The Interaction of Sulfenamide Accelerators with Sulfur, ZNO, and Stearic Acid in the Absence of Rubber
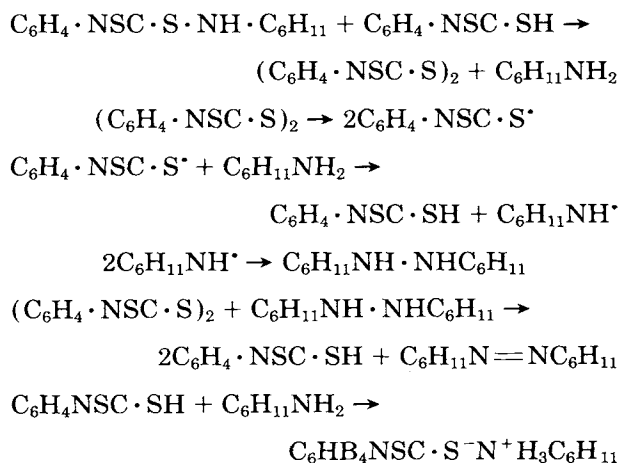
M. H. S. GRADWELL and W. J. MCGILL*

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

SYNOPSIS

The interaction of sulfur, ZnO, stearic acid, and the three sulfenamide accelerators N-cyclohexylbenzothiazole sulfenamide (CBS), 2-(4-morpholinothio)benzothiazole (MOR), and 2-t-butylaminobenzothiazole sulfenamide (TBBS) were investigated by differential scanning calorimetry in the absence of rubber. In the presence of sulfur, the same product spectrum is formed as in its absence, but at lower temperatures. 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). In the presence of sulfur, the amount of polysulfides formed initially is higher but the polysulfides are unstable, and on prolonged heating, only MBT and CB remain. MOR and TBBS form analogous product spectra. The sulfenamides do not react with ZnO or zinc stearate. The MBT-amine complex prevents MBT, formed on decomposition, from reacting to give zinc mercaptobenzothiazole (ZMBT). Reaction mechanisms are proposed to account for the formation of the products. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Kok[1] studied the interactions of N-cyclohexylbenzothiazole sulfenamide (CBS) and curatives by DSC. CBS was found to decompose at 210°C and its decomposition at lower temperatures, in the presence of sulfur, was taken as evidence of an interaction. The CBS/ZnO/stearic acid mixture was reported as energetically the most favorable for vulcanization because of the exotherm at 145°C. However, Kruger and McGill[2] attributed a peak at this temperature to the formation of zinc stearate rather than to the formation of an active sulfurating agent. Banks and Wiseman[3] isolated 2-mercaptobenzothiazole (MBT), 2-bisbenzothiazole-2,2'-disulfide (MBTS), cyclohexylammonium benzothiazolyl-2-mercaptide, and 2-N-cyclohexylaminobenzothiazole (CB) from a sample of CBS held at 140°C for 3.5 h and suggested the following reaction mechanism for the formation of some of these compounds:

$$C_6H_4 \cdot NSC \cdot S \cdot NH \cdot C_6H_{11} + C_6H_4 \cdot NSC \cdot SH \rightarrow$$
$$(C_6H_4 \cdot NSC \cdot S)_2 + C_6H_{11}NH_2$$
$$(C_6H_4 \cdot NSC \cdot S)_2 \rightarrow 2C_6H_4 \cdot NSC \cdot S^\cdot$$
$$C_6H_4 \cdot NSC \cdot S^\cdot + C_6H_{11}NH_2 \rightarrow$$
$$C_6H_4 \cdot NSC \cdot SH + C_6H_{11}NH^\cdot$$
$$2C_6H_{11}NH^\cdot \rightarrow C_6H_{11}NH \cdot NHC_6H_{11}$$
$$(C_6H_4 \cdot NSC \cdot S)_2 + C_6H_{11}NH \cdot NHC_6H_{11} \rightarrow$$
$$2C_6H_4 \cdot NSC \cdot SH + C_6H_{11}N = NC_6H_{11}$$
$$C_6H_4NSC \cdot SH + C_6H_{11}NH_2 \rightarrow$$
$$C_6HB_4NSC \cdot S^- N^+ H_3C_6H_{11}$$

The presence of $C_6H_{11}N = NC_6H_{11}$ in the reaction mixture was not reported, whereas no mechanism was suggested for the formation of CB. The sulfenamide accelerator 2-(4-morpholinothio)benzothiazole (MOR) was shown to react with sulfur to form 2-(4-morpholinodithio)benzothiazole (MDB).[4] Campbell and Wise[5,6] showed the formation of 2-bisbenzothiazole-2,2'-polysulfides (MBTP) during the induction period in the vulcanization of rubber

with MOR. Similar studies were carried out by Lieb et al.[7] and Trivette et al.[8] Sullivan et al.[9] studied the reactions of 2-t-butylaminobenzothiazole sulfenamide (TBBS) in rubber.

A previous article[10] reported on the decomposition of CBS, MOR, and TBBS, whereas this article reports on a detailed study of the interaction of these accelerators with curatives.

EXPERIMENTAL

Sulfur (99.5% purity) was supplied by AECI, South Africa, and ZnO (active grade, 99, 72% purity) by Zinc Process, South Africa. The accelerators used have been detailed.[10] Curatives were mixed in 1.0 : 1.0 mol ratios and heated in sealed aluminum DSC pans. The procedures followed for DSC,[10,11] TLC,[11] and HPLC[12] have been described. Except where otherwise indicated, HPLC analyses of reactants and products were based on retention times for the compounds described in the previous article.[10] X-ray measurements were conducted with a Philips PW2103/00 diffractometer fitted with a vertical goniometer PW1050 and a proportional detector. Powdered samples were contained in a Philips aluminum holder and scanned at a rate of $2\Theta = 1°$ per min. Used were radiation CuKα; $\lambda = 15,405$ Å; a Ni filter; 40 kV; 30 mA; and divergence slit 1°.

