the presence of the spin trap a very low amount of MBTS is formed.

The fast reaction of radical III with compounds containing weakly bonded hydrogen gives BT in particular at the first stage of the reaction. The lifetime of radical III is very short, after the addition of the spin trap into the reaction mixture the decrease of yield of BT was negligible.

Recombination of radical I with radical II gives *N*-*tert*-butyl-2-benzothiazole-disulphenamide which was observed in the reaction mixture in a small concentration (Fig. 8).



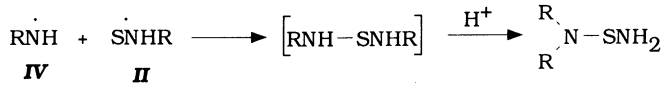
I *II*

Because at the beginning of the reaction the concentration of the formed MBTS is relatively high, from the material balance of the reaction (4) we can assume that a relatively large amount of radical IV is free for a further reaction.

Amazing is the fact that radical IV does not react with radical III because the product of this reaction was not found in the reaction mixture.

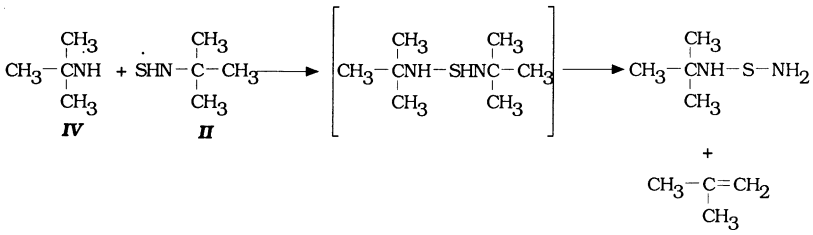
Theoretically by recombination of aliphatic radicals •SNHR and •NHR (radicals II and IV) compounds containing –HN–S–NH–, –HN–NH–, –NH–S–S–NH– groups may be formed.

It was confirmed experimentally, that *N*,*N*′-bis(*tert*-butylamino)sulphide, formed from radicals II and IV in the presence of AcOH is unstable and very rapidly rearranges to its structural isomer, *N*,*N*-bis-(*tert*-butyl)aminothioamine.



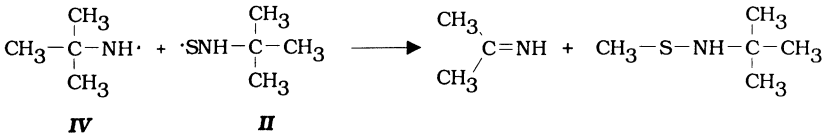
IV *II*

The steric hindrance of the relatively bulky *tert*-butyl group causes also its elimination in the form of *iso*-butylene [10] and gives *N*-*tert*-butylaminothioamine (Fig. 4).



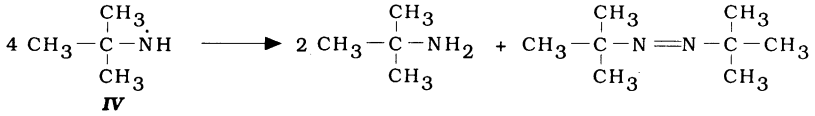
IV *II*

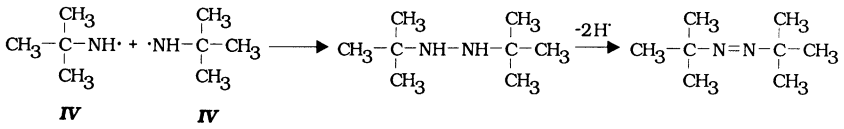
An alternative route for the recombination of radicals II and IV is the formation of $(CH_3)_3$ C–NH–S–CH_3 (Fig. 5).



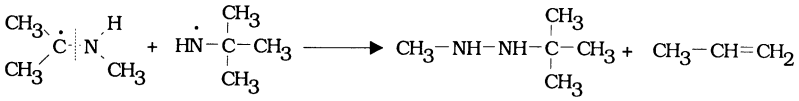
IV *II*

Radicals IV undergo not only a recombination, but also a parallel or consecutive oxidation which gives di-*tert*-butyldiazene and TBA experimentally found in the reaction mixture.



