

Rate of Formation of Polysulfides of 2-Bisbenzothiazole-2,2'-Disulfide in the Presence of Sulfur and 2-Mercaptobenzothiazole

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SYNOPSIS

2-Bisbenzothiazole-2,2'-disulfide was heated isothermally with and without sulfur at temperatures between 130 and 178°C for various periods of time and the mixture analyzed by high-pressure liquid chromatography (HPLC). 2-Bisbenzothiazole-2,2'-monosulfide formed rapidly and 2-bisbenzothiazole-2,2'-polysulfides after an induction period of about 5 min. Polysulfides of higher sulfur rank are formed by the sequential addition of sulfur atoms. 2-Mercaptobenzothiazole catalyzes the formation of 2-bisbenzothiazole-2,2'-polysulfides and eliminates the induction period. Mechanisms for the decomposition of 2-bisbenzothiazole-2,2'-disulfide and the catalytic role of 2-mercaptobenzothiazole are proposed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polysulfidic forms of accelerators such as 2-bisbenzothiazole-2,2'-disulfide (MBTS) and tetramethylthiuram disulfide (TMTD) are attributed a major role in accelerated sulfur vulcanization of diene rubbers.^{1,2} MBTS reacts with sulfur to form 2-bisbenzothiazole-2,2'-polysulfides (MBTP) in the cure delay period prior to vulcanization.³ The thermal decomposition of MBTS has been suggested to involve dissociation into benzothiazolyl radicals [BtS*].⁴⁻⁶ Cleavage of the disulfide bond occurs more readily, though experiments with ³⁵S have shown that heterolytic scission is also possible. In the absence of rubber Kapur, Koenig, and Shelton⁷ have shown the formation of 2-bisbenzothiazole-2,2'-monosulfide (MBTM) and MBTPs after 3 min at 150°C and suggested a reaction mechanism involving the homolytic scission of MBTS and the interaction of BtS radicals with MBTS to form MBTM and BtS₂ radicals. Further abstraction of sulfur by BtS radicals, followed by the recombination of radicals, would result in MBTPs of higher sulfur rank. It is stated that similar results are obtained on heating

MBTS and sulfur. Geysler and McGill⁸ have recently shown that polysulfides of TMTD (i.e., TMTP) are formed by the sequential addition of sulfur atoms; S₈ does not add to TMTD to give a TMTP of high sulfur rank which subsequently desulfurates.

2-Mercaptobenzothiazole (MBT), which may be used as an accelerator in conjunction with MBTS, has a major effect on the vulcanization reaction.⁹ While many papers^{3-5,7,10-12} suggest reaction between MBT and sulfur to form 2-hydropersulfidebenzothiazole complexes (BtS_xH), Gradwell and McGill⁹ found no evidence for the reaction. No polysulfidic MBT species could be detected in high-pressure liquid chromatography (HPLC) analysis, though Dogadkin¹³ claimed to have isolated BtS_xH from a melt of MBT and sulfur.

This study reports on the formation of MBTP on heating MBTS and MBTS-sulfur mixes to vulcanization temperatures in the absence of rubber and on the effect of MBT on MBTP formation.

EXPERIMENTAL

Materials

MBTS (chemical purity 93%, Orchem, South Africa), MBT (Thiotax, chemical purity 95%, Mon-