RESULTS

Sulfenamide/Sulfur

The thermogram of a CBS/sulfur mix (1 : 1 mol ratio) showed the melting of the sulfur and that of

the CBS as a single endothermic peak at 95°C (108°C)[4] (Fig. 1). Under the hot-stage optical microscope, the CBS crystals were seen to float in the liquid sulfur and then to dissolve at 95°C, which is below the normal melting points of sulfur and CBS. The compounds interact at higher temperatures (125–150°C) when a rapid mass loss occurs (Fig. 1). Kok[1] observed that the presence of sulfur reduced the decomposition temperature of CBS by 20°C and concluded that a reaction could have taken place. A decrease in the decomposition temperature was also observed in this study, but it varied considerably from experiment to experiment (onset of reaction 125–150°C).

The blend of sulfur and CBS (1 : 1 mol ratio) was heated to 110°C, i.e., to above the melting point of the mixture, and held at that temperature for times ranging between 1 and 14 min. These samples were then analyzed by HPLC (Fig. 2). Initially, only CBS and sulfur are evident, but after an induction period of about 3 min, MBTS and two peaks that are attributed to N-cyclohexylamino-2-benzothiazole polysulfides (CBP) of the type BTSS$_x$NR appear. Until all the CBS has reacted, the concentrations of CBP are significantly higher than observed when CBS is heated in the absence of sulfur (cf. Ref 10). No MBTM is formed. In mixes heated to above the temperature at which rapid decomposition occurs, CB forms rapidly, the concentrations of MBTS, MBTP, CBS, and CBP decrease with time, and, finally, only MBT, CB, and sulfur are left [Fig. 2(d)]. All the sulfur is recovered.

CBS/sulfur interact even at room temperature.
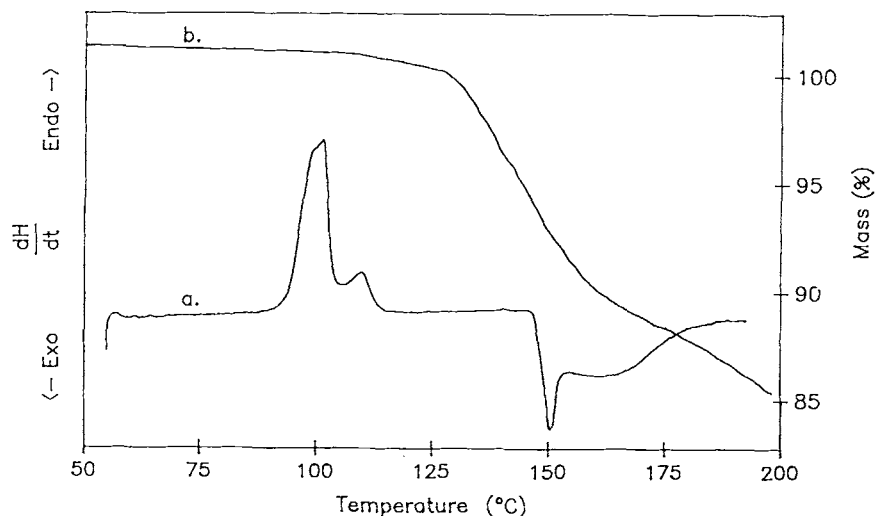
Figure 1 DSC thermogram: scan rate 5°C/min; (a) CBS/sulfur (1 : 1 mol ratio), M_i = 10.7798 mg, M_f = 10.0633 mg. TGA thermogram: scan rate 5°C/min; (b) CBS/sulfur (1 : 1 mol ratio); M_i = 34.190 mg.
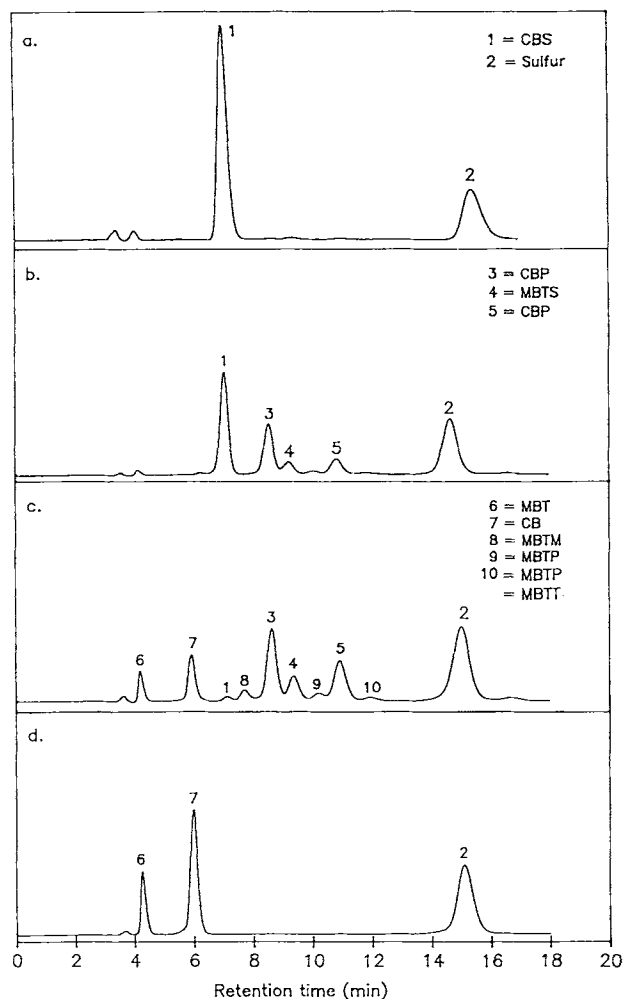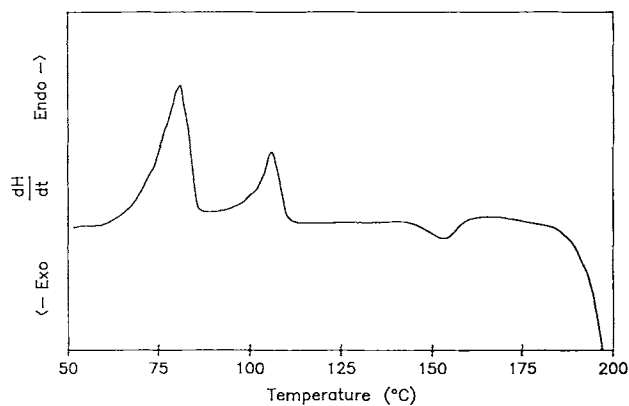
Figure 2 HPLC chromatograms: CBS/sulfur (1 : 1 mol ratio) mixture heated in the DSC at 5°C/min. (a) Unheated CBS/sulfur; (b) mix heated to 110°C and held isothermally for 4 min; (c) mix held isothermal at 110°C for 14 min; (d) mix heated to 175°C.

