Tetramethylthiuram Disulfide and 2-Mercaptobenzothiazole as Binary Accelerators in Sulfur Vulcanization. I. Exchange Reactions Between the Accelerators and Sulfur in the Absence of Rubber

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SYNOPSIS

Exchange reactions between tetramethylthiuram disulfide, 2-mercaptobenzothiazole, and sulfur were studied by heating powdered mixes to vulcanization temperatures at a programmed rate in a DSC. The reaction was stopped at points along the thermal curve and the mixture was analyzed by HPLC. On dissolution, even unheated samples undergo a sulfide exchange reaction leading to a mixed accelerator, while polysulfides of the thiuram and mixed accelerator form in low concentrations. On heating, higher concentrations of these polysulfides are formed, particularly in the presence of elemental sulfur. Dimethyldithiocarbamic acid, formed in the exchange, influences the product spectrum if it remains trapped in the DSC pan. Tetramethylthiourea is formed only at elevated temperatures when dimethylamine, a degradation product of the acid, is trapped in the DSC pan. A series of reactions is proposed to explain the product spectrum obtained under different conditions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Combinations of accelerators are commonly used in industry. Extensive studies of tetramethylthiuram disulfide (TMTD) and 2-mercaptobenzothiazole (MBT) accelerated sulfur vulcanization of polyisoprene (IR) have been conducted. This article is the first in a series reporting on the use of these as a binary accelerator system. It has been found useful to study the interaction of curatives in the absence of rubber and several articles[1-3] have reported on the interaction of TMTD and tetramethylthiuram monosulfide (TMTM) with curatives.

Bedford,[4] Dogadkin,[5] Craig,[6] and their co-workers suggested that TMTD decomposes thermally to tetramethylthiourea (TMTU), CS_2, and sulfur via TMTM as an intermediate. In contrast, Raman spectroscopic studies[7] of TMTD, heated to 145°C, reveal the formation of tetramethylthiuram polysulfides (TMTP) and the slow decomposition to TMTU and CS_2. It was emphasized that TMTM was not formed. Geyser and McGill[3] reported that TMTP is formed rapidly between 130 and 150°C and that its formation was accompanied by TMTM formation. TMTD/sulfur mixes, likewise, readily form TMTP. No TMTU was detected unless the reaction temperature was raised to above 200°C. This is in agreement with work by Kruger and McGill[2] and by Versloot.[8] The volatilization of TMTD below 180°C occurs relatively slowly. Gradwell and McGill[9] found no evidence for the decomposition of MBT on heating to 300°C and the mass loss was due only to the evaporation of MBT.

In discussing MBT accelerated vulcanization, the formation of a 2-hydropersulfide benzothiazole accelerator complex ($BtSS_xH$) is often invoked,[10-13] though Gradwell and McGill[9] could find no evidence for its formation. In experiments involving the use of radioactive sulfur, it was shown[14] that MBT, tagged in the sulfhydril group, exchanged sulfur atoms with TMTD at curing temperatures, while Guryanova and Vasilyeva[15] proposed a mechanism

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for the isotopic sulfur exchange between TMTD and elementary sulfur. Taun et al.[16] reported on the kinetics of amine evolution in the reaction between TMTD and MBT in the absence of rubber.

This article reports on the interaction among TMTD, MBT, and sulfur in a methanol solution and in the melt at vulcanization temperatures.

EXPERIMENTAL

Materials used were sulfur CP from Halpro, TMTD and MBTS from Orchem (South Africa), TMTM (Vulkacit MS) from Bayer, MBT from Monsanto, and TMTU from Fluka.

Accelerators and curatives were mixed with a pestle and mortar, normally in 1 : 1 mol ratios. Relative molar amounts used in mixes are indicated in parentheses in the text, e.g., TMTD(1)–MBT(1). Samples (2–10 mg) were heated at 5°C/min in a DuPont 910 standard DSC cell, connected to a DuPont 9000 thermal analyzer. High-purity nitrogen, at a flow rate of 70 mL/min, was used as a purge gas. In most runs, samples were sealed in aluminum pans, though the pans did not seal hermetically and volatiles slowly escaped. In many cases, the buildup of volatiles led to pans bursting above 150°C. A series of experiments was also conducted in open pans. An empty pan served as a reference. Mass loss was determined with a DuPont 951 thermogravimetric analyzer module.

The design of the DSC cell allows it to be opened, samples to be removed rapidly (3 s), and it chilled to stop the reaction. Samples heated in the DSC cell were dissolved in 2 mL dichloromethane, made up with methanol in a 25 mL volumetic flask and analyzed by HPLC. Solutions were injected within 15 min of preparation (except in studies involving changes in solution with time).

A Waters HPLC system comprising a Model 510 pump and a Model 484 tunable absorbance ultraviolet (UV) detector was used. This was connected to a Baseline 810 chromatography workstation via a WD22 chromatography interface. Separation was affected on a μ-Bondapak C_{18} reverse-phase Radial-Pak column (Waters, 8 × 100 mm, particle size 10 μm) contained in a Waters radial compression module (RCM) 8 × 10 mm. The column temperature was maintained at 30°C and the UV detector set at a wavelength of 280 nm. A Waters Guard-Pak precolumn with a μBondapak C_{18} stationary phase was utilized. The mobile phase was methanol/water (85/15 v/v) flowing at a rate of 1.0 mL/min.

Compounds were identified from their coelution with known standards. Sulfur, TMTU, TMTM, TMTD, MBT, and 2-benzothiazole-2,2′-disulfide (MBTS) were available commercially. Dimethylaminobenzothiazole (DMABT) and *N,N*-dimethylthiocarbamylbenzothiazolesulfide (DMTBS) were prepared as described below. The 2-benzothiazole-2,2′-monosulfide (MBTM) and 2-bisbenzothiazole-2,2′-tetrasulfide (M4) used were prepared by the procedure of Gradwell and McGill.[17] TMTP and 2-benzothiazole-2,2′-polysulfides (MBTP) were identified by coelution with peaks ascribed to them by Gradwell and McGill.[17] The identification of P2 is discussed below. A typical chromatogram is depicted in Figure 1.

Calibration curves used peak heights only for TMTU and TMTM and peak areas for all the remaining compounds. Calibration coefficients for MBTP, TMTP, and *N,N*-dimethylthiocarbamylbenzothiazole polysulfides (PP) were arbitrarily assigned; in the context of this study, the changes in concentration are more important than is their quantification. It is known that the coefficient used for TMTP overestimates their concentration by 10–20 times. The coefficient of P2 was estimated from its formation from MBT and TMTD. Two compounds coeluted at the peak ascribed to P1 (see below) and the coefficient of DMTBS was used for P1 throughout. The concentrations of reaction products are always expressed in terms of the mol percentage remaining or of the total that could have formed if 100% of the reactants were converted into that product. The initial concentration of MBT was used in the calculation of the concentration percentages of P1, P2, and PP.

2-Chlorobenzothiazole (4.2408 g, 0.025 mol) and hexamethylphosphoramide (25 mL) were reacted according to a published procedure[18] to give 2-dimethylaminobenzothiazole (2.5432 g; 0.0153 mol; 61%), mp 91.9°C; $\nu_{max}(CHCl_3)$ 1550, 1442, 1226, 1211, 929, 754, 725 cm^{-1}; $\delta_H(CDCl_3)$ 3.22 (s, 6 H), 7.05–7.61 (m, 4 H), *m/e* 178 (M^+).

Calcd: C, 57.8%; H, 6.06%; N, 16.9%.
Found: C, 59.7%; H, 5.62%; N, 15.4%.

TMTD (12.2 g, 0.0507 mol), MBTS (17.0 g, 0.0507 mol), and KCN (6.5 g, 1.0 mol) were reacted according to a published procedure[19] to give *N,N*-dimethylthiocarbamylbenzothiazole sulfide (10.7042 g; 0.0421 mol; 83%), mp 121.9°C (lit. [97], mp 121–122°C); $\nu_{max}(CHCl_3)$ 1714, 1365, 1224, 531 cm^{-1}; $\delta_H(CDCl_3)$ 3.54 (s, 6 H), 7.20–8.16 ppm (m, 4 H).

Calcd: C, 54.92%; H, 4.45%; N, 12.60; S, 37.81%.
Found: C, 54.03%; H, 3.86%; N, 12.45%; S, 35.2%.