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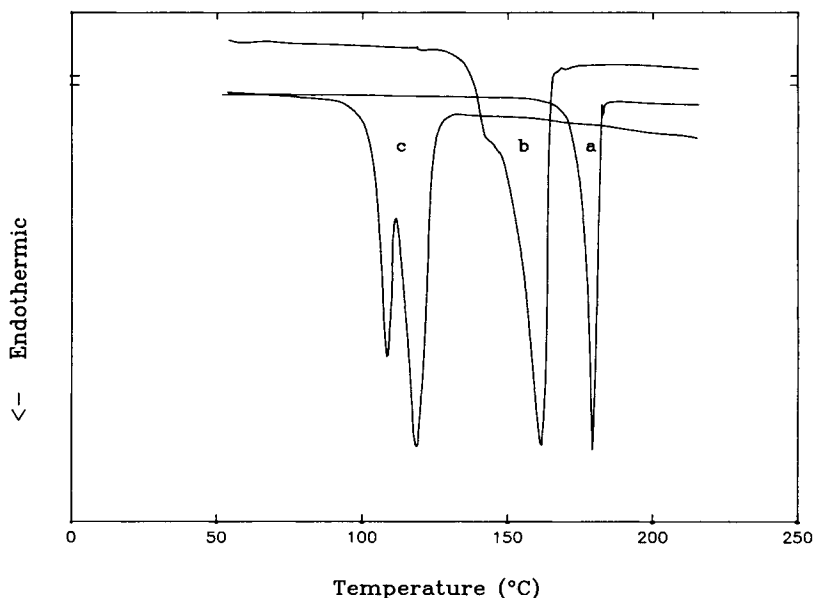


Figure 1 DSC thermograms of (a) MBTS, (b) MBTS/MBT (1 : 0.12), and (c) MBTS-MBT-sulfur (1 : 0.6 : 1) heated at 5°C/min.

santo), and sulfur (98% soluble in CS₂, AECI, South Africa) were used.

Mixtures of curatives were prepared by grinding the components with a pestle and mortar, the molar composition of each mix being given in brackets, e.g., MBTS-sulfur (1 : 1).

MBT was added to certain curative mixtures (Figs. 4, 7, and 8). In order to monitor whether the MBT concentration was affected in the reaction, the concentration of MBT initially added to the curative mixture was also expressed in terms of the mole percent MBTS present originally.

Samples (± 20 mg) were sealed in aluminum differential scanning calorimetry (DSC) pans and placed into a standard DuPont DSC cell preheated to the desired temperature. The cell design allows this operation to be completed rapidly, the cell temperature equilibrating within 30 s. Samples were held isothermally for various periods and were then rapidly removed and cooled to stop the reaction. Other details of the DSC and HPLC used to analyze the samples have been described in detail.⁸

RESULTS

MBTS

MBTS melts at 178°C (172.5°C¹⁴), producing a single endothermic peak in the DSC thermogram (Fig. 1). Holding MBTS isothermally at its melting point in a DSC results in MBTS decomposition and

MBTP production. The MBTM concentration increases linearly with time from the outset, but the MBTP production is accompanied by an induction period of 5 min or more (Fig. 2). Elemental sulfur is not produced. The reaction equilibrates after 80–100 min with the MBTS concentration at 24 mol %, MBTM at 58 mol %, and MBTP at 16 mol % of the original MBTS concentration. The 3 mol % MBT impurity remains constant throughout the reaction.

MBTS-Sulfur (1 : 1)

Heating MBTS-sulfur (1 : 1) in a DSC at 5°C/min produces three endothermic peaks (Fig. 3). The peaks at 110 and 118°C are due to the solid-solid transition in sulfur and to its melting, respectively, and the third peak, at 150°C, is due to MBTS dissolving in the molten sulfur.¹⁴ Holding MBTS-sulfur (1 : 1) isothermally at 150°C in a DSC results in MBTS decomposition and in rapid MBTP production after an induction period of 5 min (Fig. 4). The reaction equilibrates after 10–15 min. Sulfur consumption is immediate and its concentration decreases to an equilibrium value of 56 mol %. MBTM production is very low with only 2 mol % being produced after 60 min. The MBTP concentration is high at 31 mol % after 60 min (Fig. 4). At 12 mol % the trisulfide is most abundant MBTP while the tetra, penta, and hexa MBTP concentrations are lower at 8, 6, 5 mol %, respectively. The MBT con-