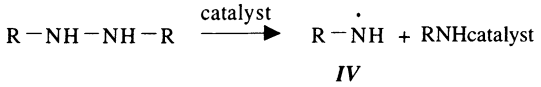


The presence of *N*,*N*′-ditert-butylhydrazine in the reaction mixture was not confirmed, however, the presence of its more volatile derivative, *N*-*tert*-butyl-*N*′-metylhydrazine, was determined in the reaction mixture by the GC–MS method (Fig. 3). This compound is probably the result of rearrangement of radical IV connected with a loss of propene. This process is thermodynamically convenient [11].

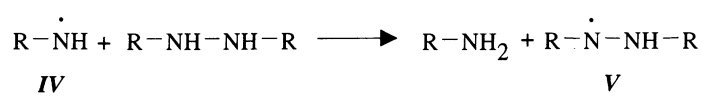


We assume that after a total conversion of TBBS, the intermediate compounds leading to the formation of TBbisBS and TBAA are MBTS, protonated compounds A or B and appropriate aliphatic compounds which contain –NH–NH– or –NH–S–NH– groups.

It is known [12] that in the presence of acid or base catalysts at increased temperature hydrazines can relatively easy form radicals.

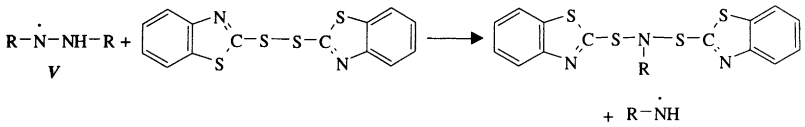


Radical IV with another molecule of dialkylhydrazine yields alkylamine and a dialkylhydrazine radical (radical V), which can also exist as a radical cation [13].



Tert-butylamine formed in this step, reacts with acetic anhydride to TBAA. This can explain the different molar ratio of TBAA and TBbisBS observed in catalyzed and uncatalyzed reactions [1].

Radical V is probably an important intermediate product which attacks the S–S bond in MBTS and gives TBbisBS.



The S–S bond of MBTS may also cleave radical IV which will formally lead to TBBS. However, under the studied reaction conditions it is a not typical way, because as it was experimentally observed, the conversion of TBBS remains total, when the yield of TBbisBS and TBAA still continuously increases.

MBTS reacts with TBA to an equilibrium formation of TBBS and a salt of 2-mercaptobenzothiazole with TBA [5]. However, under the studied reaction conditions only a salt of TBA with AcOH is formed and the amount of MBTS remains unchanged. As it was experimentally observed, the reaction of MBTS with TBA in AcOH does not lead to TBBS and TBbisBS formation.

From the obtained results we suggest that recombination of aliphatic radicals leads to the formation of a variety of reaction products. Isolation of individual reaction components from this mixture is complicated. For that reason reactions of these compounds with other compounds present in the reaction mixture were not investigated in detail.

5. Conclusions

The uncatalyzed reaction of *N*-*tert*-butyl-2-benzothiazolesulphenamide with acetic anhydride proceeds via a heterolytic pathway. In a nonpolar solvent and at sufficient concentration of acetic acid acting as catalyst, the reaction is preferable homolytic. Recombination of the formed radicals leads to the formation of MBTS, BT, *N*-*tert*-butyl-2-benzothiazoledisulphenamide, *N*-methyl-*N*′-*tert*-butylhydrazine, ditert-butyl-diazene, *N*-*tert*-butylaminothioamine, *N*,*N*-bis (*tert*-butyl)aminothioamine and *N*-*tert*-butyl-methanesulphenamide. In the formation of TBbisBS by a homolytic pathway probably *N*,*N*′-dialkylhydrazine radicals and $RNH^{\bullet}$ radicals, produced by decomposition of *N*,*N*′-dialkylhydrazine play an important role.

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