A mixture of CBS/sulfur (1 : 1 mol ratio), left in a sealed pill vial, reacted to form a different product spectrum to that observed when heated to above the decomposition exotherm. The products of this low-temperature interaction were analyzed after several weeks and were found to be composed of CBP, MBTS, MBTP, and a small amount of MBT. CBS had reacted completely and no CB had formed.

The DSC of a MOR/sulfur mix (1 : 1 mol ratio) (Fig. 3) shows the melting of MOR at 81°C and the dissolution of part of the sulfur in the melt. A further endotherm appears at 105°C, which represents the rest of the sulfur melting. The exotherm at 154°C has been identified[4] as the reaction of the MOR with sulfur to form MDB. Decomposition starts at 190°C.

HPLC analysis of the decomposition products of

Figure 3 DSC thermogram: scan rate 5°C/min; MOR/sulfur (1 : 1 mol ratio); M_i = 14.492 mg; M_f = 12.142 mg.

a MOR/sulfur (1 : 1 mol ratio) mixture showed an analogous product spectrum to that observed with the CBS/sulfur mix (Fig. 4). The MDB peak is more prominent than in the absence of sulfur (cf. Ref. 10), while peaks that, from their position in the spectrum, may be due to $BTSS_xNR$ (MORP), where x = 2 and 3, are also observed. A prominent MBTS
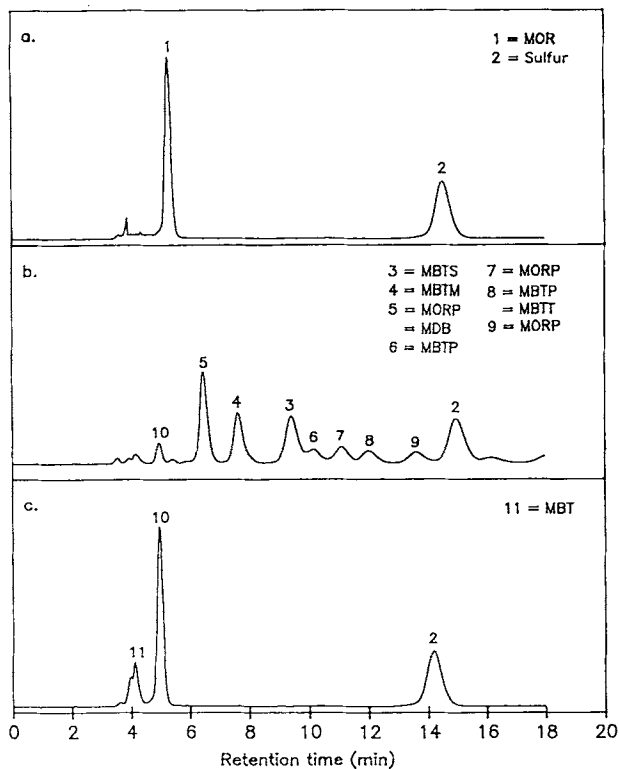
Figure 4 HPLC chromatograms: MOR/sulfur (1 : 1 mol ratio) mixture heated in the DSC at 5°C/min; (a) unheated MOR/sulfur; (b) mix heated to 185°C; (c) mix heated to 200°C.
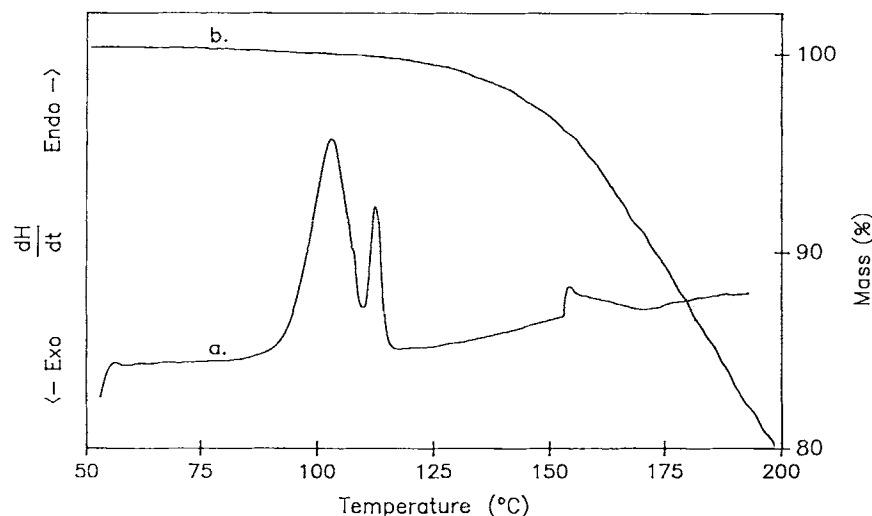
Figure 5 TBBS/sulfur (1 : 1 mol ratio): (a) DSC thermogram: scan rate 5°C/min; M_i = 17.650 mg; M_f = 12.373 mg, (b) TGA thermogram: scan rate 5°C/min; M_i = 19,080 mg.