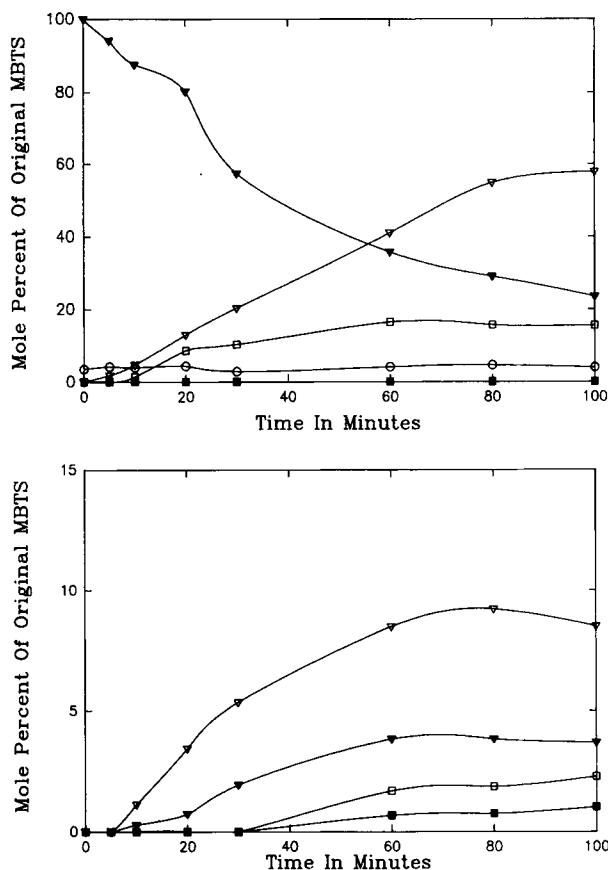


Figure 2 Products formed from the reaction of MBTS as function of time at 178°C. Upper diagram: (▼) MBTS, (▽) MBTM, (○) MBT, (■) sulfur, and (□) additive tri, tetra, penta, and hexa MBTPs. Lower diagram: (▽) BtS₃Bt, (▼) BtS₄Bt, (□) BtS₅Bt, and (■) BtS₆Bt.

centration remains constant at 3 mol % throughout the reaction.

MBTS-MBT (1 : 0.12)

The addition of 0.12 mol MBT to 1 mol MBTS results in a 18°C decrease in the MBTS melting temperature when heated at 5°C/min on a DSC (Fig. 1). Holding MBTS-MBT (1 : 0.12) isothermally at 160°C results in MBTS decomposition and MBTM, MBTP, and sulfur production, with no induction period being detected for MBTP formation. The reaction equilibrates after 20 min (Fig. 5).

The 2-bisbenzothiazole-2,2'-trisulfide (BtS₃Bt) concentration is the highest and passes through a maximum of 9 mol % at 10 min, with the corresponding 2-bisbenzothiazole-2,2'-tetra-(BtS₄Bt), penta-(BtS₅Bt), and hexasulfide (BtS₆Bt) concentrations being successively lower (Fig. 5). The 12 mol % MBT remains constant throughout.

MBTS-MBT-Sulfur (1 : 0.12 : 1)

Upon the addition of 0.12 mol MBT to the MBTS-sulfur (1 : 1) system, the MBTS dissolution peak merges with the peak attributed to the melting of sulfur (Fig. 6). The reaction proceeds immediately, with no induction period for any of the species (Fig. 7). The MBTS and sulfur interaction occurs quickly with only 20 mol % MBTS remaining after 60 min. The sulfur concentration decreases to a minimum of 50 mol % at 10 min but then increases to 56 mol % at 30 min.

MBTP production reaches a maximum of 29 mol % at 5 min and then a slight decrease occurs in the concentration of each of the MBTPs, except in the case of the hexasulfide (Fig. 7). MBTM production is initially slow, but after 60 min 20 mol % has formed. The reaction equilibrates after 5–10 min. The MBT concentration remains constant at the original value (12 mol %).

MBTS-MBT-Sulfur (1 : 0.6 : 1)

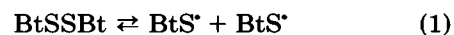
Increasing the MBT concentration from 0.12 to 0.6 mol causes no significant change in the DSC peaks discussed previously, though the second peak, at 118°C, is sharper (Fig. 1).

