Thiuram-Accelerated Sulfur Vulcanization. I. The Formation of the Active Sulfurating Agent

M. GEYSER and W. J. MCGILL*

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

SYNOPSIS

Mixtures of tetramethylthiuram disulfide (TMTD)/ZnO and TMTD/sulfur/ZnO were heated in a DSC to various temperatures. Zinc dimethyldithiocarbamate ($Zn_2(dmtc)_4$) formed only in undried TMTD/ZnO mixes, the reaction being catalyzed by water on the ZnO surface. The presence of ZnO delays the decomposition of TMTD by adsorbing thiuram sulfenyl radicals, which are needed to initiate tetramethylthiuram monosulfide (TMTM) and tetramethylthiuram polysulfide (TMTP) formation. Increased amounts of TMTM are formed in mixes where ZnO is present, and TMTP are detected prior to TMTM formation. $Zn_2(dmtc)_4$ does not react with sulfur under conditions where labile hydrogen atoms are not available. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the absence of ZnO, tetramethylthiuram polysulfides (TMTP) are regarded as the active sulfurating agent in tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization of rubber.[1-5] However, the nature of the active sulfurating agent for vulcanization in the presence of zinc has been the subject of considerable debate. The role has been attributed to both zinc perthiomercaptides[6-9] and to thiuram polysulfides.[1]

Zinc Perthiomercaptides

The formation of zinc dimethyldithiocarbamate ($Zn_2(dmtc)_4$) is considered to be the first step in the crosslink formation in the vulcanization of diene rubbers with TMTD, sulfur, and ZnO.[6-9]

Kawaoka[10] found that TMTD and ZnO reacted vigorously at 147°C to form largely zinc dimethyldithiocarbamate dimethylthiocarbamate and sulfur, but little $Zn_2(dmtc)_4$. Craig et al.[11-14] expressed conflicting opinions with regard to the reaction of TMTD and ZnO, but it seemed that TMTD and ZnO showed little tendency to react. McCleverty[15]

reported that $Zn_2(dmtc)_4$ was the only zinc-containing product in the TMTD/ZnO reaction, while Raman spectroscopy revealed that $Zn_2(dmtc)_4$ and sulfur were formed in high yield when a TMTD/ZnO mixture was heated at 125°C. The findings of Duchacek[8,9] and the kinetic investigations by Scheele et al.[16] provided further evidence that a reaction between TMTD and ZnO is the first step in thiuram-based vulcanization in the presence of ZnO. Kruger and McGill[1] obtained only limited reaction on heating a dried TMTD/ZnO mixture (1 : 1 mol ratio) to 150°C in the DSC. Various attempts were made to increase the yield of $Zn_2(dmtc)_4$, but proved unsuccessful. Kruger and McGill[2,17,18] suggested that, in rubber, $Zn_2(dmtc)_4$ is formed as a byproduct of crosslink formation, initiated by TMTP.

$Zn_2(dmtc)_4$ is postulated to react with sulfur to yield zinc perthiomercaptide, which is the active sulfurating agent for vulcanization,[6] though no direct evidence for its existence has been obtained. Kawaoka[19] claimed the synthesis of a polysulfidic homolog of $Zn_2(dmtc)_4$ by fusion of sulfur with $Zn_2(dmtc)_4$ at 140–150°C. It was inferred that an unstable addition compound of the type zinc diethyldithiocarbamate ($Zn_2(detc)_4) \cdot S_8$ formed between sulfur and $Zn_2(detc)_4$ in benzene at 30°C.[20] Molecular mass determinations involving cryoscopy, however, revealed that $Zn_2(detc)_4$ and sulfur existed as unassociated molecules at lower temperatures.[20]

Table I HPLC Analyses of TMTD/ZnO (1 : 1 mol ratio) Mixtures Heated to 150°C

Compound	$Zn_2(dmtc)_4$ (%)	TMTU (%)	TMTM (%)	TMTD (%)	TMTP (%)
1	2.0		28.5	41.4	24.9
2	8.5		24.1	37.6	21.4
3	28.3		15.4	26.4	19.7
4	43.0		12.5	24.5	

1 = dried mixture heated in sealed DSC pan at 5°C/min and held at 150°C for 15 min.
2 = rewetted mixture heated in sealed DSC pan at 5°C/min and held at 150°C for 15 min.
3 = dried mixture heated in open glass tube at 150°C for 15 min.
4 = rewetted mixture heated in open glass tube at 150°C for 15 min.