peak and lesser peaks attributed to MBTP (BTSS$_x$SBT, where x = 1 and 2) are evident, as well as a strong bisbenzothiazole-2,2'-monosulfide (MBTM) peak. The formation of MB is observed, while the MBT peak is small. On completion of the decomposition, only MBT and 2-morpholinobenzothiazole (MB) are found, together with the sulfur peak. Morita et al.[4] found that MOR reacted with the sulfur to form MDB, but the literature does not refer to any of the other products detected in this study.

The combination of TBBS/sulfur (1 : 1 mol ratio), scanned in the DSC, gives the characteristic sulfur and accelerator melting endotherms (Fig. 5). The endothermic decomposition occurs at a temperature some 80–90°C lower than in the absence of sulfur.[10]

The TGA of a TBBS/sulfur (1 : 1 mol ratio) mix shows a rapid mass loss in the temperature region associated with the reaction endotherm (Fig. 5). HPLC analysis of this combination (Fig. 6) heated to 200°C gives MBT, MBTM, MBTS, and MBTP (BTSS$_x$SBT, where x = 1 and 2). By analogy to the CBS and MOR systems and their positions relative to TBBS, MBTS, and MBTP peaks, peaks 7 and 8 could be associated with the presence of 2-t-butylaminobenzothiazole polysulfides (TBBP or BTSS$_x$NR, where x = 1 and 2). Likewise, because of its position in the HPLC chromatogram, peak 3 is taken to be indicative of the formation of 2-t-butylaminobenzothiazole (TBB). As is the case with CBS and MOR, the amount of BTSS$_x$NR and BTSS$_x$SBT formed is larger in the presence of free sulfur. The MBTM peak is not as prominent as in

the MOR/sulfur system, but more so than in the CBS/sulfur system, from which it is essentially absent. Again (see Ref. 10), it is found that, unlike in the case of the other sulfenamide/sulfur mixes, large amounts of MBTS, MBTP, and TBBP were still present at longer heating times. Sullivan et al.[9] reported identifying MBTM and MBTP as intermediates in a TBBS/sulfur vulcanization of natural rubber.

Sulfenamide/Sulfur/Zinc Oxide

The CBS/ZnO combination (1 : 1 mol ratio) did not show any interaction in the DSC (Fig. 7). A
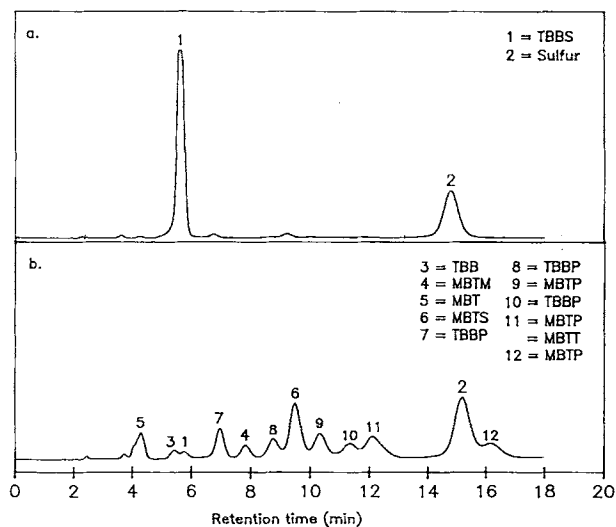
Figure 6 HPLC chromatograms: TBBS/sulfur (1 : 1 mol ratio) mixture heated in the DSC at 5°C/min; (a) unheated TBBS/sulfur; (b) mix heated to 200°C.
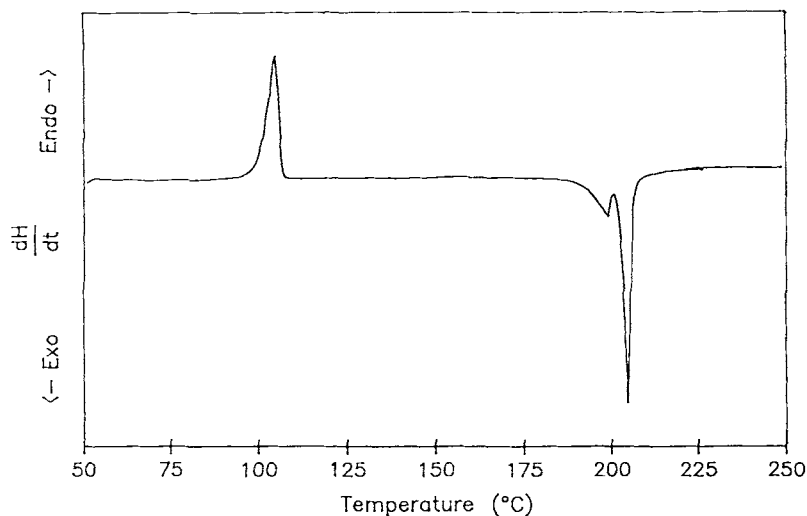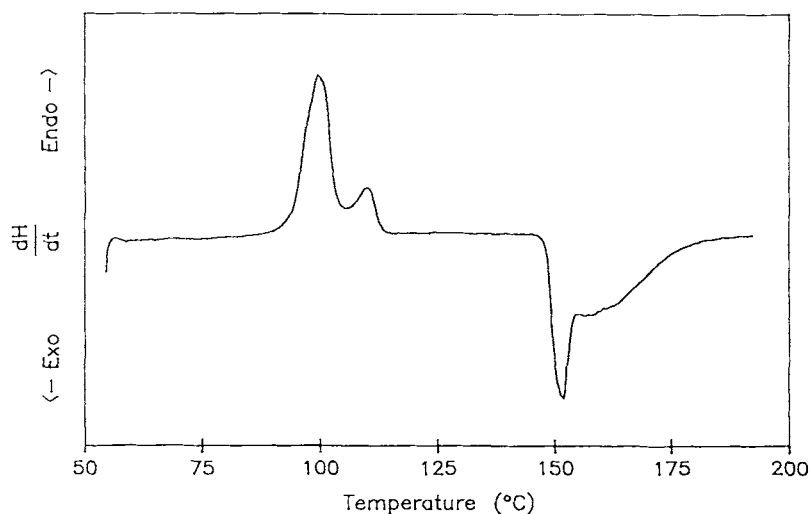
Figure 7 DSC thermogram: scan rate 5°C/min; CBS/ZnO (1 : 1 mol ratio); M_i 13.007 mg.

