

A Study of the Rate of Formation of Polysulfides of Tetramethylthiuram Disulfide

M. GEYSER and W. J. MCGILL*

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

SYNOPSIS

The rate of formation of tetramethylthiuram polysulfides (TMTP), that play an important role in vulcanization, was studied. After a short induction period (< 30 s), tetramethylthiuram disulfide (TMTD) and TMTD-sulfur mixes, heated to 130 – 150°C in the absence of rubber, rapidly form a series of TMTPs. The concentrations of TMTPs of lower sulfur rank increase most rapidly, indicating that sulfur atoms are added to the accelerator sequentially. The incorporation of sulfur molecules to give TMTPs, which subsequently desulfurate, does not occur. Equilibrium concentrations of the various TMTPs are achieved in about 2 min. Little tetramethylthiourea is formed below 200°C . Tetramethylthiuram monosulfide (TMTM) is stable, but TMTM-sulfur mixes form TMTPs. A mechanism is proposed to account for the large amount of TMTM formed on heating TMTD in the absence of sulfur and the correspondingly higher TMTP concentrations in the presence of sulfur. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the absence of sulfur, tetramethylthiuram monosulfide (TMTM) is stable at vulcanization temperatures,^{1–3} though on heating to 145°C for 120 min, Raman studies⁴ showed the presence of tetramethylthiourea (TMTU) and CS_2 , in addition to residual TMTM. Coleman et al.¹ reported that the homolysis of TMTM at 125°C is extremely slow, while in natural rubber decomposition is negligible at 145°C .² Tetramethylthiuram disulfide (TMTD), TMTM/sulfur, and TMTD/sulfur mixes decompose more readily on heating. Craig et al.⁵ synthesized TMTD in 70% yield by heating a TMTM/sulfur mixture to 120°C , while Coleman et al.⁴ reported the rapid formation of TMTD and various tetramethylthiuram polysulfides (TMTP) at 125°C after an induction period of 5 min. In the latter study, product identification was by Raman spectroscopy. Using TLC, Kruger and McGill³ identified TMTD in a TMTM/sulfur mix on heating to 180°C at $5^\circ\text{C}/\text{min}$ in a DSC. On reheating, a eutectic was observed

at 81°C , attributed to the mixture of TMTM, TMTD, and sulfur.

Dogadkin⁶ and Craig⁷ and their co-workers have suggested that TMTM is an intermediate in the thermal breakdown of TMTD to TMTU, CS_2 and sulfur. Dogadkin and Shershnev⁶ reported that the pyrolysis products of TMTD are TMTM, CS_2 and sulfur. Raman spectroscopic studies⁴ of TMTD, heated to 145°C , revealed the formation of TMTPs and the slow formation of TMTU and CS_2 . After 30 min, TMTD was still a major component of the product mix. It was emphasized that TMTM was not formed. In contrast, HPLC analysis of TMTD heated in a DSC at $5^\circ\text{C}/\text{min}$ and held at 145°C for 5 min, revealed the formation of 44 mol % TMTM and 45 mol % TMTD.⁸ No TMTU was detected. TMTU formation is accompanied by the evolution of CS_2 and the mass loss of only 0.3% supported the absence of TMTU. On reheating, the sample showed the characteristic TMTM/TMTD/sulfur eutectic.^{3,8}

Coleman et al.⁴ showed the formation of substantial amounts of TMTPs in a TMTD/sulfur mix heated to 145°C . TMTU formation was detected, but only after 15 min. HPLC analysis by Kruger and McGill⁸ of a TMTD:sulfur (1:1 mol ratio) mixture, held isothermally at 146°C for 5 min, yielded

* To whom correspondence should be addressed.

5 mol % TMTM together with 71 mol % TMTD. A mass loss of only 0.65% was recorded and no TMTU was formed. A decrease in sulfur concentration could not be detected, and this was attributed to the instability of higher thiuram polysulfides in solution during workup.⁸ More recently, Versloot⁹ reported a number of product peaks in addition to residual TMTD and sulfur in the HPLC spectrum of a TMTD/sulfur mix heated to 140°C. Following Coleman et al.,⁴ who had presented Raman spectroscopic evidence of the formation of TMTPs, these HPLC peaks were attributed to TMTPs of sulfur rank 3–13. The formation of TMTM was not mentioned.