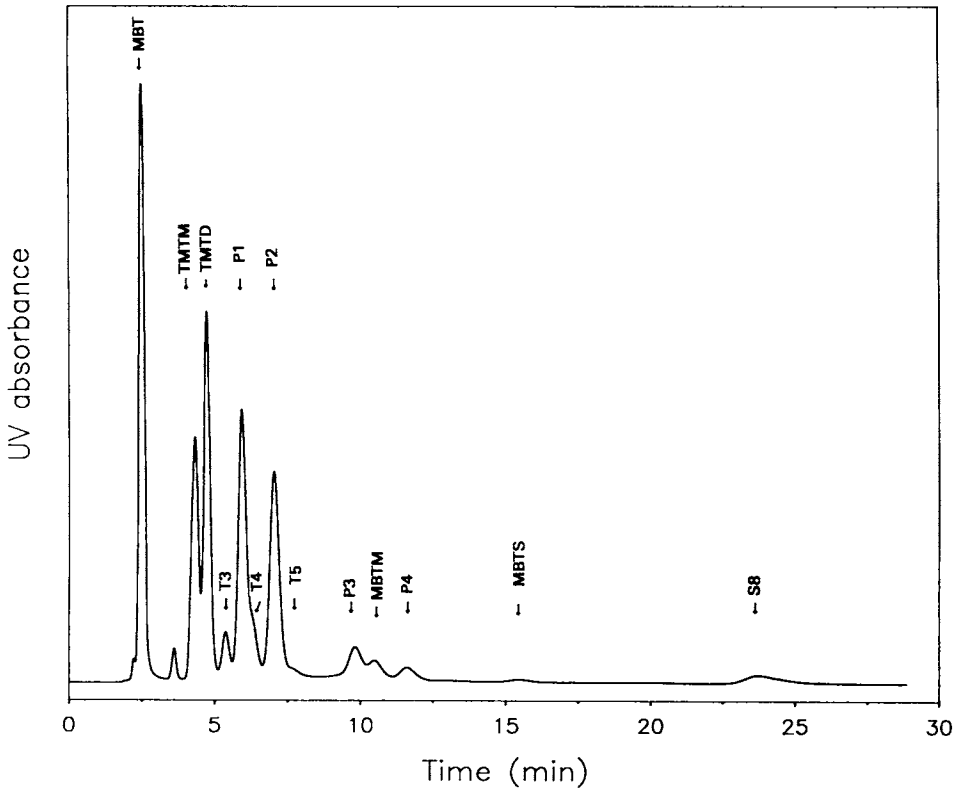


Figure 1 Typical HPLC chromatogram of some of the most common products found in this study.

A Harrison Research Chromatotron Model 7924T was used for separation of the compounds. The adsorbent layer constituted 2 mm silica gel 60 PF_{254} with $CaSO_4$ (Merck) using dichloromethane as the mobile phase. The compounds synthesized were characterized by NMR (Varian Gemini 200 MHz), mass spectrometry (Hewlett-Packard 5985A linked to a Hewlett-Packard 5840A gas chromotograph with a capillary column), CHN, and sulfur analysis (combustion).

RESULTS AND DISCUSSION

Due to the large number of product species formed, detailed plots of their concentration vs. reaction time or temperature become cluttered and difficult to interpret; hence, changes in concentration of selected species only are presented by smoothed curves. The concentrations of all reactants and products are shown in the tables and these must be read in conjunction with the figures.

Reactions in Solution

As discussed below, HPLC analysis shows the formation of a number of products on heating a TMTD(1)–MBT(1) mixture to vulcanization temperatures. However, a product with a retention time of around 7 min (P2) formed very readily and was detected by HPLC immediately after dissolution of a TMTD(1)–MBT(1) mixture in dichloromethane/methanol. Consequently, interaction between species in solution, as distinct from reactions that occur on heating, must first be considered to avoid misinterpretation of data obtained during the heating process.

The concentration of TMTD in the solution of a TMTD(1)–MBT(1) mixture (Fig. 2) is roughly 80% that in the original mix. Though the quantitative analysis of MBT presented certain difficulties, some MBT, too, had clearly been consumed in the formation of P2. On aging in the dark at 25°C, the concentration of P2 in solution increased rapidly and after 30–40 min reached an equilibrium concentration some 2.5 times than that present in the freshly prepared solution. The TMTD concentration decreased gradually with time, while the MBT concentration at first decreased and later showed an increase. The reason for this is not apparent and may be associated with difficulties in analyzing for MBT.

Nelander and Sunner[20] found that the thermal disproportionation (at 25 and 60°C) of dialkyl di-

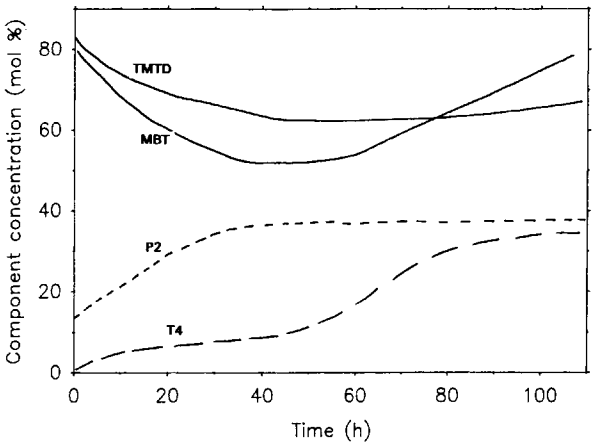


Figure 2 HPLC analysis showing changes in a solution of TMTD(1)–MBT(1) in a methanol/dichloromethane (21/4 v/v) at room temperature as a function of time.

sulfides in most cases gives an equilibrium mixture close to the statistical value, $K \approx 4$:

$$R^1SSR^1 + R^2SSR^2 \rightleftarrows 2R^1SSR^2$$

Similarly, the reduction of protein disulfide groups occurs according to the following reaction:

$$R^1SH + R^2SSR^2 \rightleftarrows R^2SH + R^1SSR^2$$

It is reasonable to suggest that P2 is an exchange product formed by reactions of this type, i.e., P2 = XSSBt, where X = $(CH_3)_2CS$ and Bt = C_7H_4NS. Exhaustive attempts to isolate P2 chromatographically from TMTD and MBT proved unsuccessful, indicating that a rapid equilibrium exists among TMTD, MBT, and P2. P2 is also formed in a solution of TMTD(1)–MBTS(1) where its initial concentration is more than double that in the corresponding TMTD(1)–MBT(1) solution. Only three species are present in the solution, as would be expected if disproportionation, as envisaged by Nelander and Sunner,[20] involved scission of the weaker S—S bond only in TMTD, MBTS, and P2. This further supports the contention that P2 is XSSBt. These three species are formed rapidly and their concentrations remain constant with time (TMTD and MBTS $\approx$ 62 mol %).

The amount of P2 formed in solution changes with the dichloromethane/methanol ratio and suggests that an ionic reaction may be involved. Kice and Ekman[21] found that the disproportionation of benzyl *p*-tolyl disulfide was catalyzed by strong acids.

In the TMTD(1)–MBT(1) solution, peaks attributed to tetramethylthiuram tri-(T3) and tetrasulfides (T4) are also present after a few minutes (Table I), the concentration of the former becomes stabilized after some 30 min, while the concentration of the tetrasulfide continues to increase slowly with time. On its own, TMTD is stable in solution and the formation of higher sulfides indicates that the presence of MBT facilitates the exchange reactions. It was noted that no similar polysulfides are formed in the TMTD(1)–MBTS(1) solution. After a few minutes, a small amount of another product (P3) appears (Table I), while in some cases, a further product (P4) is also just detectable. These, too, could not be isolated, and by analogy to the TMTD[3,8] and CBS and MBTS[17] systems, these are attributed to polysulfides of P2 that result during the exchange reactions.

In the TMTD–MBT exchange, dimethyldithiocarbamic acid (Hdmtc) should also be formed but this was not detected. According to Geyser and McGill,[3] the acid has a very short retention time and should be eluted before the MBT peak. The absence of Hdmtc from the product spectrum will be discussed below. It is interesting to note that in the TMTD–MBTS solution P2 is the only exchange product to form, while in the TMTD–MBT solution, a number of polysulfides of both TMTD and P2 are produced. Both TMTD and MBTS are stable in solution, suggesting that the acid (Hdmtc) formed in the TMTD–MBT exchange reaction plays a catalytic role in polysulfide formation as proposed by Kice and Ekman.[21]

Increasing the amount of TMTD in the mixture leads to a very similar product spectrum (Fig. 3 and Table I). The amount of P2 formed is higher, while a larger proportion of MBT is consumed. At long times (> 80 h), some TMTM (3%) also appears in the solution as well as a small amount (1%) of a new product P1. The formation of TMTM is not surprising, since the TMTM–TMTD–TMTP equilibrium is well documented.[2,3] The retention time for P1 suggests that it is a derivative of P2. DMTBS and DMABT were synthesized but it was found that both species coeluted at the HPLC peak represented by P1. It is likely that, by analogy to TMTM, P1 formed here in solution is the monosulfide of P2, i.e., DMTBS, formed on desulfuration of P2. Exchange reactions such as those detailed by Kice and Ekman[21] result in the sulfuration of some molecules at the expense of others.