Fackler et al.[21,22] indicated that chelate ring expansion occurred with the insertion of sulfur atoms into the complex zinc p-dithiocumate ($Zn(p\text{-}dtc_2)$, forming $Zn(p\text{-}dtc)_2S_2$. It was suggested that related zinc dithiolates such as $Zn_2(dmtc)_4$ would activate sulfur in a similar way. Coleman et al.,[3] however, performed Raman studies on a heated $Zn_2(dmtc)_4/$ sulfur mixture, and did not detect the formation of new S—S bonds. Craig et al.[11] found no indication of reaction between $Zn_2(dmtc)_4$ and sulfur up to 150°C in the absence of a solvent, nor was radioactive $Zn_2(dmtc)_4$ found when a $Zn_2(dmtc)_4/$sulfur–35/palmitic acid mixture was heated.

TMTP

Kruger and McGill[1] found that the addition of ZnO to TMTD/sulfur did not change the nature of DSC curves obtained on heating such mixtures in the absence of rubber. Analysis of the products revealed the formation of tetramethylthiuram monosulfide (TMTM). TMTM was also formed rapidly prior to crosslinking in TMTD/ZnO vulcanization of rubber.[2] Craig et al.[12] isolated fair yields of TMTM in natural rubber/TMTD/ZnO compounds and found that the amount of TMTM decreased on extended cure time. Neither Moore et al.[25] nor Scheele et al.[26,27] detected TMTM in TMTD/ZnO rubber cures. Raman spectra revealed that TMTP were rapidly formed in both TMTD/sulfur and TMTD/ sulfur/ZnO vulcanization systems, but Coleman et al.[3] found no evidence for the formation of zinc perthiomercaptides.

In an earlier article[28] we reported on the formation of TMTP on heating TMTD and TMTD/ sulfur in the absence of ZnO. This article investigates the question of TMTD/ZnO interaction, $Zn_2(dmtc)_4$ being regarded by some[6–9] as the active sulfurating agent, and studies the effect of ZnO

on the formation of TMTP, regarded by others[1,3] as the sulfurating agent.

EXPERIMENTAL

Materials

TMTD (Orac TMTD, chemical purity 97%, Orchem, SA), TMTM (vulkacit Thiuram MS, chemical purity 97.9%, Bayer, Germany), tetramethylthiourea (TMTU) (chemical purity 98%, Aldrich Chemical Co., Milwaukee, WI), and $Zn_2(dmtc)_4$ (vulkacit L, active ingredient 95%, Bayer, Germany).

Samples were heated in a DSC at 5°C /min to 150°C and held isothermally for 15 min.[28] A few larger samples were heated in sealed or open tubes immersed in an oil bath at 150°C. Product identification and HPLC analysis procedures have been described.[28]

The concentrations of reactants, intermediates, and products are expressed in terms of the initial mol concentration of reactant, i.e., as the mol % reactant remaining, or mol % intermediate/product formed from that reactant.

RESULTS AND DISCUSSION

$Zn_2(dmtc)_4$ Formation

TMTD and ZnO were dried in an evacuated oven at 60°C for 12 h, and stored over P_2O_5 in a vacuum desiccator for a further 24 h. Heating a dried TMTD/ZnO mixture (1 : 1 mol ratio; approx. 10 mg) to 150°C in the DSC and holding it at that temperature for 15 min resulted in the conversion of only 2 mol % of TMTD to $Zn_2(dmtc)_4$ (Table I). This confirmed the findings of Kruger and McGill.[1]

However, 28 mol % of TMTD was converted to $Zn_2(dmtc)_4$ on heating an approximately 1 g sample for 15 min in a tube placed in an oil bath maintained at 150°C.

