The Thermal Decomposition of Sulfenamide Accelerators

M. H. S. GRADWELL and W. J. MCGILL*

Polymer Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, South Africa

SYNOPSIS

The thermal decomposition of three sulfenamide accelerators *N*-cyclohexylbenzothiazole sulfenamide (CBS), 2-(4-morpholinothio)benzothiazole (MOR) and 2-*t*-butylaminobenzothiazole sulfenamide (TBBS) were investigated by differential scanning calorimetry. The sulfenamides decompose rapidly at 210–220°C, yielding a number of products, including reactive polysulfidic complexes. Thus, CBS gives *N*-cyclohexylamino-2-benzothiazole polysulfides (CBP), 2-bisbenzothiazole-2,2′-disulfide (MBTS), 2-bisbenzothiazole-2,2′-polysulfides (MBTP), 2-bisbenzothiazole-2,2′-monosulfide (MBTM), 2-mercaptobenzothiazole (MBT), and 2-*N*-cyclohexylaminobenzothiazole (CB). The polysulfides are unstable, and on prolonged heating, only MBT and CB remain. The amine fragment of the accelerator is present as the amine salt of MBT. At lower temperatures, the sulfenamides are relatively stable. MOR forms an analogous product spectrum. The decomposition of TBBS is endothermic, in contrast to the exothermic reaction observed with CBS and MOR, and the concentrations of the various polysulfides do not decrease on prolonged heating. Reaction mechanisms are proposed to account for the formation of the products. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

N-Cyclohexylbenzothiazole sulfenamide (CBS) is one of the most commonly used accelerators for sulfur vulcanization. Analogous accelerators of importance are 2-(4-morpholinothio)benzothiazole (MOR) and 2-*t*-butylbenzothiazole sulfenamide (TBBS). The accelerators melt in the region of 100°C but decompose only above 200°C.[1] Studies of the interactions of curatives in the absence of rubber have proved valuable in identifying reactions occurring in the scorch period and in highlighting the nature of the active sulfurating agent.[2–4] This article compares the complex spectrum of products that result on the thermal decomposition of CBS, MOR, and TBBS. Here, attention is paid largely to characterizing the products and to monitoring changes in the product spectrum as a function of degradation time. The interaction of these accelerators with curatives will be dealt with in a following article.

EXPERIMENTAL

The *N*-cyclohexylbenzothiazole sulfenamide (CBS), 2-(4-morpholinothio)benzothiazole (MOR), and 2-*t*-butylbenzothiazole sulfenamide (TBBS) used were produced by Bayer (Germany); the 2-bisbenzothiazole-2,2′-disulfide (MBTS), by Orchem (South Africa); and the 2-mercaptobenzothiazole (MBT), by Monsanto (Belgium).

Decomposition experiments were conducted at 5°C/min with a standard DuPont DSC cell with accelerators contained in sealed aluminum pans and mass loss experiments with a DuPont 951 thermogravimetric analyzer (TGA). The modules were connected to a DuPont 9000 thermal analyzer. High-purity nitrogen, at a flow rate of 20 cm^3/min, was used as a purge gas. The temperature calibration of the TGA was confirmed to be synchronized with that of the DSC by means of the dehydration pattern of copper sulfate pentahydrate. The procedures followed for the DSC decompositions, TLC,[3] and high-performance liquid chromatography (HPLC)[5] analyses of accelerators and products have been described. Dichloromethane/methanol (5/95 v/v ratio) was used as solvent for HPLC analysis.

* To whom correspondence should be addressed.