Geyser and McGill[3] proposed a mechanism for TMTM and TMTP formation in a TMTD or TMTD–sulfur melt. In essence, the mechanism involved the formation of a radical XS that abstracted sulfur from XSSX or sulfur to give XSS. The recombination of XS_x radicals would result in TMTP, while a high concentration of TMTM would result

Table I Analysis, as a Function of Time, of TMTD–MBT and TMTD–MBTS in a Methanol/Dichloromethane (21/4 v/v) Solution at Room Temperature

		Component Concentration (Mol %)						
Mixture	Time (h)	TMTD	T3	T4	MBT	MBTS	P2	P3
TMTD(1)–MBT(1)	1	81	< 1	1	70		19	
	2	76	1	2	67		18	
	3	80	3		71		22	
	4	81	3		71		25	3
	5	79	3		69		26	3
	6	77	3		68		27	5
	7	77	4	4	68		28	6
	8	79	4	5	71		29	6
	31	72	9	8	62		35	10
	51	59		9	47		34	10
	59	64		15	55		37	9
	72	70		24	59		40	9
	80	71	5	29	70		36	7
	96	69	6	31	82		37	8
	103	61	5	31	65		34	7
TMTD(3)–MBT(1)	0	72			67		33	
	1	75	< 1		67		33	
	2	71	2		57		41	
	3	74	3		59		42	4
	4	74	4	3	57		44	5
	5	74	5	3	56		43	5
	6	73	6	4	53		47	6
	7	74	12	4	55		44	5
	8	71		4	48		53	16
	31	73		6	53		61	11
	51	70			34		66	10
	59	74	3		35		68	12
	72	75	6		39		48	6
	80	68	6	14	70		52	9
	96	71	7	16	67		50	8
	103	72		17	66			

from exchange reactions in the absence of sulfur. The more stable DMABT is expected to form only at elevated temperatures. The calibration coefficient for DMTBS was used in all cases in the calculation of the concentration of P1.

HPLC results of mixtures of curatives heated to various temperatures must clearly be interpreted with caution, bearing in mind that changes in the product spectrum can result from subsequent reactions occurring in solution.

Dynamic Heating Studies of Curatives

TMTD–MBT

In several DSC thermal curves, sharp endothermic peaks were found, usually above 150°C. It was suspected that these events may be due to the bursting of DSC pans, i.e., to an artifact of the experimental procedure. In an attempt to clarify this point, sealed DSC pans, containing powder mixes, were substituted for the usual (unsealed) sample holders in a TG experiment. Figure 4 shows that the sharp endothermic events coincide with the bursting of the pans and the rapid release of volatiles. A DSC pan containing a lower sample mass required higher temperatures before the pan burst occurred. The endothermic events above 150°C are therefore not associated with the reaction, but it is clear that large amounts of volatiles form.

TMTD melts at 145°C and MBT at 182°C, while the TMTD(1)–MBT(1) mixture shows a melt/dissolution endotherm at 114°C (Fig. 5). The latter endotherm is accompanied by a mass loss, indicating

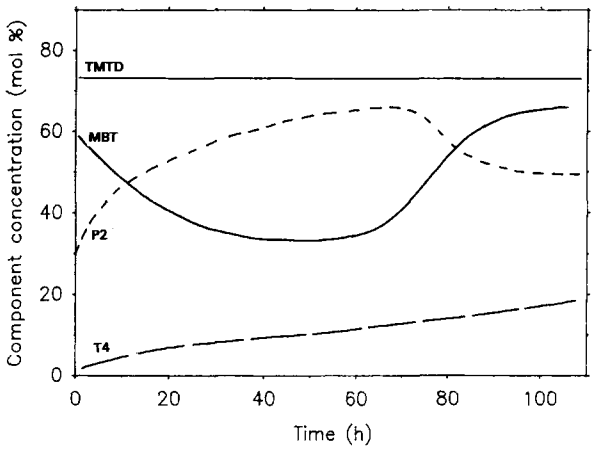


Figure 3 HPLC analysis showing changes in a solution of TMTD(3)–MBT(1) in a methanol/dichloromethane (21/4 v/v) at room temperature as a function of time.

that the liquefaction is associated with a reaction leading to the formation of volatiles. The mass loss of the TMTD(1)–MBT(1) system, as measured by TG (Fig. 6), is much higher than that found with either of the curatives alone. The TG curve shows a uniform mass loss after a rapid initial decrease and the second endotherm in the DSC thermal curve (Fig. 5) can be attributed to volatiles escaping from the DSC pan (it was impossible to seal the pans hermetically). In unsealed pans (Fig. 6), this endotherm starts earlier and is much broader. The product spectrum, too, depends upon whether volatiles were able to escape from the system (open pans) or whether such species were trapped (sealed pans). In a closed system, volatiles can clearly participate in further reactions, and by using small sample masses, the effect of pan sealability was investigated in the TMTD(1)–MBT(1) system only. In all other systems, the pressure buildup was such that the pans burst explosively at some point along the thermal curve.

At temperatures above 100°C, the concentration of TMTM, T3, and T4 increased in both sealed and open pans, and in the sealed pan system, it reached a maximum at about 130°C (Figs. 5 and 6 and Table II). In an open system, the concentration of both accelerators decreased in concert (Fig. 6), while in a closed system, the TMTD concentration decreased as the temperature was raised above 100°C but the MBT concentration remained high. The concentration of P2 decreased in parallel with the decrease in TMTD in a closed system, while in an open system, the concentration of P2 increased sharply as the TMTD and MBT disappeared. In the latter system, P3, P4, and P1 are also formed (Table II), their concentration likewise passing through a maximum. In the sealed system, the concentration of P2 and its polysulfides never reaches the same values as in the open system, while the concentration of P1 levels

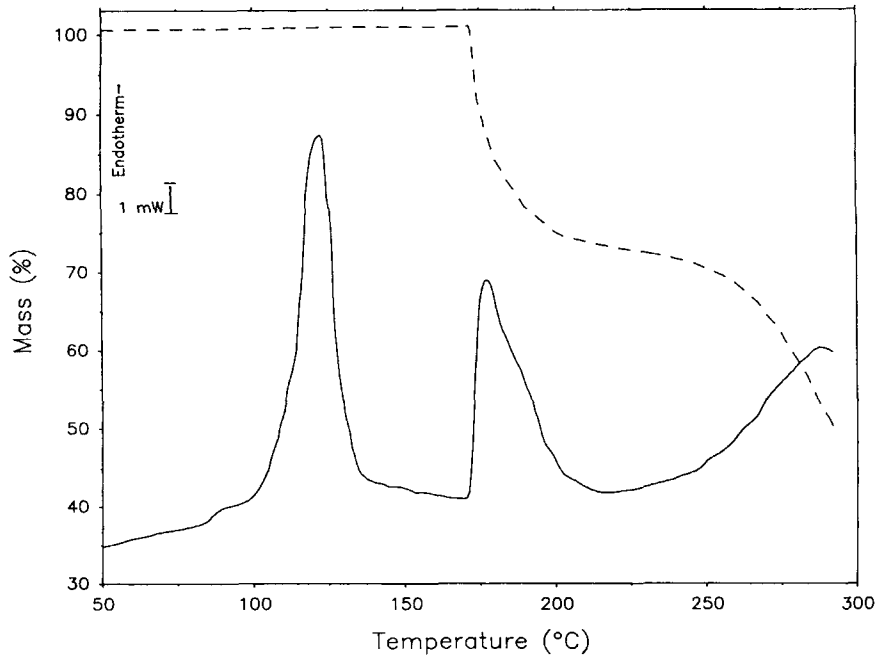


Figure 4 (——) DSC and (– – –) TG of TMTD(1)–MBT(1) heated at 20°C/min in sealed pans. In this TG experiment, a sealed DSC pan was used in place of the normal open sample holder.