TMTPs are attributed an important role in vulcanization,^{3,4,9–11} and this article reports on a study of the rate of TMTP formation on heating TMTD, TMTD/sulfur, and TMTM/sulfur mixes to vulcanization temperatures.

EXPERIMENTAL

Materials

TMTD (Orac TMTD, chemical purity 97%, Orchem, SA), TMTM (vulcavit Thiuram MS, chemical purity 97.9%, Bayer, SA), and TMTU (chemical purity 98%, Aldrich Chemical Co., USA).

Samples (± 10 mg) were heated in sealed aluminium pans with a standard Du Pont DSC cell, connected to a Du Pont 9000 thermal analyzer. Heating rates of 5°C/min were used and samples held isothermally at the desired temperatures. High-purity nitrogen, at a flow rate of 20 cm³/min, was used as a purge gas. Samples were reweighed after each DSC run. Samples (± 1 g) in open and evacuated sealed glass tubes, were isothermally heated in an oil bath set at the desired temperature. Rate studies were done isothermally in the DSC at 130°C and 150°C. The reactions were quenched by cooling the samples in liquid nitrogen.

The procedures for the high-performance liquid chromatography (HPLC) analyses¹² of accelerators and products have been described. The products were separated on a μ -Bondapak C-18 column, which is a Radial Packed Reverse phase column. Water/Methanol (15:85 v:v ratio) was used as eluent. The molar absorptivity for TMTP was calculated as follows: from the initial TMTD concentration and the concentrations of residual TMTD and TMTM formed during the reaction of TMTD with sulfur (1:1 mol ratio; 130°C), the total TMTP concentration was calculated (TMTM and TMTP being the

only products of the reaction). Using the total TMTP peak response in the HPLC chromatogram and the total TMTP concentration, an approximate molar absorptivity was calculated using Beer Lambert's law. It was assumed that the molar absorptivities of the various TMTPs were identical.

RESULTS

TMTM

TMTM melts at 111°C and is stable at 150°C, as reported earlier.^{1–3} On heating TMTM in the DSC at 5°C/min to 150°C and holding it at that temperature for 5 min, no decomposition was observed, HPLC analysis yielding the single TMTM peak only. TMTM readily decomposes at higher temperatures and on heating at 5°C/min to 220°C, the TMTU formed is equivalent to 28 mol % of the original TMTM. Based on Raman studies, Coleman et al.⁴ reported the formation of TMTU and CS₂ when TMTM was held at 145°C for 30 min. The CS₂ evolved in TMTU formation would account for a mass loss of 10%, and the 38% mass loss observed shows that part of the TMTM had either evaporated or decomposed completely.

TMTM/Sulfur

At 130°C TMTM:sulfur mixes (1:0.25 mol ratio) rapidly form TMTD and lesser amounts of TMTPs after an induction period (Fig. 1). Coleman,⁴ too, reported the rapid formation of TMTD and TMTP after an induction period of 5 min at 125°C. The thiuram tri- and tetrasulfides are the most plentiful TMTP species, while sulfur concentration decreases as expected.

TMTD

TMTD melts at 145°C. On heating TMTD rapidly to 150°C in the DSC, and holding it at that temperature, there is a gradual decrease in TMTD concentration and a corresponding increase in the amount of TMTM formed (Fig. 2), equilibrium concentrations being reached after about 2 min (TMTD 46 mol % and TMTM 32 mol %). Small amounts of thiuram tri- and tetrasulfides (5–10 mol %) are formed, together with traces of thiuram penta- and hexasulfides (< 2 mol %) (Fig. 2). After 3 min, small amounts of elemental sulfur (< 2 mol %) are detectable. The mass loss of 0.22% after 5 min shows that little CS₂, associated with TMTU