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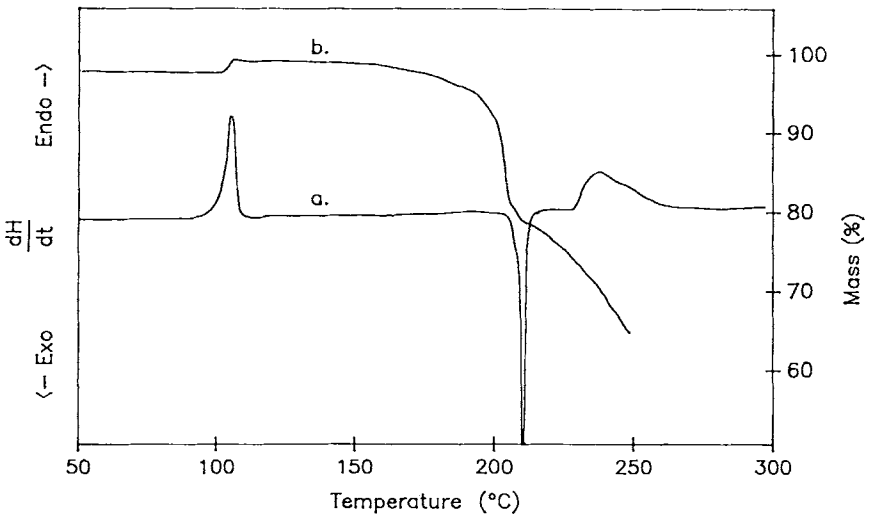


Figure 1 DSC thermogram: scan rate 5°C/min; (a) CBS, M_i = 10.5981 mg, M_f = 1.0810 mg. TGA thermogram: scan rate 5°C/min; (b) CBS, M_i = 21.504 mg.

Reaction products separated on TLC plates were identified by NMR and sulfur analysis. ^{1}H-NMR analysis of accelerators allowed the assignment of two complex series of signals to the phenyl ring (δ7.2–8.2) in the benzothiazole group, to the cyclohexyl ring (δ1–3 in CBS), or to the morpholino structure (δ3.6–3.9 in MOR). APT spectra and ^{13}C absorption further assisted in confirming the presence of these groups when they appeared in the NMR spectra of various intermediates and products. The Varian Gemini 200 Model NMR was operated at 200 MHz for proton spectra and at 50 MHz for ^{13}C spectra. Sulfur analysis of the accelerators and products was carried out using apparatus as set out by Haslam and Willis.[6] Samples were combusted in an oxygen combustion flask, dissolved in ethanol, and titrated with a barium perchlorate solution.[7]

RESULTS

DSC Thermograms

The DSC thermogram of CBS (Fig. 1) exhibits a melting endotherm at 105°C and shows decomposition occurring at 220°C. When the CBS is heated to above the melting point and is held at 120°C for

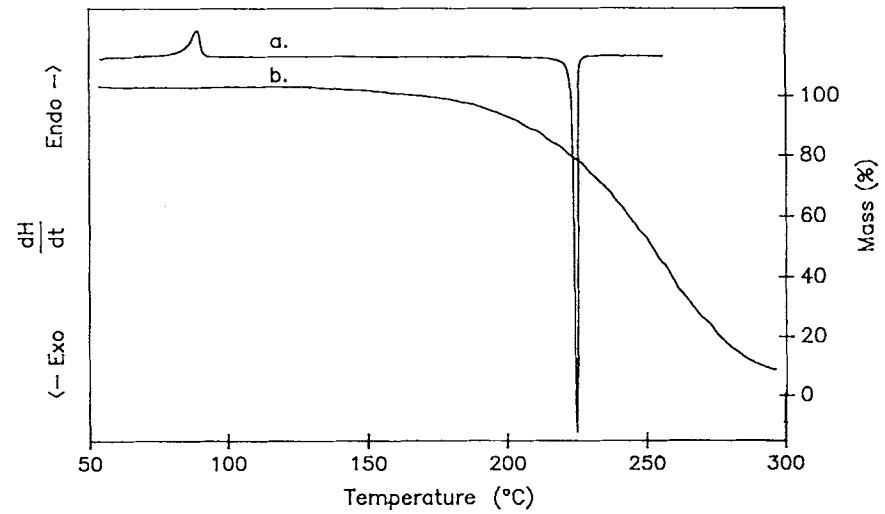


Figure 2 DSC thermogram: scan rate 5°C/min; (a) MOR, M_i = 11.606 mg, M_f = 9.721 mg. TGA thermogram: scan rate 5°C/min; (b) MOR, M_i = 18.961 mg.