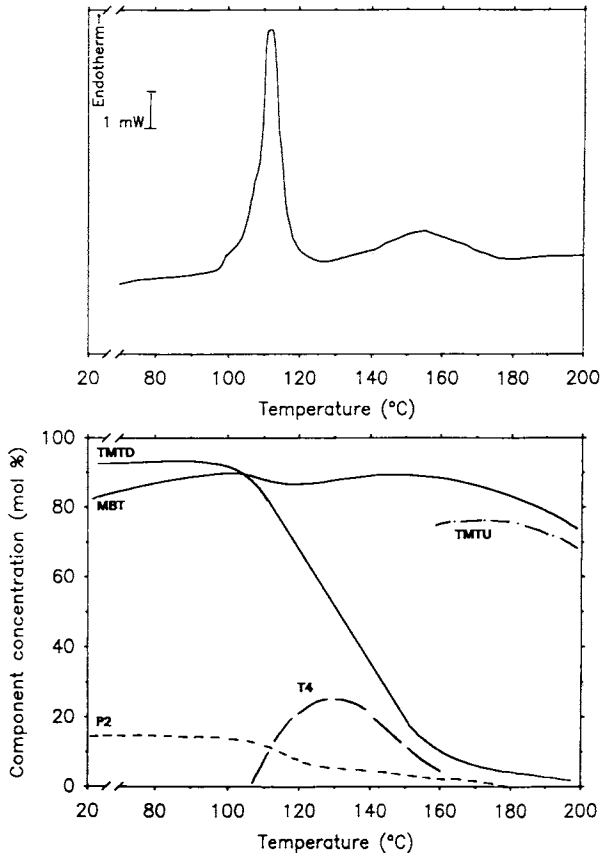


Figure 5 DSC (upper figure) and HPLC analysis (lower figure) of TMTD(1)–MBT(1) heated at 5°C/min in sealed pans.

above 140°C. It must again be noted that in view of the facile formation of P2 in solution, concentration changes must be interpreted with caution.

MBTS and its polysulfides and monosulfide are found in noticeable amounts only in the open system, the concentration of MBTM becoming particularly high above 160°C (Table II). TMTU is found only in the closed system at temperatures above the maximum in the second endotherm and is accompanied by the formation of some elemental sulfur (Table II).

The product spectrum can, in a large part, be explained in terms of the series of equilibria in Scheme 1. As noted earlier, TMTD and MBT readily undergo an exchange reaction leading to the formation of P2 (equilibrium 1). The amount of P2 detected in both systems at 100°C equals that at room temperature and can be considered to have been formed on preparation of the solution, i.e., no TMTD–MBT interaction occurred in the solid state up to this point. However, above the TMTD–MBT melt/dissolution endotherm (Figs. 5 and 6), an interaction does occur as evidenced by the presence of other species (not found in the room-temperature solution) in the product spectrum.

A rapid mass loss is observed once melting commences (Fig. 6). This may be ascribed to the decomposition of Hdmtc and the escape of dimethylamine (DMA) and CS_2 from the system or to the volatilization of Hdmtc. Craig et al.[22] claimed that Hdmtc was thermally unstable but did not indicate at which temperature decomposition commenced. $[dma]^+[dmtc]^-$, which may also form, was reported to decompose rapidly at 140°C.[3,22]

As discussed above, it was not possible to characterize the product that gives rise to the peak P1 satisfactorily, both DMTBS and DMABT having the same retention times on the HPLC. DMTBS may form from exchange reactions in which P2 gives products of lower and higher sulfur rank.[3] It may also rise from exchange reactions akin to those in reaction 1, of TMTM or MBTM with MBT or Hdmtc, respectively. The latter exchange is less likely as the TMTM and MBTM concentrations are

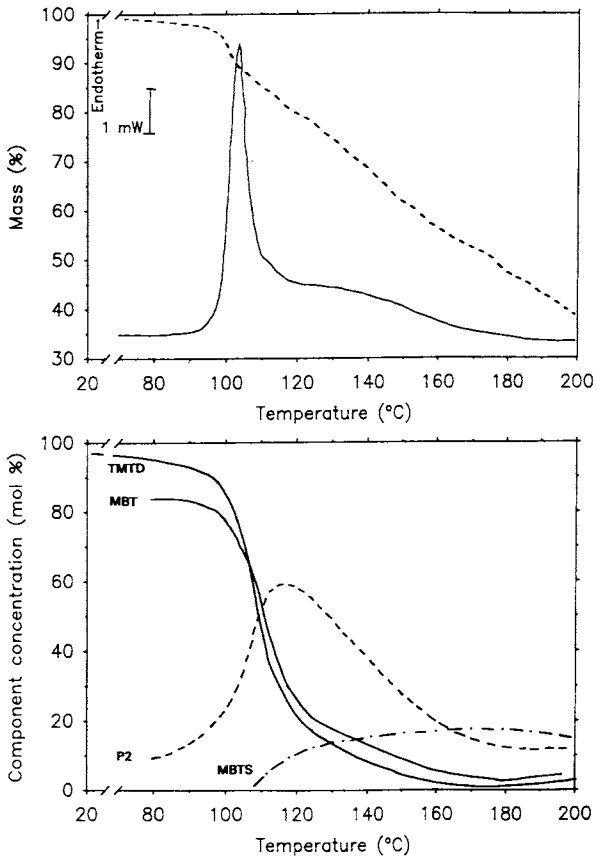


Figure 6 (– – –) TG and (——) DSC (upper figure) and HPLC analysis (lower figure) of TMTD(1)–MBT(1) heated at 5°C/min in open pans.

Table II Analysis of Mixtures Heated in the DSC at 5°C/Min in Sealed and Unsealed DSC Pans

Mixture	Temp (°C)	Component Concentration (Mol %)															
		S8	TMTM	TMTD	T3	T4	T5	TMTU	MBT	MBTM	MBTS	M3	M4	P1	P2	P3	P4
TMT(1)–MBT(1) in sealed pans	25			94					84						15		
	100			94	10	3			91						11	2	1
	110	< 1	4	88	18	6			89					1	12	6	2
	120	1	13	68	28	20	4		86					5	7	10	3
	140	5	13	37	24	19	4		90	1				10	4	5	2
	160	10		10	3	5	1	75	88	1				10	1	2	1
	180	12						75	83					11			< 1
	200	11		< 1				67	72					14			
TMTD(1)–MBT(1) in open pans	25			97					91					< 1	18		
	80			94					84						9		
	100			86	10	11			78						24	7	
	110		3	44	19	11			48		3			3	52	26	
	120		7	20	13	1			23		10	15		9	58	50	9
	140	3	6	7	6				13	4	14	21	12	20	37	50	10
	160	4	1	1					5	22	16	25	10	23	19	4	7
	180	4	< 1	1					2	20	16	23	11	12	11	7	4
	200	3		3						17	13	17	13	9	11	8	6
TMTD(3)–MBT(1) in sealed pans	25			97					86						19		
	100			92					81						15		
	110		4	83	5	3			70					5	15		
	120	1	6	71	23	15			63	1				13	17		
	140	4	15	33	19	23			76					21	16		
	160	9		6	3	1		86	63	1				19	3		
	180	12						90	58					27		1	
	200	8		1				65	62	2				1	1	4	1