melting endotherm of the CBS was evident and was also present in a rescan after cooling the sample from temperatures below the decomposition exotherm. The residue from a sample heated to 160°C was analyzed in the HPLC when only CBS was found to be present, i.e., there was no evidence for the formation of a zinc–accelerator complex. There was a 15% mass loss due to evaporation. X-ray powder diffraction of the CBS/ZnO combination, heated to below the CBS decomposition temperature, did not show any interplanar spacings characteristic of zinc mercaptobenzothiazole (ZMBT). Interplanar spacings for ZMBT were obtained from the diffraction pattern of a ZMBT sample and were correlated with those cited in the powder diffraction file

(ASTM). When heated to past the decomposition temperature of CBS, X-ray diffraction of the CBS/ZnO combination did show the formation of a small amount of ZMBT.

The DSC of a CBS/sulfur/ZnO mixture (1 : 1 : 1 mol ratio) (Fig. 8) did not differ from that of the CBS/sulfur mix, as would be expected if the ZnO did not play a role in the reaction. HPLC analysis of this mix showed the same features as those of the CBS/sulfur mix.

Up to 200°C, the DSC thermogram of MOR/ZnO (1 : 1 mol ratio) showed only the MOR melting endotherm, suggesting that no reaction had taken place. This was confirmed by HPLC analysis that showed the presence of MOR only. (Trace amounts

Figure 8 DSC thermogram: scan rate 5°C/min; CBS/sulfur/ZnO (1 : 1 : 1 mol ratio); M_i = 13.3502 mg; M_f = 12.1195 mg.
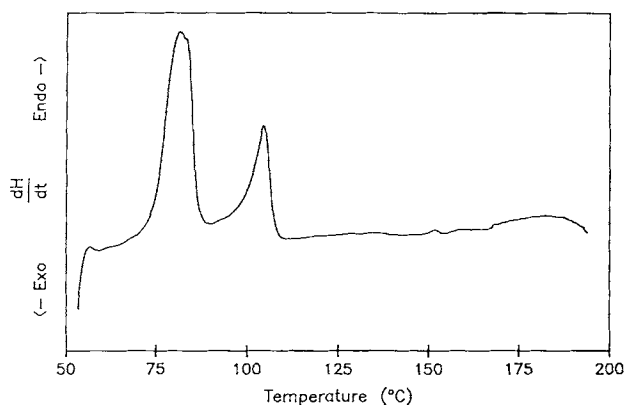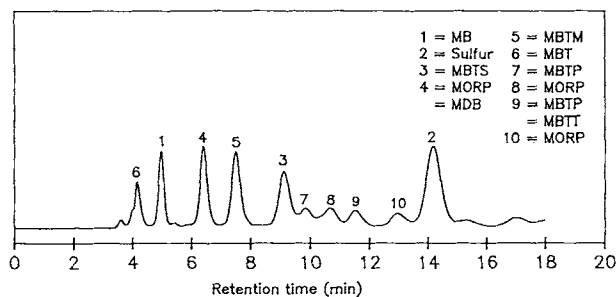
Figure 9 DSC thermogram: scan rate 5°C/min; MOR/sulfur/ZnO (1 : 1 : 1 mol ratio); M_i = 22.986 mg; M_f = 20.363 mg.