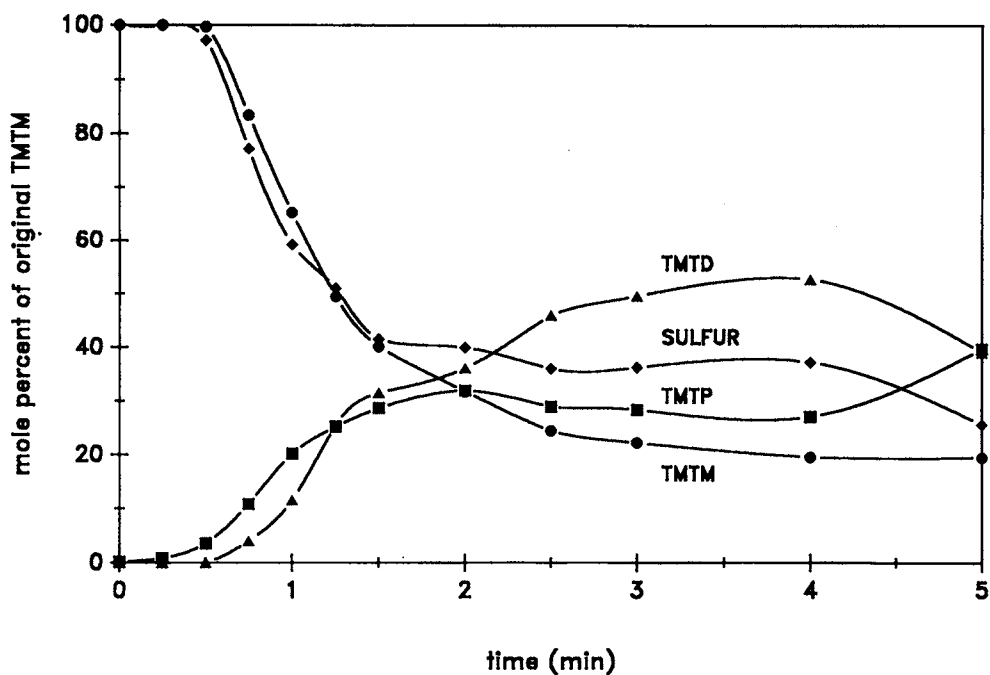


Figure 1 Products formed from the reaction of TMTM and sulfur (1:0.25 mol ratio) as a function of time at 130°C. Thiuram sulfide concentrations are expressed as a percentage of TMTM originally present.

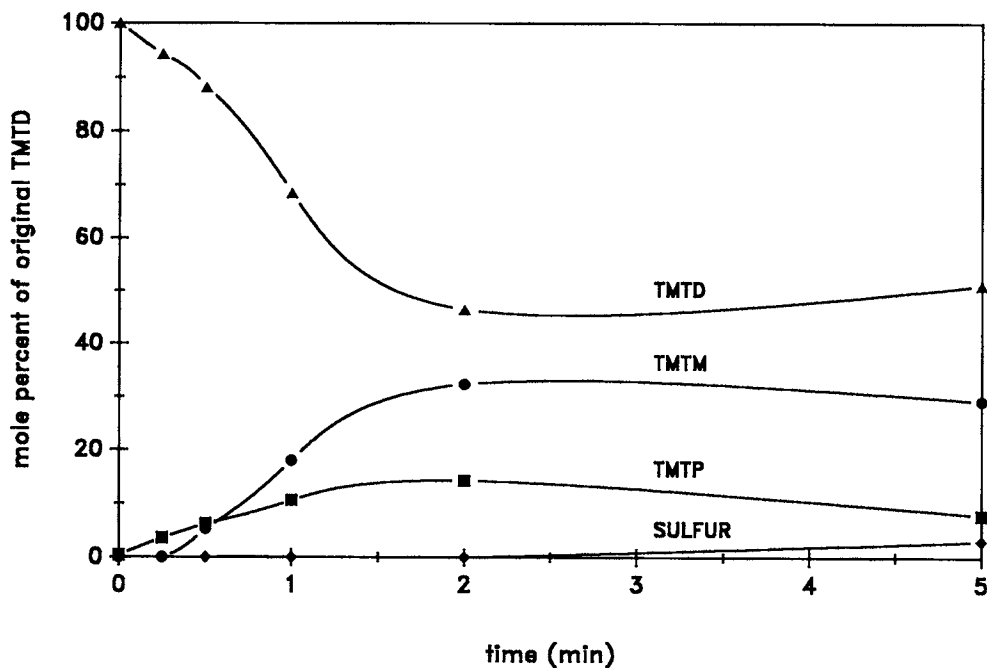


Figure 2 Products formed from the reaction of TMTD as a function of time at 150°C. Thiuram sulfide concentrations are expressed as a percentage of TMTD originally present.