15 min, no change occurs. This was verified by HPLC analysis. When the CBS sample is heated to 150°C and then stored at −30°C, it recrystallizes and again exhibits a melting endotherm at 105°C. Kok[1] obtained similar results, with melting occurring at 105°C and decomposition at 210°C. Banks and Wiseman[8] reported that CBS did decompose if held isothermally at 180°C, but only after an induction period of 60 min. This is much longer than the times involved in vulcanization.

The DSC thermogram of MOR shows that it melts at 85°C and decomposes exothermically at 219°C (Fig. 2), essentially the same temperature at which CBS decomposes. It is relatively stable below its decomposition temperature, but less so than CBS, which shows little decomposition prior to the rapid reaction at 220°C. A small conversion to MBTS takes place when heated to 185 or 200°C. A mass loss of 5.2% was found when MOR was heated to 200°C and 27 mol % decomposed to MBTS. MBTS is found as an impurity in unheated MOR [see later, Fig. 6(a)], suggesting a degradation of the sulfenamide as was shown by Leucken and Fath.[9]

When TBBS is heated in the DSC (Fig. 3), a melting endotherm is obtained at 112°C. Rapid decomposition occurs in the same temperature region as was found for CBS and MOR, viz., 210°C, but is accompanied by an endotherm, not an exotherm, as with other sulfenamides. As is the case with MOR, a slow decomposition to MBTS occurs below the decomposition temperature [see later, Fig. 7(a)].

TGA Thermograms

Heating in the TGA (Fig. 1) shows the slow evaporation of CBS from 175°C up to 220°C, where the CBS decomposes and the decomposition products evaporate rapidly. The TGA for MOR and TBBS (Figs. 2 and 3) show similar though greater mass losses that can also be attributed to the evaporation of reactants and volatile degradation products.

CBS Degradation Products

The products of the decomposition of CBS were analyzed by HPLC after a sample had been heated to 220°C [Fig. 4(d)]. No CBS remained but MBT and 2-*N*-cyclohexylaminobenzothiazole (CB) were detected. To identify the compound giving rise to peak 4 in the HPLC chromatogram, CBS was decomposed by heating to 220°C. The resinous products were separated on TLC plates and the bands lifted off the plates. An NMR analysis showed the product lifted off the band in question to contain both the cyclohexyl group (associated with the amine) and the phenyl group (associated with benzothiazole). Sulfur analysis of this compound is shown in Table I and allowed it to be identified as CB.

The CBS decomposition was stopped at various points along the DSC thermogram (Fig. 1) and HPLC analysis performed on these samples. When CBS starts to decompose at 205°C, MBTS, MBTP, MBT, and *N*-cyclohexylamino-2-benzothiazole