Figure 11 DSC thermogram: scan rate 5°C/min; TBBS/sulfur/ZnO (1 : 1 : 1 mol ratio); M_i = 13.892 mg; M_f = 11.661 mg.
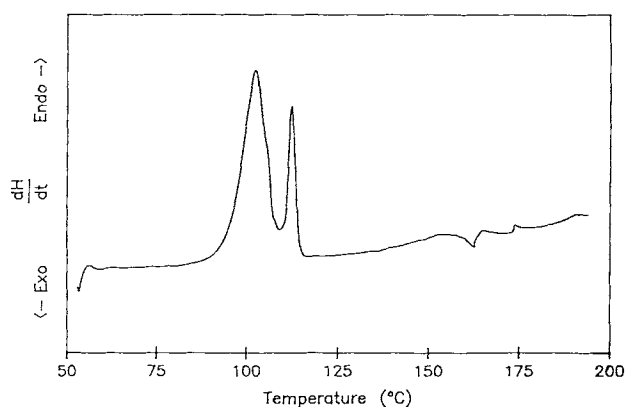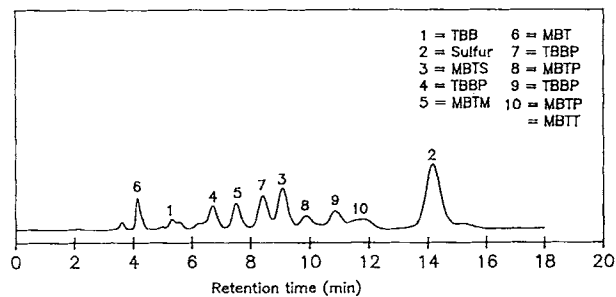
of compounds described earlier were present.) In the presence of sulfur, the decomposition of MOR occurs more readily. The DSC thermogram (Fig. 9) of a MOR/sulfur/ZnO (1 : 1 : 1 mol ratio) mixture showed no new thermal events when compared to the MOR/sulfur thermograms, whereas HPLC analysis of a mix heated to 200°C showed the same spectrum of products (Fig. 10) as observed in the absence of ZnO, viz., MBT, MBTS, MBTP, MORP, CB, and residual MOR and sulfur.

On heating, TBBS/ZnO (1 : 1 mol ratio) and TBBS/sulfur/ZnO (1 : 1 : 1 mol ratio) mixes gave analogous results to the above two sulfenamide systems. The DSC showed no new thermal events attributable to a reaction involving ZnO. HPLC analysis of a TBBS/ZnO mix, heated to 200°C, yielded MBTS and unreacted TBBS. A TBBS/sulfur/ZnO mix (Fig. 11), heated to 200°C, yielded MBT, MBTS, MBTP, TBBP, TBB, and residual TBBS and sulfur (Fig. 12).

MBTS is formed during degradation of all three sulfenamides. A DSC scan of an MBTS/ZnO (1 : 1

mol ratio) mix showed the melting peak of MBTS at 180°C as the only thermal event (Fig. 13). This concurs with an earlier study of MBTS.[13] HPLC analysis of the product after heating to 200°C showed the MBTS-to-MBTM conversion as the main reaction, whereas small amounts of MBTP were formed (Fig. 14). A 1% mass loss occurred. X-ray diffraction studies showed no evidence for the formation of ZMBT.

Sulfenamide/Stearic Acid/Zinc Oxide

Although the smaller CBS and sulfur melting endotherms observed with CBS/stearic acid and CBS/sulfur/stearic acid (1 : 1 : 1 mol ratio) mixes suggest the dissolution of these components in the stearic acid melt, the acid did not affect the decomposition exotherm (Fig. 15). Stearic acid melts at 55°C.

The temperature at which stearic acid and ZnO react to form zinc stearate depends on the presence of water in the mixture.[2] The CBS/stearic acid/ZnO (Fig. 16) thermogram shows that some zinc

Figure 10 HPLC chromatogram: MOR/sulfur/ZnO (1 : 1 : 1 mol ratio) heated at 5°C/min in the DSC to 200°C.

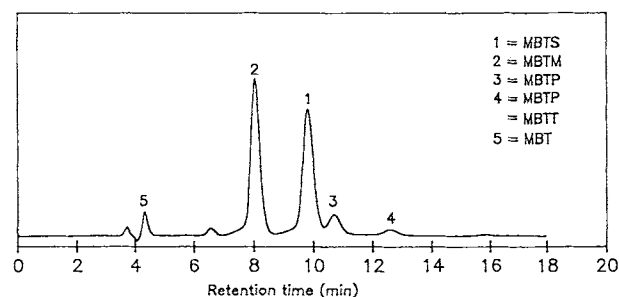**Figure 12** HPLC chromatogram: TBBS/sulfur/ZnO (1 : 1 : 1 mol ratio) heated in the DSC at 5°C/min to 200°C.
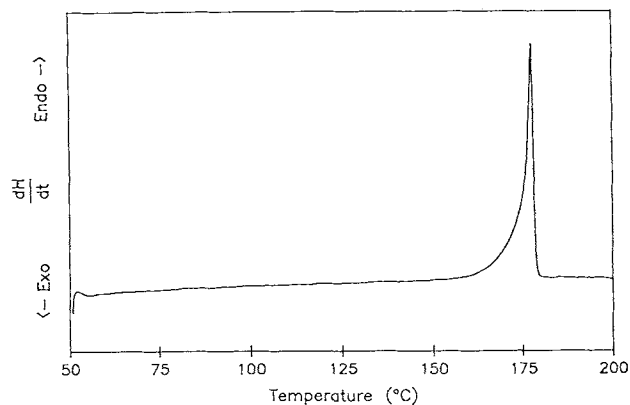
Figure 13 DSC thermogram: scan rate 5°C/min; MBTS/ZnO (1 : 1 mol ratio) heated to 200°C; M_i = 9.771 mg; M_f = 9.692 mg.