Once again no induction period is detected for the formation of any of the species (Fig. 8). The reaction proceeds quickly and equilibrates at 10–12 min. The MBTM concentration increases to 27 mol % at 60 min. The MBTP concentration peaks at 32 mol % at 5 min and then decreases to 19 mol % at 12 min. The sulfur concentration decreases rapidly to 71 mol % at 3 min, then increases to 73 mol % at 5 min and decreases again to 62 mol % at 12 min, after which there is a slow increase to 68 mol % at 60 min (Fig. 8). The concentration of the trisulfide increases more rapidly than that of MBTPs of higher sulfur rank. The concentration of all MBTPs peak at 5 min. The MBT concentration remains constant at 60 mol % throughout the reaction.

DISCUSSION

MBTP Production from MBTS

According to Kapur et al.⁷ MBTS cleaves homolytically (reaction 1) to produce BtS radicals:



However, unsymmetric cleavage is also possible (reaction 2), but it is unlikely to be a major reaction as it requires breaking of the more stable C-S bond.⁴

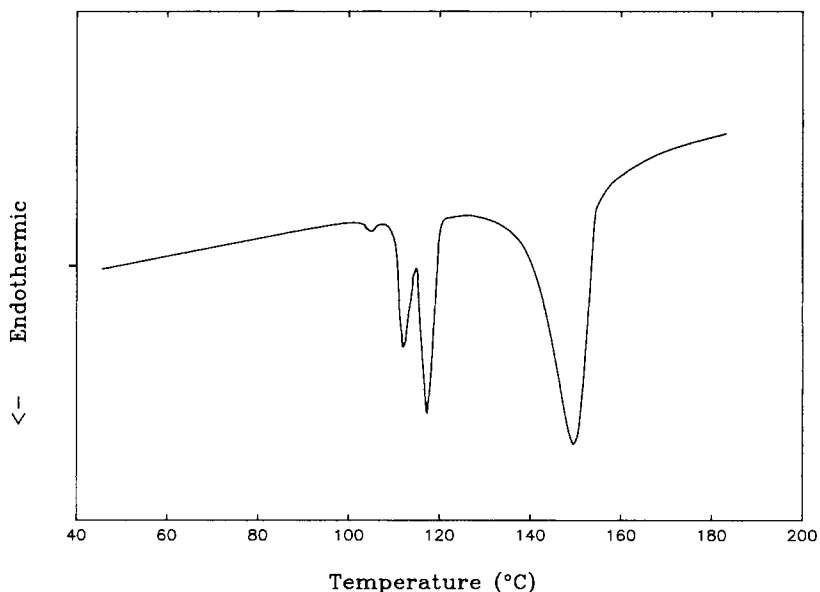


Figure 3 DSC thermogram of MBTS-sulfur (1 : 1) heated at 5°C/min.



The BtS radicals react with MBTS in a sulfur exchange mechanism to produce MBTM (reaction 3a). The activation energy is reported to be 96 kJ/mol.¹⁵



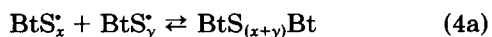
The latter radicals will continue to exchange sulfur with MBTS to produce MBTM and radicals of higher sulfur rank (reaction 3b).



Resonance and conjugation were suggested to account for the stability of the radicals of sulfur rank greater than 2.^{16,17}

Reactions 3 would account for the formation of MBTM coinciding with the onset of MBTS degradation.

There are two possibilities for MBTP production. First, the recombination of BtS_x radicals to form the appropriate MBTPs (reaction 4), and second, sulfur exchange reactions by BtS_x radicals (reaction 5).



As the BtS_x radical concentration is low initially, either or both of these reactions could account for

the induction period prior to the steady increase in MBTP concentration with time. The radicals BtS and BtSS are most abundant, thus accounting for the high 2-bisbenzothiazole-2,2-trisulfide concentration. Note that reaction 4b is unlikely to contribute significantly to MBTM production because it is dependant on reaction 2, which is a less probable reaction.

MBTP Formation from MBTS-Sulfur (1 : 1)

In the presence of elemental sulfur, MBTM production is limited, while MBTP production is increased (cf. Figs. 4 and 2). The radicals produced from the homolysis of MBTS are thought to react with sulfur to produce radicals of high sulfur rank which later desulfurate.^{1,5,6} Figure 4, however, suggests otherwise. The concentrations of MBTPs of lower sulfur rank increase more quickly than those of higher sulfur rank. Thus sulfur atoms add to the radicals sequentially.