Heating of an undried TMTD/ZnO mixture to 150°C in the DSC and holding it at that temperature for 15 min resulted in the conversion of 21 mol % of the TMTD to $Zn_2(dmtc)_4$, while 36 mol % of the TMTD was converted to $Zn_2(dmtc)_4$ in an undried TMTD/ZnO mixture of 1 : 5 mol ratio (Table II).

The discrepancy appears to be associated with an autocatalytic reaction initiated by H_2O, adsorbed onto the ZnO surface. It is proposed that thiuram sulfenyl radicals (XS radicals, where X = $(CH_3)_2NC(=S)$) from the decomposition of TMTD (during TMTP formation[28]) are adsorbed onto the ZnO surface, and react with adsorbed water to form a dimethyldithiocarbamic acid (Hdmtc) type adsorbant, which can react with ZnO.
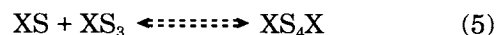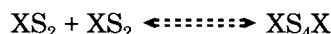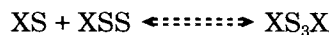

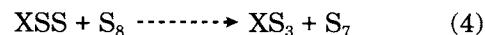ZnO surface

ZnO surface

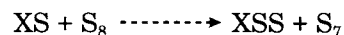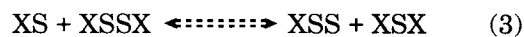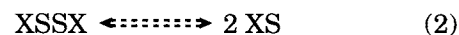$$H_2O + O_2 + Zn_2(dtmc)_4 \quad (1)$$
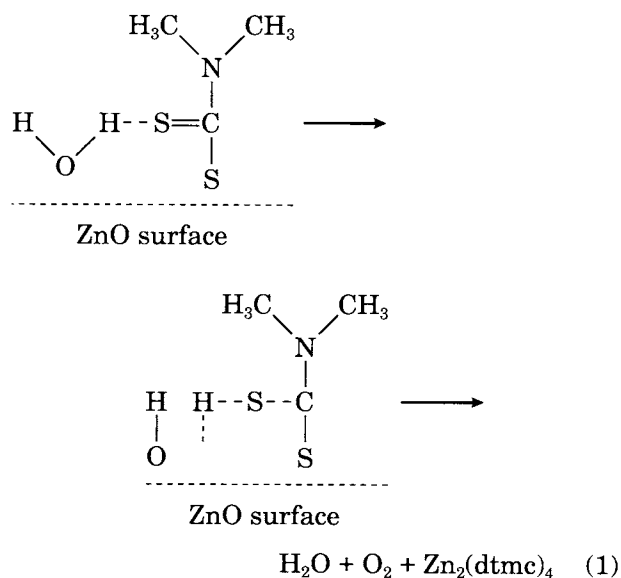
Dried ZnO rapidly readsorbs H_2O during the process of mixing it with TMTD. While on heating traces of adsorbed H_2O can readily escape from the smaller DSC samples, such H_2O is trapped in larger samples heated in glass tubes, and the autocatalytic $Zn_2(dmtc)_4$ formation is initiated. Rewetting of dried ZnO also activated $Zn_2(dmtc)_4$ formation on heating TMTD/ZnO mixtures (Table I).

In the presence of sulfur, heating even a larger sample (approx. 3 g) of the undried TMTD/ZnO mixture in a tube does not lead to appreciable $Zn_2(dmtc)_4$ formation unless the amount of ZnO in the mixture is very large (TMTD/sulfur/ZnO 1 : 1 : 5 mol ratio). This is attributed to the adsorbed water being displaced by sulfur.