Figure 15 DSC thermogram: scan rate 5°C/min; CBS/ stearic acid (1 : 1 mol ratio); M_i = 10.8937 mg; M_f = 10.3896 mg.

stearate was formed immediately when the stearic acid melted (evidenced by the stearate melting endotherm) while the reaction went to completion at 150°C.
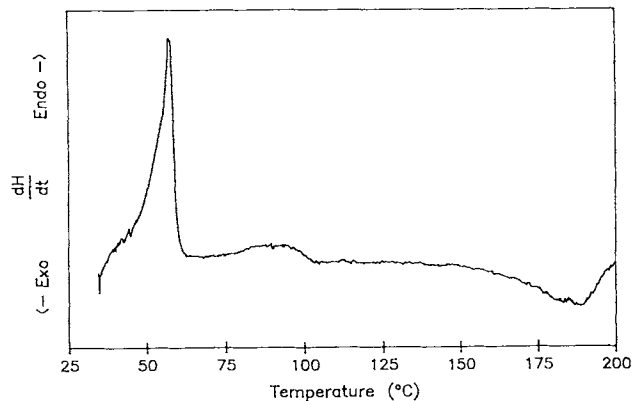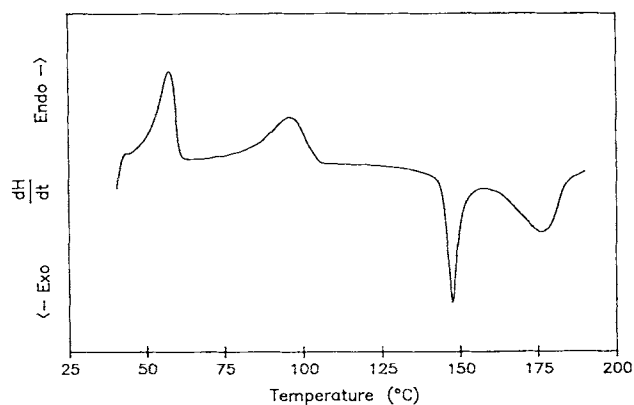
DISCUSSION

Sulfenamides/Sulfur

The addition of sulfur to CBS (and MOR) leads to degradation at a much lower temperature than in the absence of sulfur,[10] the reaction now occurring in the temperature range associated with vulcanization. The intermediate and final product spectra are the same as in the absence of sulfur though the intermediates are initially more highly sulfurated. On decomposing CBS, 55 mol % appears as MBT, and in a CBS/sulfur mixture, 55 mol % MBT is also formed. All the sulfur is recovered (99 mol %). In the TBBS decomposition, where the concentration of intermediates remains high, only 8 mol % of the TBBS is present as MBT at the end of the decomposition (200°C). TBBS/sulfur decomposition gives

a similar result and the overall reaction is again endothermic.

The fact that sulfenamides degrade at lower temperatures in the presence of sulfur indicates active participation by sulfur in initiating sulfenamide decomposition.

Catalytic Effect of MBT

MBT, which is obtained in the vulcanizate simultaneously with cross-link formation, is thought to catalyze CBS decomposition.[8] Removal of MBT by its reaction with N-(cyclohexylthio)phthalimide (CTP) was shown to increase the scorch time.[7] The ready interaction between CBS and MBT was illustrated by Banks and Wiseman[3] who showed the formation of MBTS and cyclohexylamine in ether solution after 5 min at room temperature. On heat-

Figure 14 HPLC chromatogram: MBTS/ZnO (1 : 1 mol ratio) heated in a DSC at 5°C/min to 200°C.

1 = MBTS
2 = MBTM
3 = MBTP
4 = MBTP
   = MBTT
5 = MBT

Figure 16 DSC thermogram: scan rate 5°C/min; CBS/ ZnO/stearic acid (1 : 1 : 1 mol ratio); M_i = 13.2300 mg; M_f = 10.4534 mg.
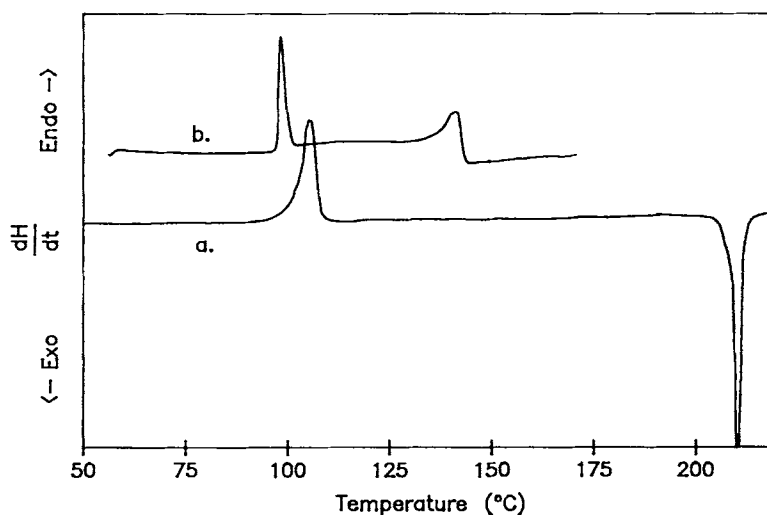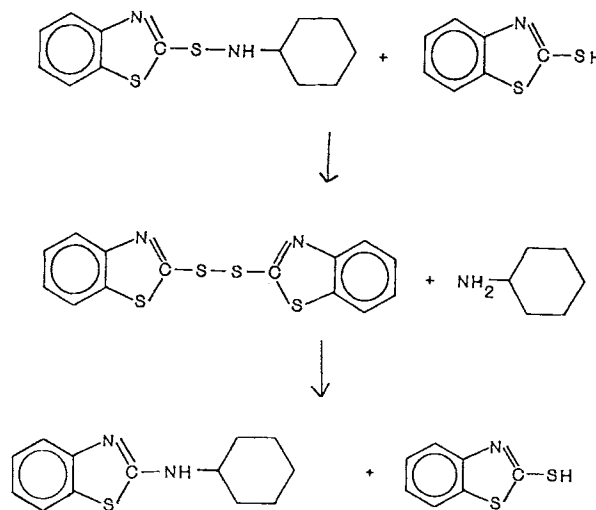
Figure 17 DSC thermogram: scan rate 5°C/min; (a) CBS, M_i = 10.5981 mg, M_f = 1.0810 mg; (b) CBS/MBT (1 : 1 mol ratio), M_i 7.3976 mg, M_f = 6.8766 mg.