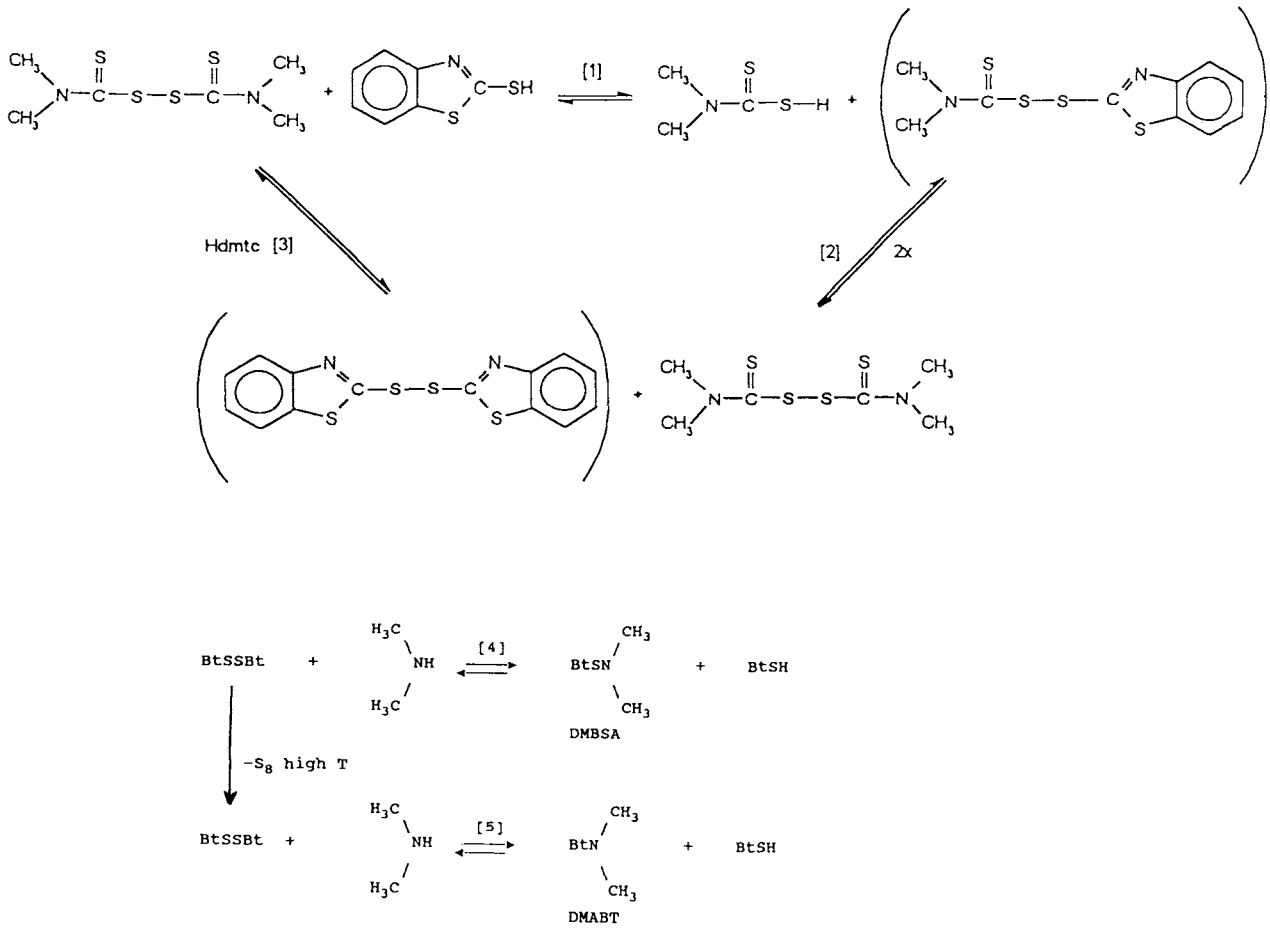
Table II (Continued)

Mixture	Temp (°C)	Component Concentration (Mol %)															
		S8	TMTM	TMTD	T3	T4	T5	TMTU	MBT	MBTM	MBTS	M3	M4	P1	P2	P3	P4
TMTM(1)–MTB(1) in sealed pans	25		100[a]						[a]								
	80		85[a]						[a]								
	120		94[a]						[a]					1	1		
	140		80[a]						[a]	5				5	3		
	160		29[a]						[a]	20				18	9		
	180		21[a]						[a]	2				12			
	200		19[a]						[a]	2				15			
TMTM(1)–MBTS(1) in sealed pans	25		85[b]						[b]		80				2		
	80		93[b]						1[b]		80				2		
	100		95[b]								83			1	3		
	150		53[b]	1					2[b]	4	41	5		32	38	5	
	200	5		9					12[b]	41	10	7		33	10		
TMTD(1)–MBTS(1) in sealed pans	25			90		2					81				8		
	100			60		4					45				47	4	
	110			72		6					51	4		45	6		
	120			46	13	5			6		39	6		4	68	14	
	140			27	12				27		29	20	3	11	66	38	4
	160			18					30		27	30	7	32	50	50	9
	180	5		16					16	7	14	26	8	31	34	35	8
	200	15		10					11	23	12	16	6		7		

Table II (Continued)

Mixture	Temp (°C)	Component Concentration (Mol %)														
		S8	TMTM	TMTD	T3	T4	T5	TMTU	MBT	MBTM	MBTS	M3	M4	P1	P2	P3	P4
TMTD(1)–MBT(1)–sulfur(1) in sealed pans	25	91		96	9				89						10	1	
	80	83		75	47	44	9		90						10	11	
	100	84		62	61	68	26		85					2	12	11	5
	120	88	5	48	47	51	13		92					5	7	13	6
	140	91	6	40	37	39	10		92					5	6	9	4
	160	96	10	15					85	< 1				13	2	2	2
	180	99	12						79					18	< 1		
	200	90	10						76	2				21	2		
TMTD(1)–MBTS(1)–sulfur(1) in sealed pans	25	92									66				27		
	80	91				6					59				30	5	
	100	67			34	46	24				18	85	28		33	83	25
	200	103							15	12	12	25	11	33	12	15	5
DMTBS(1)–sulfur(1) heated in sealed pans	25	95												99	6		
	135	80									5			89	6		
	150	73		5						1	4			84	8		
	160	62								2	4			70	7		
	180	44		10	7		11		3	8	8			33	16		
	190	48		8	6	18	16		2	11	9			12	18		
	200	51		4	5	15	8		2	12	10			9	17		

[a] TMTM and MBT not separated. Total indicated here as TMTM.
[b] Poor separation of TMTM and MBT.



Scheme 1

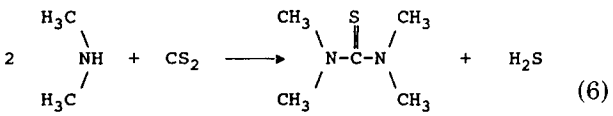
low. At high temperatures, the decomposition of Hdmtc into DMA and CS_2 occurs more readily and DMABT can form in the presence of DMA (in sealed systems) via reaction 5. In an experiment to determine whether a reaction occurs between MBTM and DMA, DMABT was found in a 52% yield upon heating the mixture to 150°C at 5°C/min in a DSC pan. DMBSA (*N,N*-dimethylbenzothiazole-2-sulfenamide) is essentially the sulfurated form of DMABT and may result from MBTS and DMA in reaction 4. It may likewise coelute at the retention time of P1. Reactions 4 and 5 may also occur in open pans, the amine reacting rapidly at higher temperatures before it can escape from the system. In general, therefore, it appears that P1 is composed mainly of DMTBS at low temperatures and of DMABT and DMBSA (formed from MBTM and MBTS, respectively) at higher temperatures.

In the open system, the concentration of P2 and its polysulfide P3 increase sharply above 100°C, while the concentration of both TMTD and MBT decrease. The loss of Hdmtc by decomposition or evaporation from the open system would move equilibrium 1 to the right, decreasing both the TMTD and MBT concentration and increasing the P2 concentration. This, in turn, would lead to a buildup of MBTS via equilibrium 2 and the TMTD thus formed would be available for further reaction according to equilibrium 1. Thus, MBTS and its polysulfides are found only in the open system. The high concentrations of P2 and P3 that build up in the open system (Fig. 6) when the TMTD and MBT concentrations decrease must be attributed to BtS being more important than is XS in initiating the sulfuration–desulfuration exchange process.[3] (Whether the BtS and XS species are ionic or radical in nature is unknown and therefore not indicated.) MBTP and PP are formed in high concentrations only when MBTS is present, the dissociation of MBTS generating BtS for the sulfuration–desulfuration sequence. The formation of mono- and polysulfides of MBTS is consistent with other studies.[23] As the temperature increases, the concentration of P1 passes through a maximum as more ma-

terial volatilizes from the system and equilibria change. DMA is lost from the system and DMBSA and DMABT do not form in high concentrations, while the MBTM concentration increases.

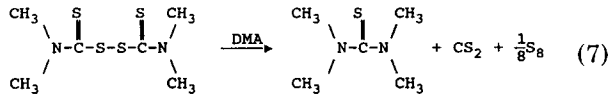
In the closed system, the amount of P2 decreases above 100°C and demonstrates the effect of Hdmtc on the reverse reaction in equilibrium 1. It also suggests that the acid decomposes slowly, sufficient acid being present to limit the consumption of MBT and restrict the formation of increasing amounts of P2. At low temperatures, the concentration of MBT remains high and could further be accounted for by reaction 3 that regenerates MBT (plus $\frac{1}{2}$ TMTD). No MBTS is detected due to its destruction by Hdmtc in reaction 3. Reaction 3 is, of course, the reverse of reactions 1 and 2, but is included for the situations in which TMTD and MBTS do not exist together. At high temperatures, the destruction of MBTS proceeds preferentially via reactions 4 and 5 to produce P1, here identified with DMBSA and, at even higher temperatures, with DMABT. In the closed system, the DMA trapped in the DSC pan causes a steady increase in P1 concentration, with only a small amount of MBTM detected. The decrease in TMTD may be ascribed to the formation of large amounts of TMTP and TMTM. This is consistent with their formation in other systems.[2,3] XS would now be the important species giving rise to the sulfuration–desulfuration exchange and it would act principally on TMTD which is present (initially) in the highest concentration. Note that at lower temperatures the P1 (DMTBS) concentration increases in line with the increase in TMTM. P2 would not escape desulfuration by XS in the exchange sequence.