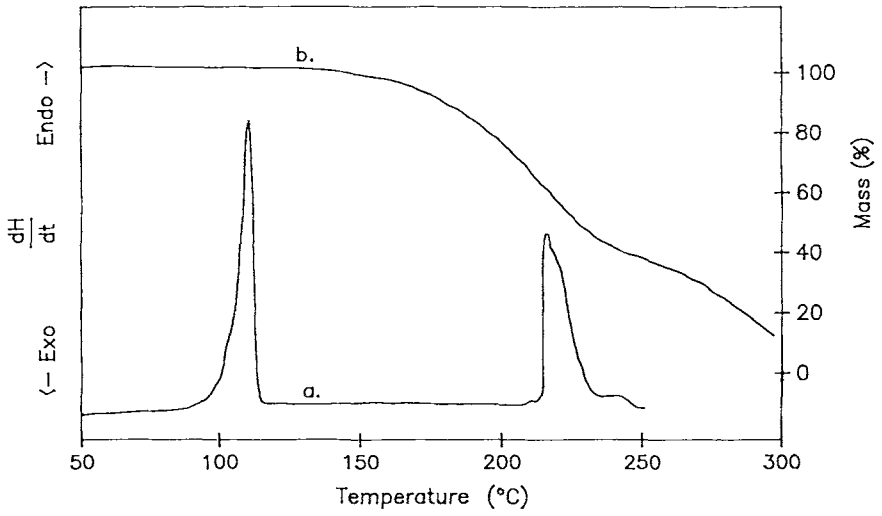


Figure 3 DSC thermogram: scan rate 5°C/min; (a) TBBS, M_i = 12.012 mg, M_f = 4.335 mg. TGA thermogram: scan rate 5°C/min; (b) TBBS, M_i = 25.664 mg.

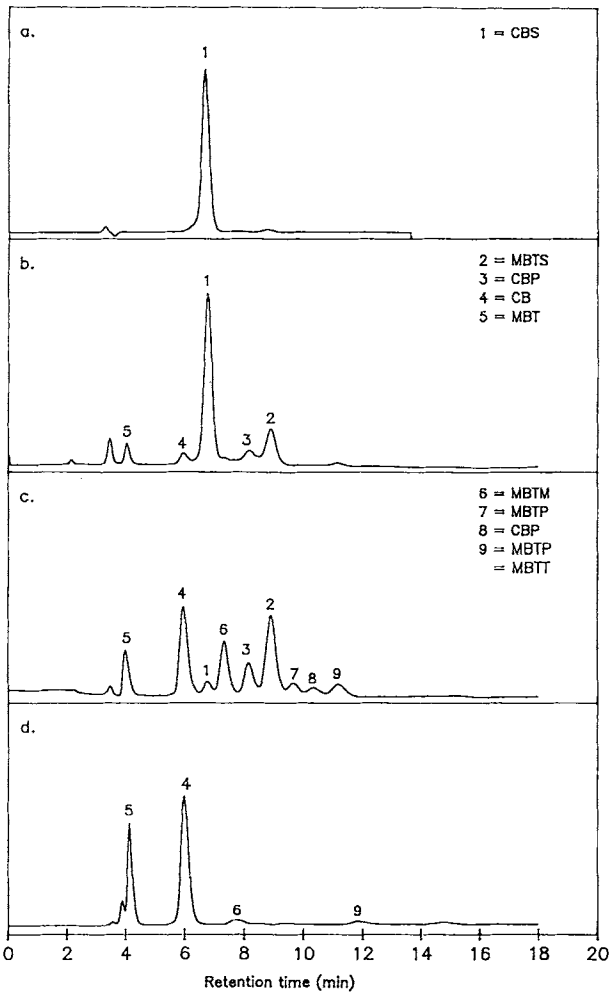


Figure 4 HPLC chromatogram: (a) Unheated CBS; (b) CBS heated in the DSC at 5°C/min to 204°C; (c) CBS heated in the DSC at 5°C/min to 205°C; (d) CBS heated to 220°C.

Table I Sulfur Determinations of Accelerators and Reaction Products

Compound	% Sulfur Theoretical	% Sulfur Found
MBT	38.3	39.4
MBTM	32.0	33.2
MBTS	38.6	39.7
CB	13.9	14.4
CBS	24.4	25.1
MB	14.6	13.9
MOR	25.4	24.7
MDB	33.8	33.2

polysulfides (CBP) of the type $BTSS_xNR$ and CB are formed. To identify the MBTPs, 2-bisbenzothiazole-2,2′-tetrasulfide (MBTT) was prepared by the method of Levi.[10] Sulfur monochloride (1.3 mL) and the zinc salt of 2-mercaptobenzothiazole (MBT), zinc mercaptobenzothiazole (ZMBT) (2.6 g), were reacted at room temperature in sodium-dried ether for 5 h. The reaction produces a series of 2-bisbenzothiazole-2,2′-polysulfides, a major component being the tetrasulfide, MBTT. The precipitate was dissolved in dichloromethane/methanol (5/95 v/v ratio) and injected into the HPLC. A series of peaks, similar to that reported by Campbell[11] was obtained (Fig. 5). The major peak 4 was attributed to MBTT whereas the peak occurring between MBTS and MBTT was assigned to the trisulfide. Peaks with longer retention times than MBTT were ascribed to higher polysulfides.