formation, was evolved. This is in contrast to Coleman et al.,⁴ who found that, after 60 min at 145°C, little TMTD remained. Raman spectra indicated that the product mix comprised mainly TMTU, CS₂ and TMTPs. Craig⁵ reported TMTU formation on pyrolysis of TMTD at 160 to 230°C.

TMTD/Sulfur

On heating TMTD to 150°C in the presence of sulfur (TMTD:sulfur 1:1 mol ratio), the concentration of TMTD decreases more rapidly and stabilizes at 18 mol % of the original TMTD after 1 min (Fig. 3). TMTM forms rapidly, but in smaller amounts than in the absence of sulfur, 10 mol % of the original TMTD being present as TMTM after 1 min. Larger amounts of TMTPs are formed. The most prominent TMTP species present is still the thiuram trisulfide, while progressively smaller amounts of thiuram polysulfides of higher sulfur rank form. It is noticeable that TMTM initially forms more rapidly than any of the TMTPs, but its concentration decreases on reaching a maximum after 1 min, and after 1.5 min, thiuram trisulfide is the most plentiful product species. The concentration of thiuram trisulfides increases more rapidly than that of poly-

sulfides of higher sulfur rank. Coleman et al.⁴ observed the maximum concentration of TMTPs between 5 and 15 min on heating to 145°C. After 15 min, the TMTD and TMTP concentrations decreased while increased amounts of TMTU, CS₂ and sulfur were formed. In the present study, no TMTU was detected, even after 1 h at 130°C. Only at higher temperatures was TMTU formation observed, e.g., above 200°C mass losses of greater than 30% were recorded for DSC samples, the bulk of the residue being identified as TMTU (Table I).

The TMTD-sulfur system was further studied at 130°C, where the reaction is less rapid. Higher mol ratios of TMTD to sulfur lead to the formation of lesser amounts of TMTPs, while the amount of TMTD at equilibrium is higher (cf., Figs. 4 and 5). The induction period before the onset of rapid reaction, evident in Figures 2 to 4, is very considerable (45 s) at low sulfur loadings (Fig. 5).

Although most experiments were conducted in DSC pans in a nitrogen atmosphere, larger samples (1 g) were heated for 5 min in both sealed and open tubes immersed in an oil bath at 150°C. The same product spectrum resulted in all cases (Table I). Reaction times used are very short and quantitative differences can be ascribed to longer times being required for the larger samples to reach the bath temperature.