The data could be explained in terms of sulfur extraction from elemental sulfur by BtS radicals (reaction 6).



The high elemental sulfur concentration would favor sulfur extraction via reaction 6, more than extraction from MBTS (reactions 3 and 5). The

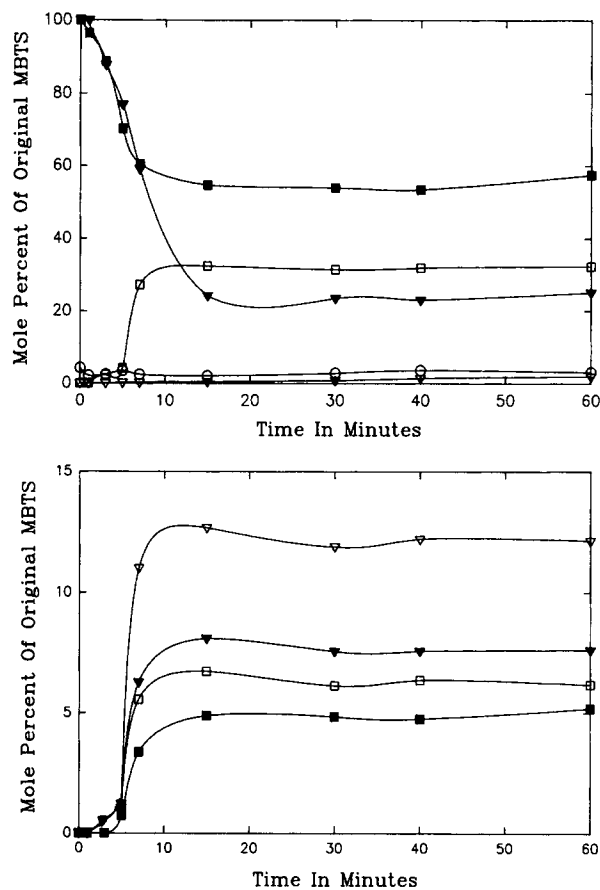


Figure 4 Products formed from the reaction of MBTS-sulfur (1 : 1) as function of time at 150°C. Upper diagram: (\blacktriangledown) MBTS, (∇) MBTM, (\circ) MBT, (\blacksquare) sulfur, and (\square) additive tri, tetra, penta, and hexa MBTPs. Lower diagram: First four detectable MBTPs: (∇) BtS_3Bt , (\blacktriangledown) BtS_4Bt , (\square) BtS_5Bt , and (\blacksquare) BtS_6Bt .

MBTM concentration would be correspondingly low. The very rapid formation of MBTP after an induction period of about 5 min (Fig. 4) suggests MBTP formation via the recombination of radicals (reaction 4), and not from reaction 5, as the latter reaction would lead to a more gradual MBTP production. The reaction for MBTM and MBTP formation are analogous to those suggested by Geyser and McGill⁸ for the formation of mono- and polysulfides of TMTD.

MBTP Formation from MBTS-MBT (1 : 0.12)

Addition of 0.12 mol % MBT to MBTS changes the mechanism of MBTP production, no induction period for MBTP formation being observed (Fig. 5). It is proposed that MBT undergoes an exchange reaction with MBTS similar to that observed for MBT and TMTD¹⁸ (reaction 7).



The formation of 2-hydropersulfidebenzothiazoles by the interaction of MBT and sulfur has been proposed by various authors but questioned by Gradwell and McGill.⁹ If, however, such species were formed in an exchange reaction (exchange reactions have been found to be extremely rapid¹⁸), they may participate in further rapid exchanges before decomposition (reactions 8).



BtS_3Bt would be produced via reaction 8a but reaction 8b could also occur, thus producing MBTM. Reaction 7 would also be producing MBTM and hence the high MBTM concentration.