The retention times of these peaks were used in subsequent analyses. It was not possible to separate the tetrasulfide from the other components of the reaction mix for further analysis; it decomposed on TLC plates, giving rise to broad bands that, on lifting from the plates and injecting into the HPLC, gave a similar product spectrum to the original mixture. Analysis of the ether solution yielded a similar product spectrum to the precipitate. The compounds giving rise to peaks at 8 and 10.5 min (Fig. 4) could not be separated in sufficient quantity and purity to be analyzed and were thus not specifically identified, but, from their relative positions in the HPLC product spectrum and by analogy to the accelerator polysulfides of MBTS (recorded above) and MOR (see below), it is proposed that they represent polysulfides of CBS (i.e., CBP).

As decomposition progresses, the CBS concentration decreases and the MBTS and MBT concentrations increase. The CB peak becomes very prominent as the CBS disappears (Fig. 4). 2-Bisbenzo-

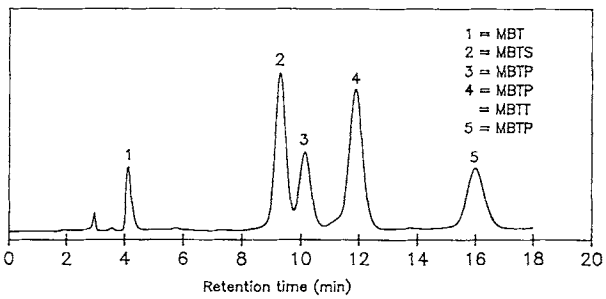


Figure 5 HPLC chromatogram: Analysis of the precipitate of the S_2Cl_2/ZMBT reaction.

thiazole-2,2'-monosulfide (MBTM) is formed from MBTS as the concentration of the latter builds up. MBTM used to identify peak 6 in the HPLC was synthesized according to the method of D'Amico et al.[12] MBT (45.1 g) was dissolved in benzene and 21 g of oxalyl chloride was added dropwise. The stirred reaction mixture was refluxed for 24 h (benzene bp 80.1°C). NMR analysis of the solid precipitate revealed the presence of the phenyl group only in the benzothiazole fragment. Sulfur analysis of the compound is in agreement with the sulfur content of MBTM (Table I). The retention time of the major peak obtained on injection of the compound into the HPLC was used to identify MBTM in subsequent analyses. A small peak due to unreacted MBT was observed.

Continued reaction sees the disappearance of MBTM and MBTS, and on prolonged heating, only MBT and CB remain. Banks and Wiseman[8] found that MBTS was a minor product of CBS decomposition. An examination of Figure 4 shows that it is the extent of reaction, or heating, that determines the amount of MBTS present. It is, however, not one of the final decomposition products. The fate of the amine fragment of the accelerator is dealt with in the Discussion.