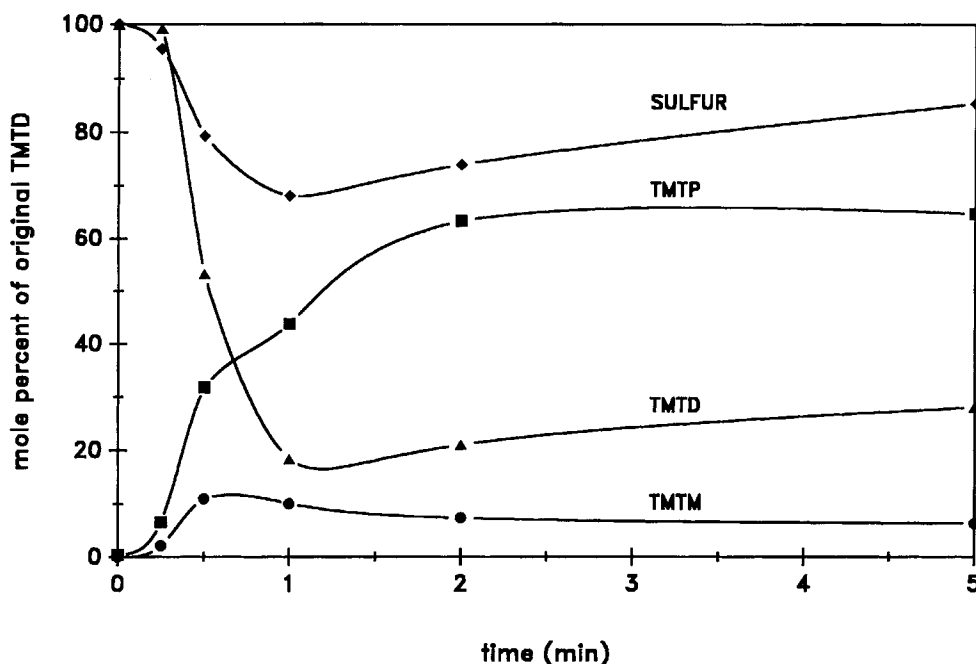


Figure 3 Products formed from the reaction of TMTD and sulfur (1:1 mol ratio) as a function of time at 150°C. Thiuram sulfide concentrations are expressed as a percentage of TMTD originally present.

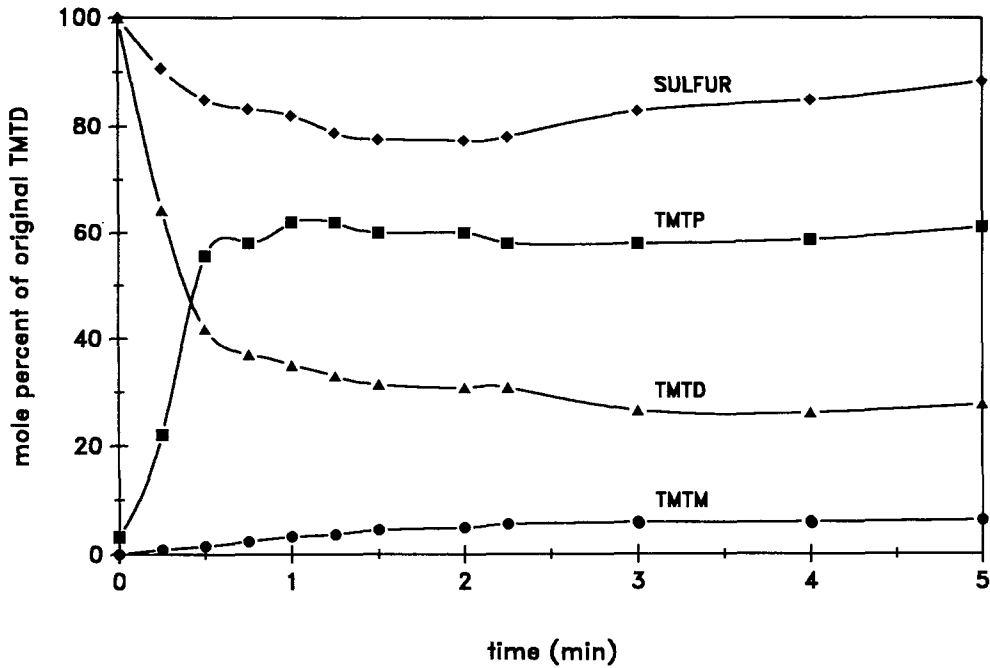


Figure 4 Products formed from the reaction of TMTD and sulfur (1:1 mol ratio) as a function of time at 130°C. Thiuram sulfide concentrations are expressed as a percentage of TMTD originally present.