TMTU forms rapidly at 160°C in the sealed system where it could result from the interaction of DMA and CS_2 liberated on decomposition of Hdmtc. It may also point to the decomposition of Hdmtc becoming important only at higher temperatures:



(6)

Interaction between DMA and TMTD would likewise yield TMTU[3,24] together with increasing amounts of elemental sulfur as observed in Figure 5 and Table II:



(7)

Geyser and McGill[3] found that Hdmtc did not attack TMTD in a closed system at 140°C, but this may be because DMA was trapped as $[dma]^+[dmtc]^-$, which is still stable at this temperature.[3,22]

Three endothermic peaks are observed in the DSC thermal curve of a TMTD(3)–MBT(1) mixture (Fig. 7). The first endotherm coincides with the eutectic in the TMTD(1)–MBT(1) system and is followed by a second endotherm which may be due to the remainder of the TMTD dissolving in the eutectic liquid. The final endotherm is associated with the rapid reactions and evolution of volatiles that lead to the bursting of the DSC pans. As for the system with only 1 mol TMTD, the onset of the mass loss coincides with the melting of the curatives and the product spectrum is very similar to that found earlier, viz., the MBT concentration remains high though there is a slightly larger decrease in concentration at higher temperatures (Table II). TMTD decreases as the reaction progresses and TMTU and elemental sulfur form in the higher-temperature regions. The shape of the P1 curve

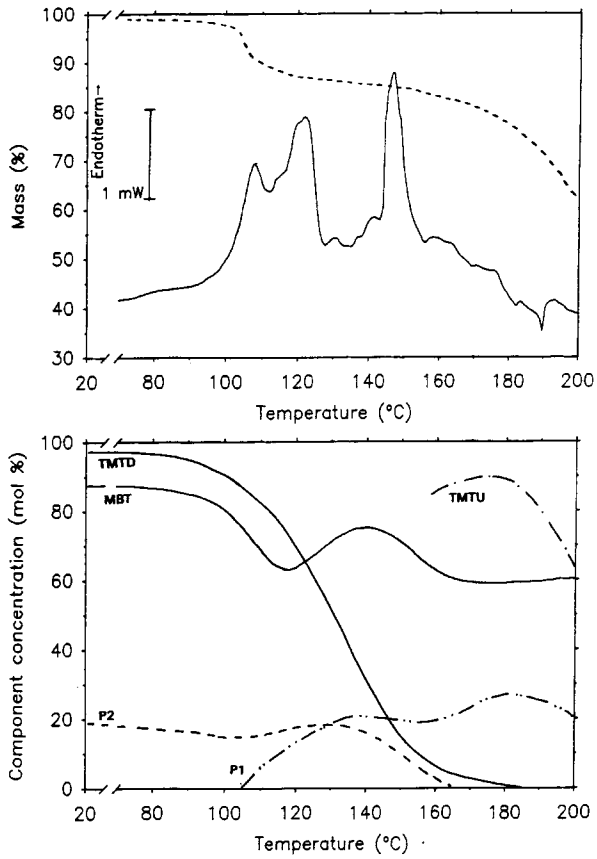


Figure 7 (– – –) TG and (——) DSC (upper figure) and HPLC analysis of (lower figure) TMTD(3)–MBT(1) heated at 5°C/min in sealed pans.

shows that P1 forms via the low- and high-temperature reactions. It forms in higher concentrations than in the TMTD(1)–MBT(1) system because the higher proportion of TMTD produces more DMA which drives reactions 4 and 5, Scheme 1, forward.

TMTM–MBT

In the TMTM(1)–MBT(1) system, the eutectic has an onset temperature of 89°C and a comparison of the DSC and TG curves (Fig. 8) shows that the melt endotherm is not associated with a rapid mass loss as for the TMTD–MBT system. HPLC analysis of the mixture, heated to 114°C (beyond the endotherm), showed that no reaction had occurred. However, at higher temperatures (above 140°C), some exchange reactions occur, yielding P2, P1, and MBTM (Table II). It was not possible to separate TMTM from MBT in this series of experiments, but the HPLC peak area was attributed to the two species that decreased as the reaction progressed; the TMTM peak area calibration coefficient was used for the single peak (Table II). The product spectrum can be explained by a sequence of equilibria analogous to that in Scheme 1. P1 (DMTBS) is a prominent product as would be expected; it will form directly in the exchange. Decomposition of Hdmtc formed in the exchange would account for the mass loss and would drive the exchange equilibrium 1 (Scheme 1) to the right, i.e., lead to a decrease in accelerator concentration while the high concentration of MBTM would result from equilibrium 2. The reason for the interaction between TMTM and MBT becoming rapid only above 140°C may be attributed to the greater stability of TMTM compared to TMTD. The unsymmetrical break that occurs in the exchange between TMTM and MBT is not unexpected. At high temperatures, the proportion of the contribution of DMBSA and DMABT to P1 increases in preference to that of DMTBS, as evidenced by the consumption of MBTM above 160°C.

TMTM–MBTS

Exchange reactions in solution for the unheated TMTM(1)–MBTS(1) system (Fig. 9 and Table II) are very limited compared to that in the TMTD(1)–MBTS(1) system (cf. Fig. 10) and may be attributed to the stability of TMTM. Ready exchange does occur at higher temperatures. The sequence of equilibria in Scheme 1 suggests that P2 and P1 (DMTBS) should be the principal products, as indeed is found at 150°C.

At higher temperatures, TMTM and MBTS decrease in concert as do TMTD and MBTS in Figure 9. (The clear separation of TMTM and MBT was difficult, though the concentration of the latter can be expected to be very low.) At 200°C, the more stable species P1 and MBTM dominate while some 2-bisbenzothiazole-2,2′-trisulfide (M3) and sulfur are formed (Table II). The composition of P1 at high temperatures is expected to be mainly DMTBS in this system, since no Hdmtc is produced (a low mass loss due mainly to evaporation and not decomposition is observed) and reactions 4 and 5, Scheme 1, do not occur. This is further evidenced by the presence of MBTM at 200°C.

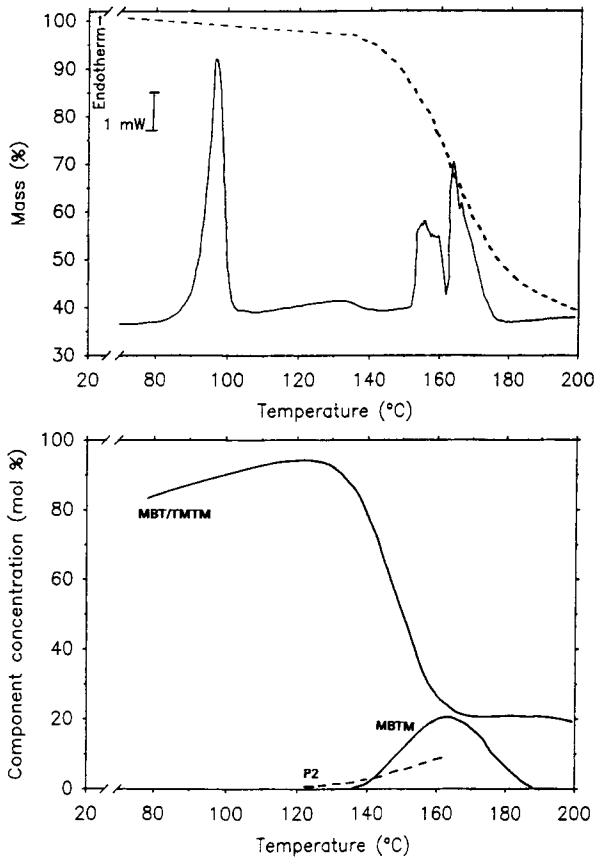


Figure 8 (– – –) TG and (——) DSC (upper figure) and HPLC analysis (lower figure) of TMTM(1)–MBT(1) heated at 5°C/min in sealed pans. MBT and TMTM peaks not separated, indicated here as MBT/TMTM.