TMTP Formation in the Presence of ZnO

TMTD and sulfur react in the presence of ZnO to form TMTM and TMTP (Figs. 1 and 2).

We have previously[28] proposed that in the absence of ZnO, TMTP are formed via the homolysis of TMTD (reaction 2), followed by sulfur exchange reactions between XS radicals and TMTD (reaction 3), resulting in the formation of thiuram persulfenyl radicals (XS_X) and TMTM. The presence of elemental sulfur would favor sulfur extraction from S_8 (reaction 4) and reduce the likelihood of extraction from TMTD. Radical recombinations (reaction 5) would ultimately lead to TMTP.

$$XSSX \Longleftrightarrow 2 XS \quad (2)$$

$$XS + XSSX \Longleftrightarrow XSS + XSX \quad (3)$$

$$XS + S_8 \dashrightarrow XSS + S_7$$

$$XSS + S_8 \dashrightarrow XS_3 + S_7 \quad (4)$$

$$XS + XSS \Longleftrightarrow XS_3X$$

$$XS_2 + XS_2 \Longleftrightarrow XS_4X$$

$$XS + XS_3 \Longleftrightarrow XS_4X \quad (5)$$

An induction period before the rapid formation of products is ascribed to the slow decomposition of TMTD.[28] The low concentration of XS radicals during the early stages of the reaction would limit the formation of further XS and XS_x via reactions 3 and 4. At some point the accumulation of these radicals will result in the formation of TMTP.

ZnO increases the induction period before the onset of rapid reaction between TMTD and sulfur, and increases the amount of TMTM formed. TMTP are detected well before TMTM is observed (Fig. 3). Despite the fact that no $Zn_2(dmtc)_4$ is formed in the presence of sulfur, more TMTD is decomposed, the TMTP concentration being higher than in the absence of ZnO.[28]

The increased induction period observed in the reaction between TMTD and sulfur in the presence of ZnO implies that ZnO removes some reaction intermediate from the system. Adsorbtion by ZnO of XS radicals, which it is suggested are slowly produced on the decomposition of TMTD,[28] will delay the buildup of the concentration of radicals necessary to ensure rapid reaction in terms of reactions 3-5. Not all XS radicals will be adsorbed onto the surface, but as sulfur exchange with cyclic sulfur is favored over exchange with TMTD, negligible amounts of TMTM will be produced. The XSS rad-

Table II   HPLC Analyses of TMTD/ZnO and TMTD/S/ZnO Heated to Various Temperatures

Compound[a]		Temp (°C)	$Zn_2(dmtc)_4$ (%)	TMTU (%)	TMTM (%)	TMTD (%)	TMTP (%)	S_8 (%)	Mass Loss (%)
TMTD/ZnO	1	150	20.7		20.1	30.9	23.0		0.3
	2	150	55.5		11.4	21.9	9.2	0.6	
	3	150	43.3		12.5	26.0	10.6	1.4	
(1 : 5)	1	150	36.3		12.9	23.5	18.7	0.1	
	4	190	69.9	27.2			2.9	6.0	
	5	200	75.4	20.2		0.7	3.5	6.0	
	5	280				0.2			64.2
TMTD/S_8/ZnO	1	150	0.1		6.9	18.6	60.3	49.8	0.1
	2	150	12.4		5.8	16.5	65.2	66.2	
	3	150	5.1		6.9	17.2	64.1	54.2	
(1 : 1 : 5)	1	150	13.4		5.3	16.6	58.8	62.1	
	4	190	74.4	29.8			7.1	98.5	
	5	225	77.2	29.6		0.3	2.2	101.5	
	5	280				0.5		89.0	41.2

[a] Mol ratio (1 : 1) or (1 : 1 : 1) except where otherwise indicated.
1 = heated in sealed DSC pan at 5°C/min and held at 150°C for 15 min.
2 = heated in open glass tube at 150°C for 15 min.
3 = heated in sealed glass tube at 150°C for 15 min.
4 = heated in open glass tube at 190°C for 15 min.
5 = heated in sealed DSC pan at 5°C/min to temperature stated.

icals produced in exchange with sulfur will partake in further sulfur extraction, and will combine with other thiuram radicals to form TMTP, i.e., thiuram tri- and tetrasulfide will be observed before TMTM. (cf. Figs. 2 and 3).