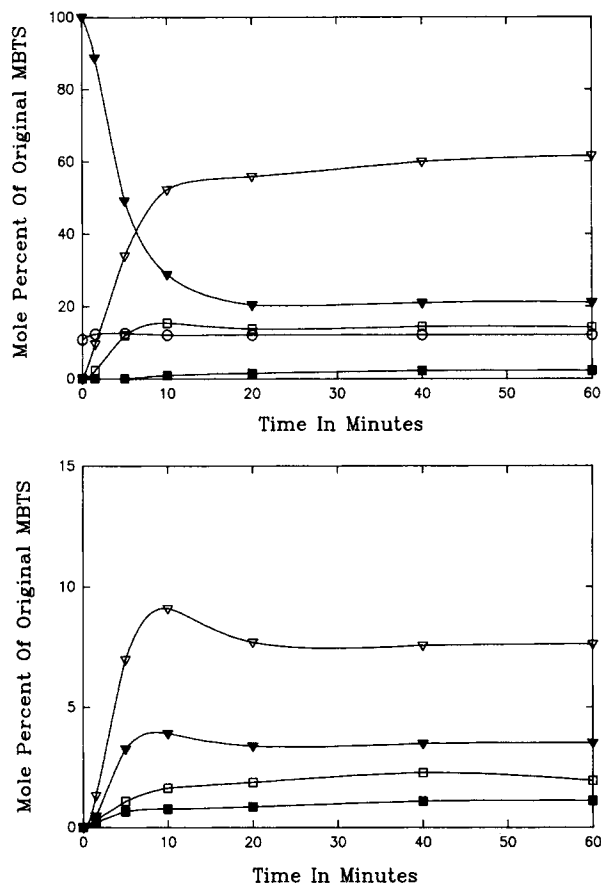


Figure 5 Products formed from the reaction of MBTS-MBT (1 : 0.12) as function of time at 160°C. Upper diagram: (\blacktriangledown) MBTS, (∇) MBTM, (\circ) MBT, (\blacksquare) sulfur, and (\square) additive tri, tetra, penta, and hexa MBTPs. Lower diagram: First four detectable MBTPs: (∇) BtS_3Bt , (\blacktriangledown) BtS_4Bt , (\square) BtS_5Bt , and (\blacksquare) BtS_6Bt .

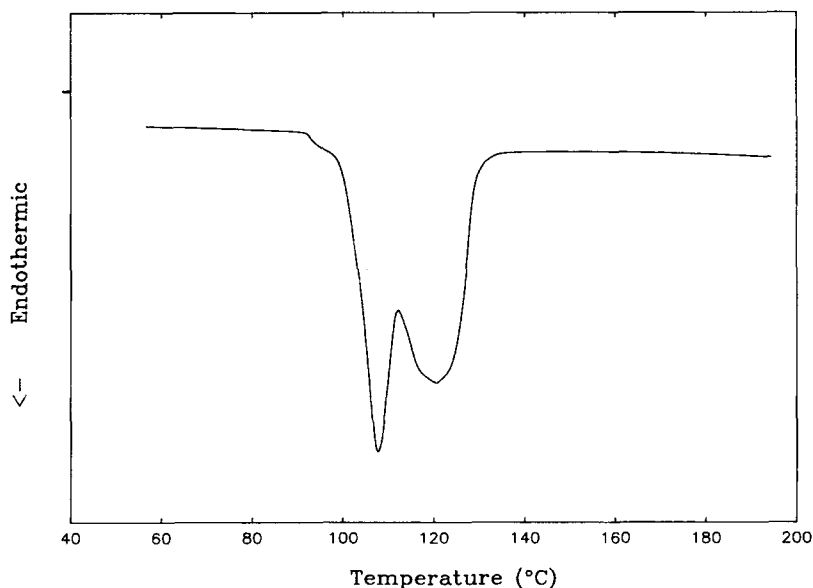


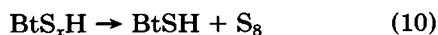
Figure 6 DSC thermogram of MBTS-MBT-sulfur (1 : 0.12 : 1) heated at 5°C/min.

BtS₄Bt would be produced via reactions 9. However, either reaction would produce a low BtS₄Bt concentration; BtSSH would react with BtSSBt before reacting with BtSSSBt because the former is higher in concentration than the latter; while in 9b the BtSSSH concentration would be even lower than the BtSSH concentration because of the extra step involved in its formation (reactions 7 and 8b).