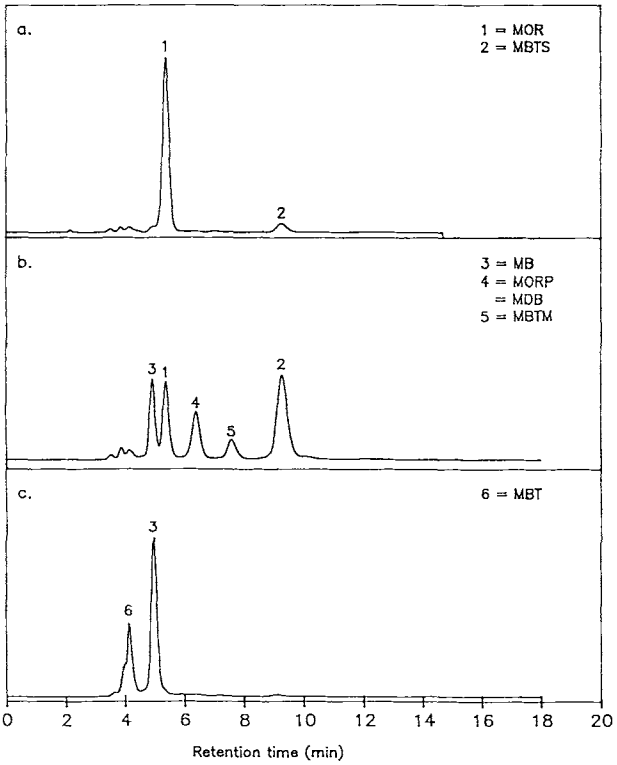


Figure 6 HPLC chromatogram: (a) unheated MOR; (b) MOR heated in the DSC at 5°C/min to 205°C; (c) MOR heated in the DSC at 5°C/min to 250°C.

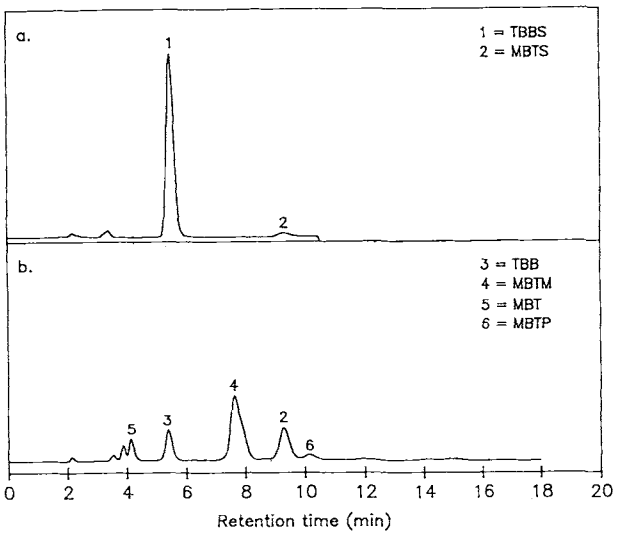


Figure 7 HPLC chromatogram: (a) unheated TBBS; (b) TBBS heated in the DSC at 5°C/min to 250°C.

MOR Degradation Products

HPLC analysis was conducted on samples of MOR heated to two temperatures. The important components in the product spectrum [Fig. 6(b)] are analogous to those found on heating CBS, viz., MBTS, MBTM, 2-morpholinobenzothiazole (MB), and a MOR disulfide 2-(4-morpholinodithio)benzothiazole (MDB). In the early stages of decomposition of MOR, only a trace amount of MBT is present. At the end of the decomposition exotherm, only MB and MBT are found, together with a small amount of MBTM. MB in the reaction mixture was separated by TLC, and NMR analysis of the relevant TLC band showed the presence of benzothiazole and morpholino groups.

Sulfur analysis supports the contention that the product is MB (Table I). MB has also been found to be a product of MDB heated to vulcanization temperatures.[13] Following Hardman,[14] MDB was prepared by heating MBTS and 4,4'-dithiomorpholine (1 : 1 mol ratio) in the DSC to 185°C. The reaction mix was dissolved in a dichloromethane/methanol (5/95 v/v ratio) and injected into the HPLC. A peak coinciding with the retention time for MBTS showed the presence of unreacted MBTS, whereas a small 2-(4-morpholinothio)benzothiazole (MOR) peak was also found. The major peak was attributed to MDB and its retention time was used

to identify MDB in subsequent analysis. NMR studies of the product separated from residual reactants by TLC revealed the presence of both benzothiazole (phenyl group) and the morpholino group. The sulfur content corresponds with that of MDB (Table I).

TBBS Degradation Products

HPLC analysis (Fig. 7) of the decomposition products of TBBS showed that it forms MBTS, MBTM, MBT, and a compound that, by its position on the chromatogram and by analogy to CBS and MOR, was attributed to 2-*t*-butylaminobenzothiazole (TBB). The amount of TBB formed was small and it could not be isolated as was done with the analogous product from CBS and MOR. Unlike with the other sulfenamides, large amounts of MBTS and MBTM are still evident at 250°C.