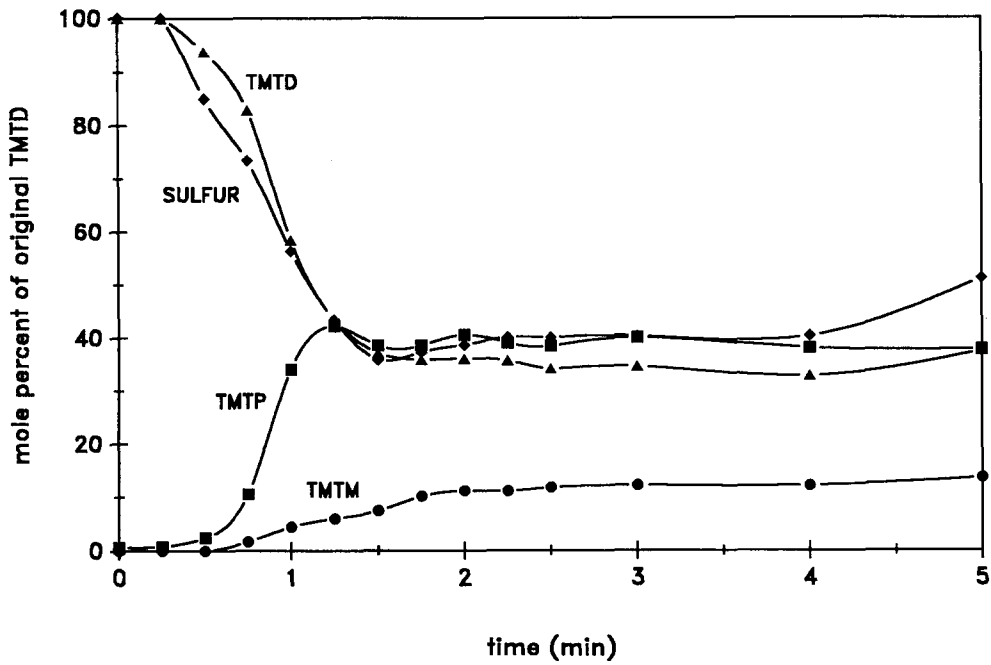


Figure 5 Products formed from the reaction of TMTD and sulfur (1:0.25 mol ratio) as a function of time at 130°C. Thiuram sulfide concentrations are expressed as a percentage of TMTD originally present.

Table I Products Formed on Heating Accelerators to Various Temperatures

Compound	Temp °C	TMTU %	TMTM %	TMTD %	TMTP %	Sulfur %	Mass Loss %
TMTM	150 ^a		102				0.2
	150 ^b		105				
	150 ^c		77				
	220 ^d		28				38.1
	280 ^d						99.7
TMTD	150 ^a		35	43	28		0.2
	150 ^b		17	74	17		
	150 ^c		35	63	31	1	
	200 ^d	103		7	12	7	29.3
	280 ^d						97.4
TMTD/S ₈	150 ^a		7	17	62	49	0.2
	150 ^b		9	23	66	61	
	150 ^c		6	18	70	69	
	210 ^d	72		1	4	101	18.5
	280 ^d					90	45.6

^a Heated in sealed DSC pan at 5°C/min and held at 150°C for 5 min.

^b Heated in open glass tube at 150°C for 5 min.

^c Heated in sealed glass tube at 150°C for 5 min.

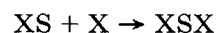
^d Heated in sealed DSC pan at 5°C/min to temperature stated.

DISCUSSION

A reaction mechanism to account for the TMTD decomposition must be consistent with three observations: (1) the rapid formation of TMTM, (2) the step-wise addition of sulfur to form TMTPs of progressively higher sulfur rank, and (3) an induction period before the onset of rapid reaction. In the presence of sulfur, too, step-wise addition of sulfur to yield TMTPs of higher sulfur rank, occurs.

Current Mechanisms for TMTP Formation

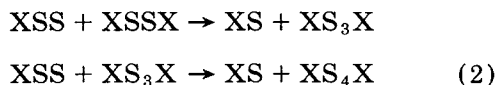
We will first discuss the data presented in this article in terms of reaction mechanisms that have been proposed for the TMTD, TMTD/sulfur, and TMTM/sulfur reactions. Koenig^{4,13} suggested that TMTP and MBTP formation occurred via symmetric and unsymmetric homolysis of TMTD and MBTS, respectively, on heating. TMTM and TMTP (as well as MBTM and MBTP) could result from the recombination (reactions 4) of radicals formed in symmetric and unsymmetric homolysis reactions (reactions 1 and 2),^{4,13} while the recombination of radicals from the scission of thiuram tri- and tetrasulfides would lead to thiuram polysulfides of progressively higher sulfur rank ($X = (\text{CH}_3)_2\text{C}(\text{S})\text{S}-$