ing a mixture of CBS and MBT (1 : 1 mol ratio) in the DSC, decomposition was seen to occur at much lower temperatures than in the absence of MBT (Fig. 17). HPLC analysis (Fig. 18) of the mixture at 130°C (just prior to the onset of the decomposition exotherm) showed that CB was formed in addition to MBTS. Analysis at 145°C showed MBTT and sulfur now added to the product spectrum.

It has been suggested[10] that CB results from the interaction of MBTS and cyclohexylamine. MBT is simultaneously regenerated and may interact with CBS, producing more MBTS and cyclohexylamine.
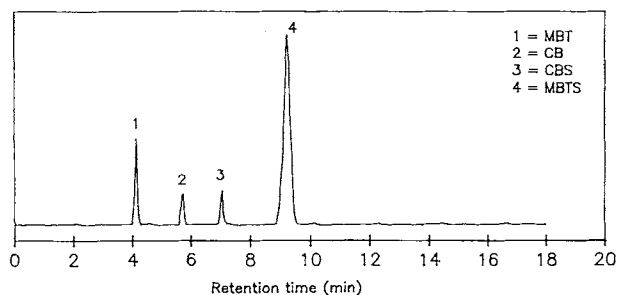
The reaction scheme would account for the catalytic action of MBT in decomposing CBS. In the CBS/MBT mixture, there is a large excess of MBT initially and the amine released in the reaction may well be present as the cyclohexylamine salt of MBT. This may react with MBTS to form CB:

Figure 18 HPLC chromatogram: CBS/MBT (1 : 1 mol ratio) heated in the DSC at 5°C/min to 130°C.

Banks and Wiseman[3] proposed a more complex mechanism for the formation of the cyclohexylamine salt of MBT in the MBT accelerated degradation of CBS. Their mechanism also involves MBTS as an intermediate, but requires the formation of $C_6H_{11}N{=}NC_6H_{11}$, which was not mentioned in their product analysis. They could not account for the formation of CB.

Reactions with Zinc Oxide

ZnO does not react with any of the three sulfenamides on heating to 200°C, i.e., to below their decomposition temperature but well above normal vulcanization temperatures. MBTS also does not react with ZnO to give ZMBT. Thus, as in the case

of TMTD,[14] there is no evidence for the formation of a zinc-accelerator complex in the absence of rubber.

In the presence of sulfur, the decomposition of CBS takes place at a much lower temperature and the reactions in the presence of ZnO suggest that cyclohexylamine, formed in the degradation of CBS, may well be present as the cyclohexylamine salt of MBT. MBT is a decomposition product of CBS/sulfur, but when ZnO is added to a CBS/sulfur mixture, there is only very limited evidence of an MBT/ZnO reaction despite the ease with which such a reaction occurs on heating an MBT/ZnO mixture.[15] This suggests that most of the MBT is not available for reaction, which would be the case if it were present as the amine salt of MBT. Similar results were obtained with MOR/sulfur/ZnO and TBBS/sulfur/ZnO mixes, the accelerator/sulfur DSC thermograms and product spectra being unaffected by the addition of ZnO.

CONCLUSION

The spectrum of polysulfidic accelerator complexes (CBP, MDB, TBBP, MBTS, MBTP) that forms in the presence of sulfur is similar to that found on decomposition of these accelerators at 210–220°C[10] in the absence of sulfur. The products are more highly sulfurated and the reactions are rapid at vulcanization temperatures. There is no evidence for the formation of a zinc–accelerator complex (ZMBT) with any of the sulfenamides or with MBTS. MBT, which is very reactive toward ZnO, is a major product of the decomposition of the sulfenamides, but is present in the mix as a MBT–amine salt and is not free to react with ZnO.

REFERENCES

1. C. M. Kok, *Eur. Polym. J.*, **21**, 579 (1985).
2. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2643 (1991).
3. D. J. Banks and P. Wiseman, *Tetrahedron*, **24**, 6791 (1968).
4. E. Morita, J. J. D'Amica, and E. J. Young, *Rubber Chem. Tech.*, **41**, 721 (1968).
5. R. H. Campbell and R. W. Wise, *Rubber Chem. Tech.*, **37**, 635 (1964).
6. R. H. Campbell and R. W. Wise, *Rubber Chem. Tech.*, **37**, 650 (1964).
7. R. I. Leib, A. B. Sullivan, and C. D. Trivette, *Rubber Chem. Tech.*, **43**, 1188 (1970).
8. C. D. Trivette, E. Morita, and O. W. Maender, *Rubber Chem. Tech.*, **50**, 570 (1977).
9. A. B. Sullivan, C. J. Hann, and G. H. Kuhls, American Chemical Society, Rubber Division Meeting, Ontario, 1991.
10. M. H. S. Gradwell and W. J. McGill, *J. Appl. Polym. Sci.*, to appear.
11. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2661 (1991).
12. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **44**, 581 (1992).
13. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2651 (1991).
14. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2669 (1991).
15. A. S. Luyt, W. J. McGill, and D. Shillington, *Br. Polym. J.*, **23**, 135 (1990).