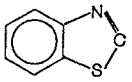
DISCUSSION

CBS is more stable than are MOR and TBBS, both of which decompose at measurable rates above 185°C. CBS, too, will decompose at this temperature, but only after a lengthy induction period.[8] All three sulfenamides decompose rapidly at 210–220°C, suggesting an identical initiation step, but in the case of TBBS, the overall reaction is endothermic; an exothermic process is obtained with CBS and MOR. The endotherm is quite small in magnitude compared to the exotherms.

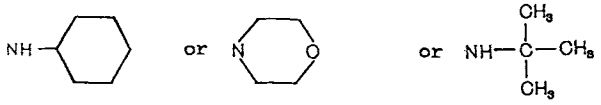
Most of the intermediates and final products of the degradation process in the three accelerators are similar or analogous, the major difference lying in the amine fragment. Amines are said to form on degradation of CBS and are trapped as the amine salt of MBT.[15] Should these amines escape from the system, the endotherm might be explained in terms of the rapid evaporation of the highly volatile *t*-butylamine liberated from TBBS (*t*-butylamine, bp 44°C;[16] morpholine, bp 128.3°C;[16] and cyclohexylamine, bp 134°C).[16] The overall mass loss at any temperature is greater in TBBS than with the other sulfenamides. However, various products are lost from the system and an HPLC analysis of volatiles trapped on decomposing CBS showed MBT as the major component, together with lesser amounts of sulfur and MBTS. TGA curves do not show a rapid change in the rate of mass loss at the decomposition temperature, which is surprising, and supports the idea that the amine fragment remains trapped. It appears more feasible to suggest that the endotherm is associated with differences in the reaction sequence following the initiation of degradation, as will be discussed below.

Decomposition exotherms are very narrow, indicating a rapid reaction as is also evidenced by the HPLC analysis of the system at temperatures close to the onset and completion of the exotherm in CBS; the CBS concentration is high in the first case and essentially nil in the second (Fig. 4). Dogadkin et al.[17] proposed that at vulcanization temperatures of 140–160°C *N*,*N*-diethyl-2-benzothiazole sulfenamide dissociates into benzothiazyl thiyl and diethylamine radicals. We suggest that scission of the weaker S—N bond in the sulfenamides would initiate the following reactions, which would explain the formation of CBP, MBTS, MBTM, and MBTP. The mechanism is similar to that suggested for MBTP and TMTP formation from MBTS and TMTD,[3,4] respectively:

$$XSNHR \leftrightarrow XS^{\cdot} + {}^{\cdot}NHR$$
$$XS^{\cdot} + {}^{\cdot}SX \leftrightarrow XSSX$$
$$XSSX \leftrightarrow X^{\cdot} + {}^{\cdot}SSX$$
$$XS^{\cdot} + X^{\cdot} \leftrightarrow XSX$$
$$XSS^{\cdot} + XSS^{\cdot} \leftrightarrow XSSSSX$$
$$XSS^{\cdot} + {}^{\cdot}NHR \leftrightarrow XSSNHR$$

where X = 

and NR =



The fate of the amine fragment is more difficult to follow as the species cannot be monitored by the ultraviolet detector of the HPLC. The following suggests that, in the early stages of decomposition, it may be present as the amine salt of MBT. CBP, MBTM, MBTS, and MBTP are intermediates of the degradation reaction; their concentrations initially increase and later decrease. In the vulcanization process, too, the concentrations of these products are found to pass through a maximum during the induction period.[18–20] The final degradation products are MBT and CB. CB cannot form from the above intermediates alone and there must clearly be an intermediate that contains the amine fragment. This species must react with and eliminate