TMTD–MBTS

The DSC melting/dissolution endotherm of TMTD(1)–MBTS(1) occurs at 116°C (Fig. 10). As in the TMTM(1)–MBTS(1) system, the mass loss is small as no Hdmtc is produced and occurs only at temperatures well above the melting endotherm. As noted earlier, the concentration of P2 in a TMTD(1)–MBTS(1) solution is considerably higher

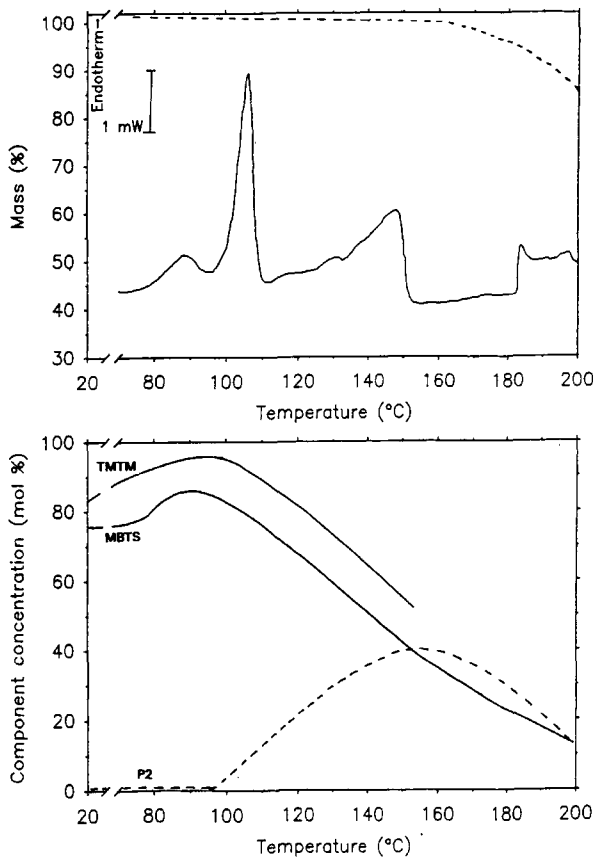
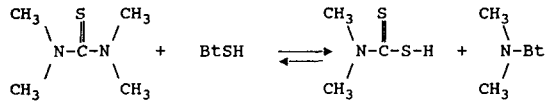


Figure 9 (– – –) TG and (——) DSC (upper figure) and HPLC analysis (lower figure) of TMTM(1)–MBTS(1) heated at 5°C/min in sealed pans. TMTM and MBTS peaks poorly separated.

than in a similar TMTD(1)–MBT(1) solution (Table II). As no Hdmtc is formed in this system, the equilibrium reactions are much simpler. On heating, very large amounts of P2 and P3 form while the concentrations of TMTD and MBTS decrease in concert. The formation of PP (polysulfides of DMTBS) and MBTP are favored over the formation of TMTP, and compared to the MBT system, the formation of polysulfidic compounds occurs more readily. MBT forms above 120°C, the source of the proton being uncertain, but possibly it is abstracted from H_2O adsorbed onto the powdered sample. Whether MBT or Hdmtc forms first is a moot point. The formation of either will give rise to an equilibrium from which the other will result. Again, the detection of P1, MBTM, and MBTP together at 200°C suggests that it is chiefly composed of DMTBS.

TMTU–MBT

Some TMTU forms in a TMTD(1)–MBT(1) mixture heated in sealed pans and the possibility that P1 (DMABT) formed from the interaction of TMTU and MBT was investigated:



(8)

The onset of the mutual dissolution of the TMTU(1)–MBT(1) mixture occurs at 60°C. On heating to 200°C, a mass loss of 6% was measured for DSC samples and HPLC analysis returned only MBT and TMTU. A reaction occurs when the sample is heated to 300°C and only MBT and P1 remain, the DSC sample showing a mass loss of 56%. A sample of TMTU(1)–MBT(1) was heated to 250°C for 60 min under nitrogen. It was possible to separate P1 from MBT chromatographically in this sample and the MS and NMR spectra were found to coincide with that of DMABT sample that was synthesized. However, the reaction of MBT and TMTU to produce P1 recorded here occurs at temperatures well above those of importance to vulcanization and it

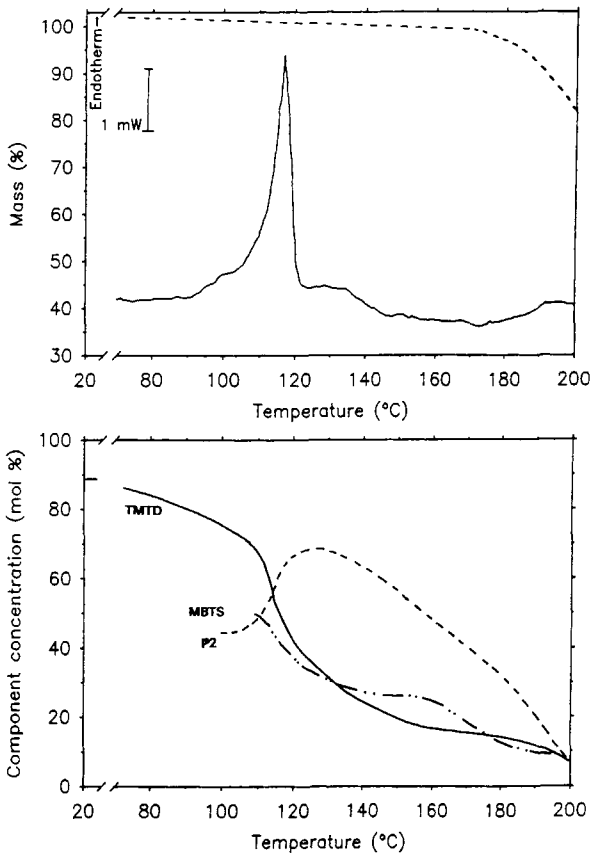


Figure 10 (– – –) TG and (——) DSC (upper figure) and HPLC analysis (lower figure) of TMTD(1)–MBTS(1) heated at 5°C/min in sealed pans.

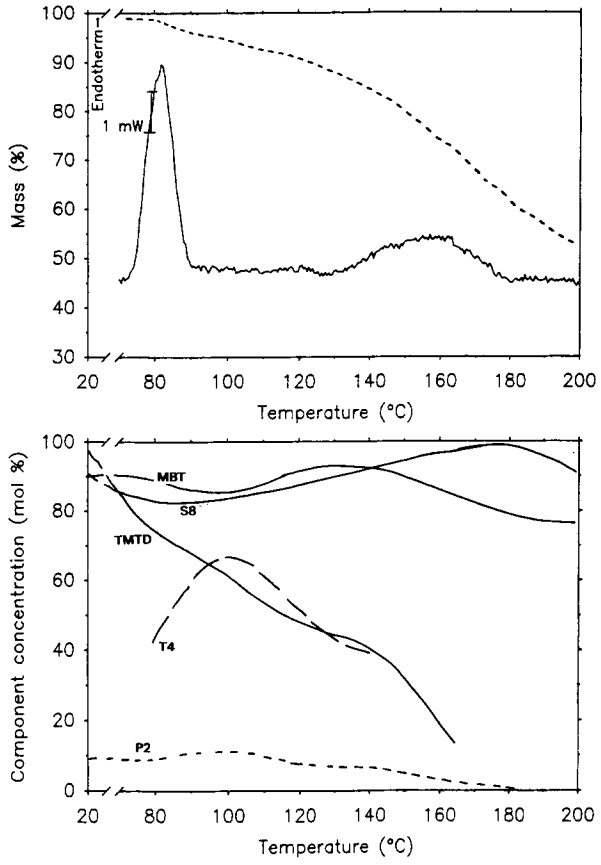


Figure 11 (- - -) TG and (——) DSC (upper figure) and HPLC analysis (lower figure) of TMTD(1)–MBT(1)–sulfur(1) heated at 5°C/min in sealed pans.

is unlikely that P1 reported above was DMABT formed as a result of TMTU–MBT interaction. Its formation via reactions in Scheme 1 is more plausible.

TMTD–MBT–Sulfur

The DSC thermal curve for the TMTD(1)–MBT(1)–sulfur(1) system (Fig. 11) has the same general features as that for the system without sulfur. A very low temperature melt/dissolution endotherm at only 82°C is observed, followed by a second endotherm, due to escape of volatiles from the pans. This occurs in the same temperature region as in the TMTD(1)–MBT(1) system. Mass loss from the mixture again begins concurrently with the melt/dissolution endotherm, albeit at a slower initial rate. TG shows that when the volatiles can readily escape a large mass loss of 48% occurs on heating to 200°C.