As the ZnO surface becomes saturated with XS radicals, rapid interaction between the adsorbed species could occur and lead to TMTM formation with the elimination of atomic sulfur. A small amount of sulfur was detected in heated TMTD/ZnO mixtures. TMTM formation, once initiated, is more rapid than in the absence of ZnO, and could

result from reaction between adsorbed accelerator fragments.

The TMTM concentration passes through a maximum and can be ascribed to the sulfuration of desorbed TMTM by thiuram sulfenyl and persulfenyl radicals produced in the bulk melt.

## Interaction of $Zn_2(dmtc)_4$ With Sulfur

While $Zn_2(dmtc)_4$ is an ultraaccelerator with sulfur, no interaction is observed at vulcanization temperatures in the absence of rubber (Table III).
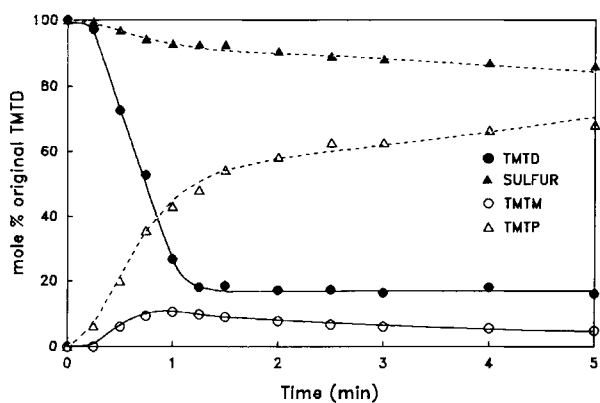
Figure 1   HPLC analyses of reactants and products in the TMTD/sulfur/ZnO reaction (1 : 1 : 1 mol ratio; 130°C).
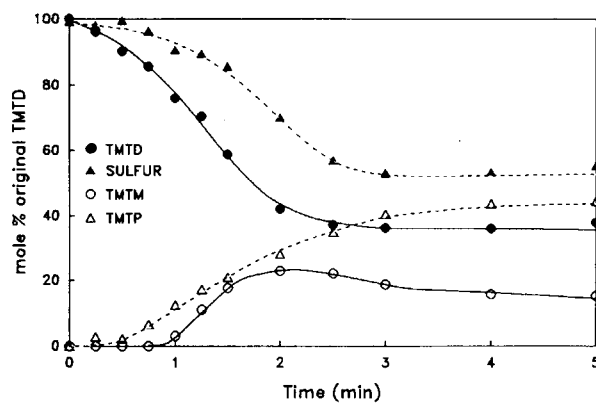
Figure 2   HPLC analyses of reactants and products in the TMTD/sulfur/ZnO reaction (1 : 0.25 : 1 mol ratio; 130°C).
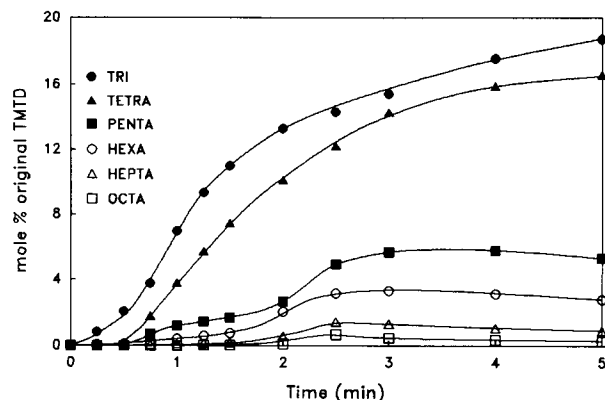
Figure 3 HPLC analyses of TMTP formed in the TMTD/sulfur/ZnO reaction (1 : 0.25 : 1 mol ratio; 130°C).