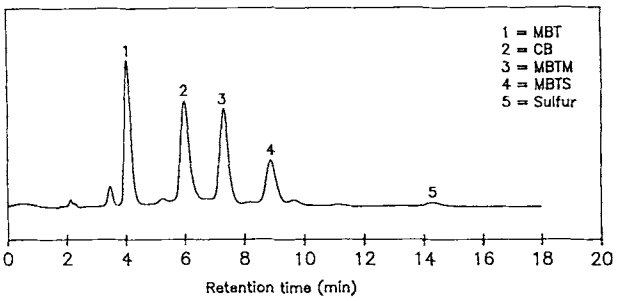
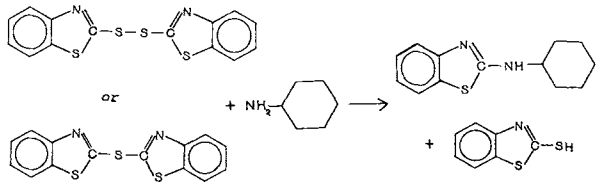


Figure 8 HPLC chromatogram: MBTS/cyclohexylamine mix heated to 150°C.

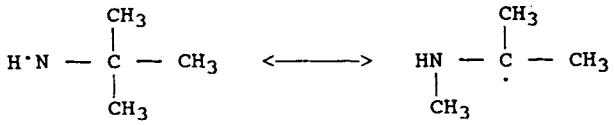
the MBTS derivatives. Cyclohexylamine is said to be a degradation product of CBS.[15] Some evidence for the formation of the amine salt of MBT is supplied by infrared studies. The infrared spectrum, in chloroform, of the decomposition products of CBS, heated to 220°C, shows three strong, well-defined peaks at 1598.8, 1546.6, and 1489.0 cm^{-1}. Amine salts[21] show an asymmetric NH_3^+ deformation in the 1625–1560 cm^{-1} region and a symmetric deformation at 1550–1505 cm^{-1} and these peaks may be indicative of the cyclohexylamine salt of MBT. NH stretching and deformation bands at 2800 and 2610 cm^{-1}, respectively, are present in the undecomposed CBS and cannot be used in identification.

On heating an MBTS/cyclohexylamine (1 : 1 mol ratio) mixture to 150°C, the formation of MBT, MBTM, and CB were observed (Fig. 8). MBTM is a major degradation product of MBTS decomposition[22] and it appears that CB results from either of the following reactions:



The reaction also accounts for the formation of MBT, which is the other final product. An analogous reaction would be the MDB reaction with morpholine to form the morpholine salt of MBT.[19] On degradation, MOR yielded a similar spectrum of intermediates, viz., MDB, MBTM, MBTS, and MBTP and final degradation products MBT and MB.

In contrast to CBS and MOR reactions, TBBS degradation was endothermic, as noted earlier. The intermediate product spectrum was analogous to that obtained with CBS and MOR, but there was essentially no change at longer degradation times. Very little TBB was formed. The tertiary butylamine radical, formed on scission of the S—N bond in TBBS, may readily rearrange to a more stable radical, reducing the amount of *t*-butylamine formed:



In this case the destruction of the MBTS derivatives and the formation of TBBS and MBT would be limited.

CONCLUSION

Although the sulfenamides decompose to give a range of reactive polysulfidic complexes (CBP, MDB, TBBP, MBTS, MBTP, etc.) that could couple to the polymer chain, thereby initiating crosslinking, these reactions occur at temperatures well above those of vulcanization (210–220°C). The formation of most products can be accounted for by mechanisms involving scission of the S—N bond in sulfenamides and the S—S or S—X bond in MBTS and its derivatives. Monosulfidic complexes are thermally more stable and their concentrations build up as the reaction progresses. The final degradation products are CB (or MB) and MBT and these result from the action of the amine on MBTM or MBTS. The decomposition of TBBS differs in that the decomposition reaction is endothermic and the concentrations of MBTM, MBTS, and TBBP remain high. This is attributed to the ready rearrangement of the *t*-butylamine radical and this inhibits the amine–MBTM interaction. The final TBB concentration is correspondingly low.

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