A similar product spectrum is obtained to that in the absence of sulfur, though certain quantitative differences apply (Table II). The MBT concentration remains high up to 200°C, as does the sulfur concentration. As Hdmtc cannot escape the reverse reaction in equilibrium 1, Scheme 1, is important. T3 forms in the solution at room temperature. This is consistent with the earlier findings. It is worth noting that P3 is now also detected in the solution at room temperature. In the presence of sulfur, exchange reactions would lead to the even more ready formation of higher polysulfides of the accelerator. At the melt/dissolution endotherm maximum, a relatively large amount of TMTP is present, with the maximum TMTP concentration occurring just after this endotherm at 100°C. The formation of larger amounts of more highly sulfurated accelerator species can readily be explained in terms of the findings of Gradwell and McGill[9] and Geyser and McGill.[3] The decrease in TMTP parallels the decrease in TMTD at higher temperature. It is noteworthy that the addition of sulfur increases the concentration of TMTP relative to that of P2 and PP. This shows that any MBTS and MBTP formed in equilibrium 2 (Scheme 1) are eliminated by Hdmtc via reaction 3. There is a steady increase in the concentration

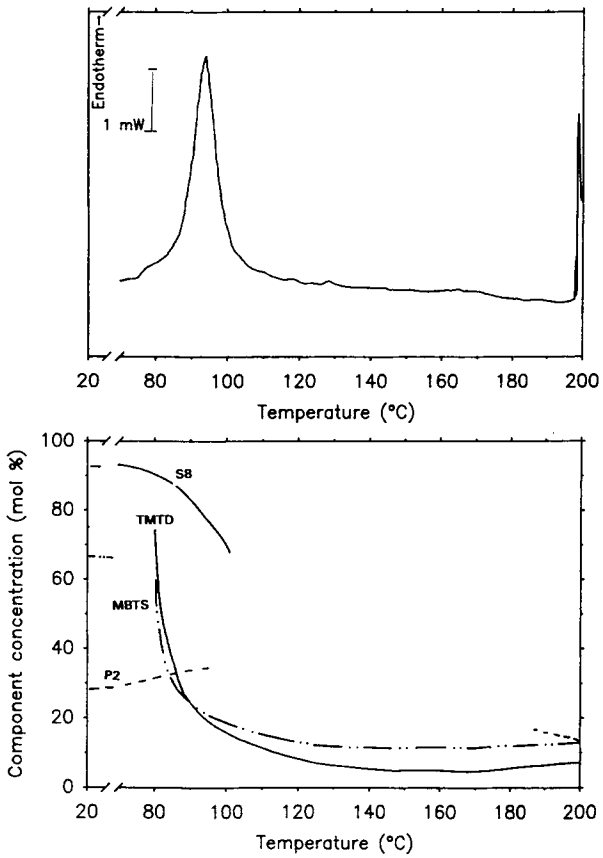


Figure 12 DSC (upper figure) and HPLC analysis (lower figure) of TMTD(1)–MBTS(1)–sulfur(1) heated at 5°C/min in sealed pans.

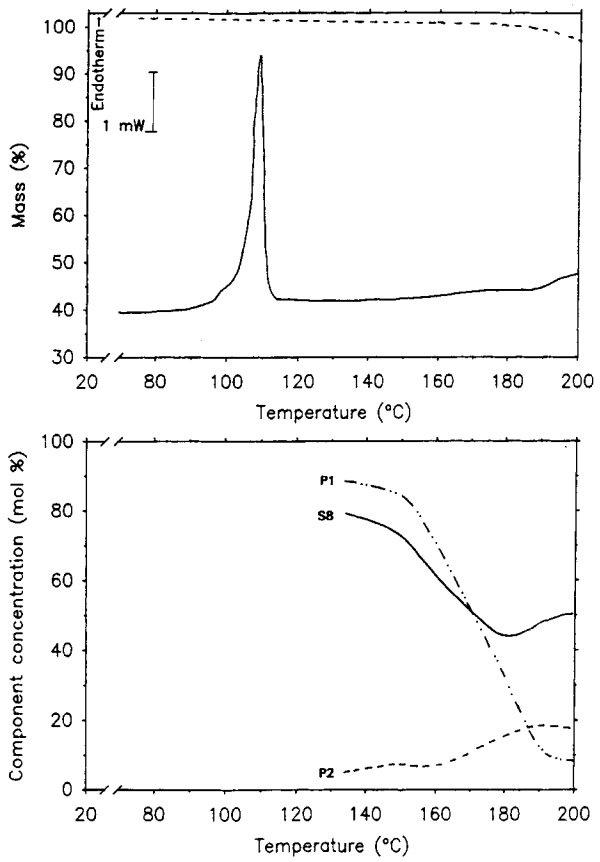


Figure 13 (- - -) TG and (——) DSC (upper figure) and HPLC analysis (lower figure) of DMTBS(1)–sulfur(1) heated at 5°C/min in sealed pans.

of the more stable products P1 and TMTM from 100 to 200°C. No TMTU forms, presumably, as the CS_2 and amine escape from the system when the DSC pans burst. The product spectrum can be explained in terms of the reactions proposed above for the corresponding system without sulfur.

TMTD–MBTS–Sulfur

A limited study of the TMTD(1)–MBTS(1)–sulfur(1) system (Fig. 12) was conducted. Melting/dissolution occurs somewhat earlier (94°C) than in the absence of sulfur (cf. Fig. 10), while the TMTD and MBTS concentrations again decrease in concert as the temperature is raised. However, the drop in their concentrations is very sudden and low concentrations are reached at 100°C; immediately, the melting process is completed. In contrast to the TMTD(1)–MBT(1)–sulfur(1) system, the addition of sulfur also leads to high MBTP and PP concentrations (Table II). This would be expected in the absence of Hdmtc (which destroys MBTP in reaction 3, Scheme 1). At 200°C, the more stable P1 dominates. The product spectrum is readily explained in terms of the reactions discussed for the TMTD(1)–MBTS(1) system.

DMTBS–Sulfur

DMTBS, the monosulfide of P2, was synthesized. It is relatively stable, and in a DMTBS(1)–sulfur(1) mixture, it interacts with sulfur in solution at room temperature to form only a small amount of P2 (Fig. 13 and Table II). Only above 160°C are measurable quantities of TMTD, MBT, MBTM, TMTP, and MBTP formed. These would result from exchange reactions involving attack of XS or BtS on sulfur.

CONCLUSIONS

TMTD (and TMTM) readily undergo exchange reactions with MBT (and MBTS) to give a mixed accelerator P2 (XSSBt). At vulcanization temperatures, polysulfides of TMTD and P2 form, their formation being enhanced by the presence of sulfur. Equilibrium between the main species can be explained in terms of Scheme 1. The product spectrum obtained on heating is dependent on the ability or otherwise of Hdmtc or its degradation products to escape from the system. The presence of Hdmtc favors the formation of TMTP by reversing the TMTD–MBT exchange and by reacting with MBTS and its polysulfides, while its degradation products, when trapped in sealed pans (and not by ZnO), lead to TMTU and DMABT. In the absence of Hdmtc, the formation of MBTP and PP rather than TMTP is favored.

We wish to thank the South African Foundation for Research Development and Karbochem, Division of Sentrachem, for financial assistance.

ABREVIATIONS

Bt^-	C_7H_4NS
$[dma]^+[dmtc]^-$	dimethylammonium dimethyldithiocarbamate
DMA	dimethylamine
DMABT	dimethylaminobenzothiazole
DMBSA	*N,N*-dimethylbenzothiazole-2-sulfenamide
DMTBS	*N,N*-dimethylthiocarbamulbenzothiazole sulfide
dmtc	dimethyldithiocarbamate
Hdmtc	dimethyldithiocarbamic acid

IR	*cis*-1,4-polyisoprene
MBT	2-mercaptobenzothiazole
MBTM	2-bisbenzothiazole-2,2′-monosulfide
MBTP	2-bisbenzothiazole-2,2′-polysulfides
MBTS	2-bisbenzothiazole-2,2′-disulfide
P1	unresolved peak of DMTBS and/or DMABT and/or DMBSA
P2	*N,N*-dimethylthiocarbamylbenzothiazole disulfide
P3	*N,N*-dimethylthiocarbamylbenzothiazole trisulfide
P4	*N,N*-dimethylthiocarbamylbenzothiazole tetrasulfide
P5	*N,N*-dimethylthiocarbamylbenzothiazole pentasulfide
PP	*N,N*-dimethylthiocarbamylbenzothiazole polysulfide
T3	tetramethylthiuram trisulfide
T4	tetramethylthiuram tetrasulfide
T5	tetramethylthiuram pentasulfide
TMTD	tetramethylthiuram disulfide
TMTM	tetramethylthiuram monosulfide
TMTP	tetramethylthiuram polysulfides
TMTU	tetramethylthiourea
X—	$(CH_3)_2NC(=S)$—

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