Clearly, MBTPs can be formed via two routes, viz. BtS_x radical recombination (reaction 4) and exchange reactions 7, 8, and 9. The former mechanism will lead to the rapid production of MBTP after an induction period. This would lead to a MBTP concentration in excess of the equilibrium values that would be established by reactions 7, 8, and 9 alone. In the presence of MBT, the reverse reactions in 8 to 9 allow equilibrium to be reestablished, with a decrease in the MBTP concentration. The decrease is most noticeable in the case of BtS₃Bt, the most prominent MBTP.

The small amount of elemental sulfur produced in the reaction is postulated to result from decomposition of BtS_xH species. The MBT concentration remains constant, pointing to its catalytic role in the overall reaction.



MBTP Formation from MBTS-Sulfur-MBT (1 : 1 : 0.12)

Four major changes occur when adding the 0.12 mol MBTS to the 1 : 1 mol ratio MBTS-sulfur system (Fig. 7): (1) no induction period is observed for MBTP production, (2) high MBTM concentrations develop, (3) the sulfur concentration passes through a minimum, some sulfur being liberated after 10 min, and (4) MBTP concentrations pass through a maximum at 5 min.

As in the MBTS-MBT system, MBTP will form via two routes: (i) the combination of BtS_x radicals produced following scission of BtSSBt and the reaction of these radicals with sulfur (reactions 1, 4a, and 6) and (ii) exchange reactions between MBT and MBTS and their analogs of higher sulfur rank (reactions 7-9). The latter reactions lead to the immediate production of MBTM and MBTP, while in the former reaction rapid MBTP production follows only after an induction period. Once MBTPs are rapidly formed via the former route, the reverse reaction in reactions 8 and 9, in which exchange with MBT desulfurates MBTPs of high sulfur rank, dominates. Hence MBTP concentrations pass through a maximum (Fig. 7) while there is an increase in the sulfur concentration, some sulfur being released during desulfuration.

As in earlier systems the MBT concentration does not change during the reaction; it acts as a catalyst, BtS_xH species being unstable and decomposing to regenerate MBT and sulfur.

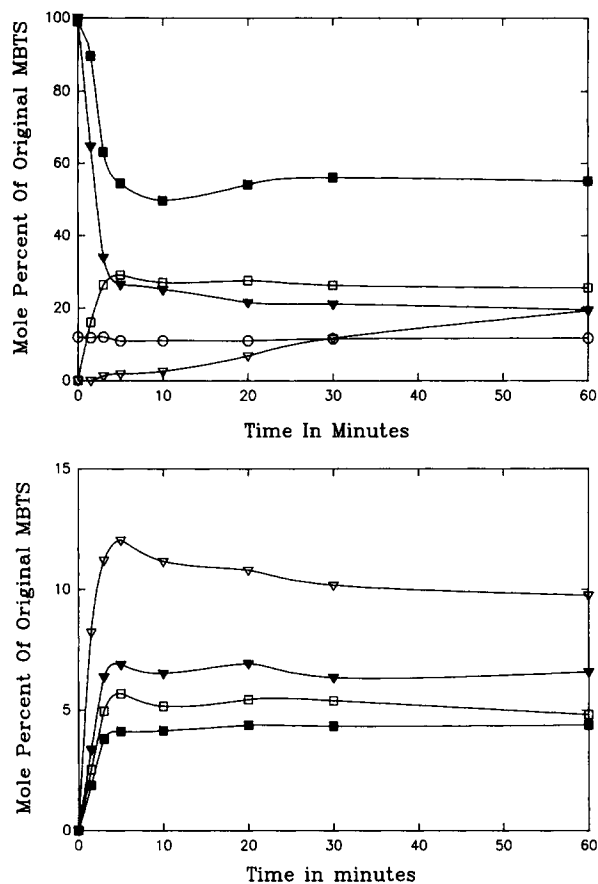


Figure 7 Products formed from the reaction of MBTS-MBT-sulfur (1 : 0.12 : 1) as function of time at 130°C. Upper diagram: (▼) MBTS, (▽) MBTM, (○) MBT, (■) sulfur, and (□) additive tri, tetra, penta, and hexa MBTPs. Lower diagram: First four detectable MBTPs: (▽) BtS₃Bt, (▼) BtS₄Bt, (□) BtS₅Bt, and (■) BtS₆Bt.