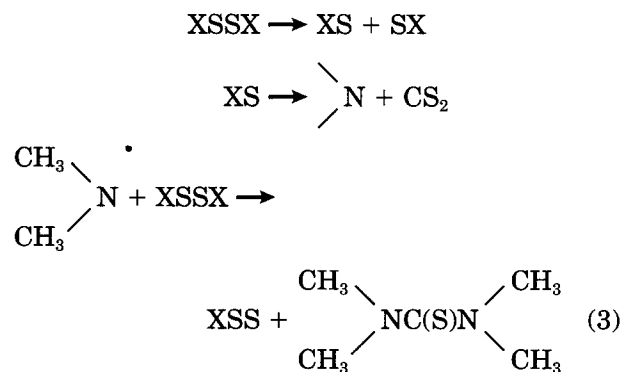
However, it is difficult to see how such radical recombinations would lead to the product spectrum observed on heating TMTD. For example, although recombination of fragments as in reactions 4 would lead to TMTM and thiuram tri- and tetrasulfides, the formation of high TMTM concentrations (Fig. 2) would require scission of the more stable C—S bond to be a frequent event. The symmetrical and unsymmetrical homolysis of TMTD would make XS, XSS, and X radicals the most plentiful. If the high concentration of TMTM observed in the absence of sulfur resulted from a recombination of XS and X radicals, XSS and XS radicals should combine with equal frequency resulting in an equivalent concentration of XS₃X. The concentration of XS₄X would be low, certainly not comparable with that of XS₃X. TMTPs could result from the combination of XS with thiuram persulfenyl radicals of progressively higher sulfur rank, but if X, and not XS, were the main species extracting sulfur from S₈, the source of these persulfenyl radicals would have to be the homolysis of thiuram tri- and tetrasulfides already formed and, again, unsymmetric homolysis of the stronger C—S bond would be required. The

induction period would be difficult to explain in terms of reactions 1.

Coleman et al.⁴ proposed the formation of TMTPs by the interaction of XSS radicals with TMTD or TMTP, the radicals sulfurating thiuram di- and polysulfides of lower sulfur rank.



Their source of XSS radicals did not involve the unsymmetrical homolysis of TMTD. Instead, they suggested that XSS radicals were produced during the formation of TMTU.



However, this article shows that, in the early stages of reaction, high concentrations of TMTM are produced. Even after 30 min at 130°C, no TMTU is detected and the mass loss (CS₂) is negligible. TMTU only forms at higher temperatures (> 200°C) and in rubber during vulcanization.¹⁰ Indeed, Coleman et al.,⁴ themselves, found that TMTP concentrations reached a maximum after 5 to 15 min at 145°C. Although TMTU was detectable at this point, its concentration increased at longer heating times, although TMTD and TMTP concentrations decreased. Thus, an alternative reaction mechanism for the formation of XSS radicals or an alternative mechanism to reactions 3 is required.

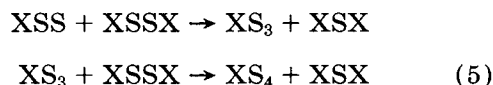
An analogous mechanism to reactions 3 was suggested for the decomposition of TMTM.⁴ Again, the slow formation of TMTU mitigates against this reaction route. Furthermore, it is difficult to see why, if TMTM formed XS radicals, TMTD would not result from the recombination of two XS radicals in the absence of sulfur.

A Mechanism for TMTP Formation from TMTD

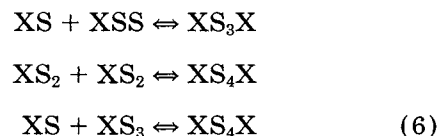
We suggest the following reaction mechanism. Homolysis of TMTD, followed by sulfur exchange reactions between XS and TMTD (reaction 4), resulting in the rapid formation of high concentrations of TMTM as is observed.