$Zn_2(dmtc)_4$ melts at 250°C. In the presence of sulfur, $Zn_2(dmtc)_4$ does not melt, but decomposes rapidly above 230°C, with a mass loss of 54.1%. This corresponds to all of the $Zn_2(dmtc)_4$ present in the $Zn_2(dmtc)_4$/sulfur mixture (Table III).

It is suggested[6,19] that zinc perthiomercaptide, formed by the interaction of $Zn_2(dmtc)_4$ and sulfur, is the active sulfurating agent in the vulcanization of rubber, though such species have never been isolated. Although, as detailed in part IV of this series of articles,[29] $Zn_2(dmtc)_4$ and sulfur do react in the presence of compounds containing labile hydrogens, the data in Table III shows no evidence of a $Zn_2(dmtc)_4$/sulfur interaction in their absence. This argues against zinc perthiomercaptide performing the role of active sulfurating agent in vulcanization,

i.e., zinc perthiomercaptide being formed by the interaction of $Zn_2(dmtc)_4$ and sulfur prior to interaction with rubber.

CONCLUSIONS

The present study confirms that no $Zn_2(dmtc)_4$ is formed on heating dried TMTD/ZnO mixtures to vulcanization temperatures. $Zn_2(dmtc)_4$ is formed via an autocatalytic reaction initiated by H_2O adsorbed onto the ZnO surface. No $Zn_2(dmtc)_4$ is formed in the TMTD/sulfur/ZnO reaction, the H_2O being displaced by sulfur.

TMTM and TMTP are formed on heating TMTD/sulfur/ZnO mixtures. Their formation is consistent with the proposed mechanism of TMTM and TMTP formation in the reaction of TMTD with sulfur in the absence of ZnO. The induction period is increased in the presence of ZnO due to thiuram sulfenyl radicals being adsorbed onto the ZnO surface. TMTP are produced before TMTM, but TMTM formation, once initiated, is more rapid than in the absence of ZnO.

Zinc perthiomercaptides are not formed by the interaction of $Zn_2(dmtc)_4$ and sulfur prior to interaction with rubber, and the present data does not support the postulated role of zinc perthiomercaptide as the active sulfurating agent in TMTD-accelerated sulfur vulcanization with ZnO.

Table III HPLC analyses of $Zn_2(dmtc)_4$ and $Zn_2(dmtc)_4$/Sulfur (1 : 1 Mol Ratio) Heated to Various Temperatures

Compound		Temp (°C)	$Zn_2(dmtc)_4$ (%)	TMTU (%)	TMTM (%)	TMTD (%)	TMTP (%)	S_8 (%)	Mass Loss (%)
$Zn_2(dmtc)_4$	1	150	93.4			0.1			0.1
	2	150	99.7		0.1	0.5			
	3	150	96.4		0.3	0.2			
	4	190	94.4						
	5	280	94.0	4.8		0.2			0.1
$Zn_2(dmtc)_4/S_8$	1	150	83.6			0.3		96.1	0.1
	2	150	100.4		0.1	1.4		93.6	
	3	150	93.3					94.5	
	4	190	85.0			1.0		95.7	
	5	220	91.5			0.6		100.5	
	5	280				0.4		75.6	54.1

1 = heated in sealed DSC pan at 5°C/min and held at 150°C for 15 min.
2 = heated in open glass tube at 150°C for 15 min.
3 = heated in sealed glass tube at 150°C for 15 min.
4 = heated in open glass tube at 190°C for 15 min.
5 = heated in sealed DSC pan at 5°C/min to temperature stated.

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