MBTS-Sulfur-MBT (1 : 1 : 0.6)

With still higher MBT loading the decrease in the MBTP concentration after 5 min is more prominent (Fig. 8), and the relative concentration of sulfur utilized in the reaction is lower. The higher MBT loading ensures that reaction route (ii) is more favorable for MBTP production as compared to reaction route (i). Thus the sulfur utilized would be lower and hence its higher concentration (cf. Figs. 7 and 8). The higher MBT loading ensures that the reverse reactions in reactions 8a and 9 are more rapid, thus shifting the equilibrium for these reactions further to the left, resulting in MBTP concentrations being lower than in Figure 7.

The very rapid rate of the reverse reaction 9 when the MBTP concentrations peak, and the accompanying degradation of BtS_xH (reaction 10), may ac-

count for the increase in elemental sulfur concentration at 5 min.

CONCLUSIONS

The homolytic scission of MBTS, followed by sulfur, exchange between the radicals and MBTS leads to the rapid production of MBTM and the formation of MBTP after an induction period. In the presence of sulfur, exchange with elemental sulfur occurs in preference to exchange with MBTS, high MBTP, and low MBTM concentrations developing. MBTPs of higher sulfur rank result from the sequential addition of sulfur atoms. MBT will undergo a sulfide exchange reaction with MBTS leading to the immediate formation of MBTPs, no induction period being observed. MBT acts as a catalyst for MBTP formation as the 2-hydropersulfidebenzothiazoles

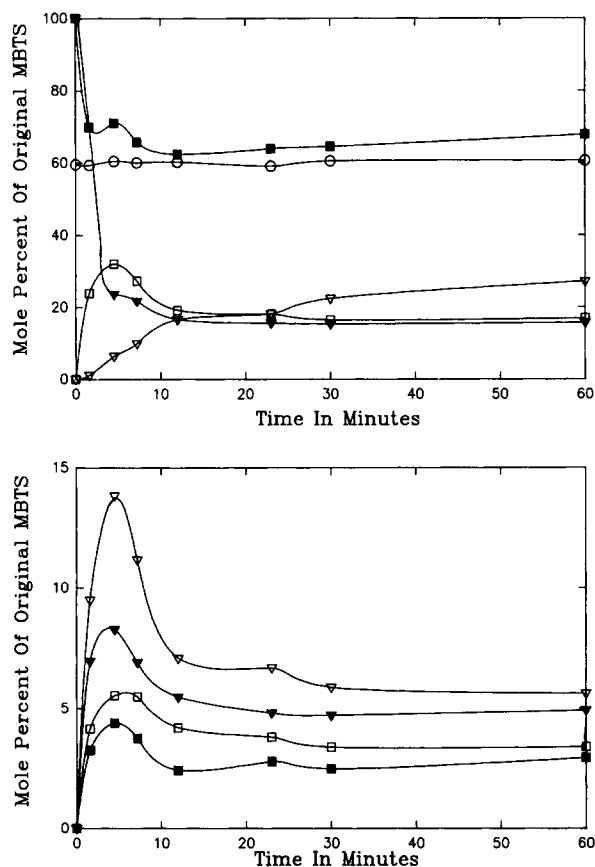


Figure 8 Products formed from the reaction of MBTS-MBT-sulfur (1 : 0.6 : 1) as function of time at 130°C. Upper diagram: (▼) MBTS, (▽) MBTM, (○) MBT, (■) sulfur, and (□) additive tri, tetra, penta, and hexa MBTPs. Lower diagram: First four detectable MBTPs: (▽) BtS₃Bt, (▼) BtS₄Bt, (□) BtS₅Bt, and (■) BtS₆Bt.

formed are unstable and decompose to MBT and sulfur.

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