As the TMTD/XS ratio is high, further sulfur extraction by persulfenyl radicals (reactions 5) is possible, i.e., it is suggested that sulfur exchange involving persulfenyl radicals abstracts rather than adds sulfur to TMTD.

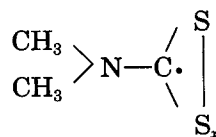


Radical recombinations (reactions 6) would ultimately lead to TMTPs, though initially recombination reactions would be limited due to the low concentrations of the species involved in these reactions.



The formation of TMTPs of higher sulfur rank require more sulfur extraction steps, and their concentrations would be correspondingly lower. Such TMTPs would also be more unstable and their rates of decomposition greater.

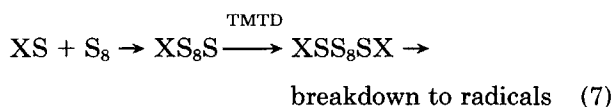
Various ways, whereby persulfenyl radicals, generated in reactions 4 and 5, may be stabilized, have been suggested. The activation energy for the homolysis of RS_nR (*n* ≥ 4) is similar to that for the dissociation of S₈, indicating that RS_n (*n* > 1) radicals are more stable than thiyl radicals.¹⁵ A high concentration of persulfenyl radicals is expected in TMTD/sulfur mixtures, yet the signal at *g* = 2.02 is low and the singlet signal at *g* = 2.006 in the ESR spectra of TMTD, heated with sulfur to 150°C, has been interpreted⁴ as evidence that the higher thiuram persulfenyl radicals are stabilized by cyclization, the radical residing on the C atom,



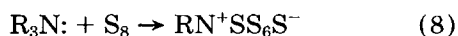
Fairbrother et al.¹⁵ suggested that the reduced reactivity of RS_x (*x* > 2) could be ascribed to the radicals being partly stabilized by resonance. Such conjugation may be involved in stabilizing radicals involved in the formation of polysulfides of MBTS and CBS,¹⁶ where cyclic sulfide formation is not possible.

A Mechanism for TMTP Formation from TMTD and Sulfur

In the presence of cyclic sulfur, TMTM formation is limited, while more TMTPs form (Fig. 3). In both the TMTD/sulfur and TMTM/sulfur reactions, sulfur, which is regarded as a radical trap, is thought to interact with radicals from the homolysis of TMTD and TMTM to give persulfenyl radicals of high sulfur rank which later desulfurate.^{4,17,18}

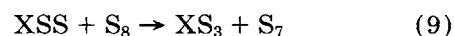
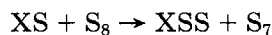


Bateman et al.,¹⁹ too, discussed the addition of sulfur to nonionic nucleophiles to yield persulfenyl radicals.



However, the data in Figure 6 clearly disprove this sequence of events. It is clear that the concentrations of TMTPs of lower sulfur rank increase faster than that of TMTPs of higher sulfur rank, i.e., TMTPs of high sulfur rank, that subsequently desulfurate, are not produced initially. Sulfur atoms are added sequentially. This applies both to TMTM/sulfur and TMTD/sulfur interactions.

The main product of the TMTM/sulfur reaction is TMTD, i.e., the addition of a single sulfur atom represents the most frequent occurrence. The XS radical concentration obtained on heating TMTM must be very low; otherwise, some TMTD would be expected to form, even in the absence of cyclic sulfur. Thiuram tri- and thiuram tetrasulfides initially form at similar rates but their concentrations do not continue to increase at the same rate as that of TMTD. As in the absence of sulfur, the data could be explained in terms of the extraction of sulfur atoms by XS radicals, extraction occurring from S₈ (reaction 9).



A high sulfur concentration would favor sulfur extraction from S₈ (reaction 9) and reduce the likelihood of abstraction from TMTD (reactions 4 and 5), which leads to TMTM. The higher the sulfur concentration, the more frequently will extraction from cyclic sulfur rather than from TMTD occur and, hence, less TMTM would result. The step-wise increase in the number of sulfur atoms in the persulfenyl radicals would be consistent with the progressive increase in sulfur rank of TMTPs formed on their recombination.

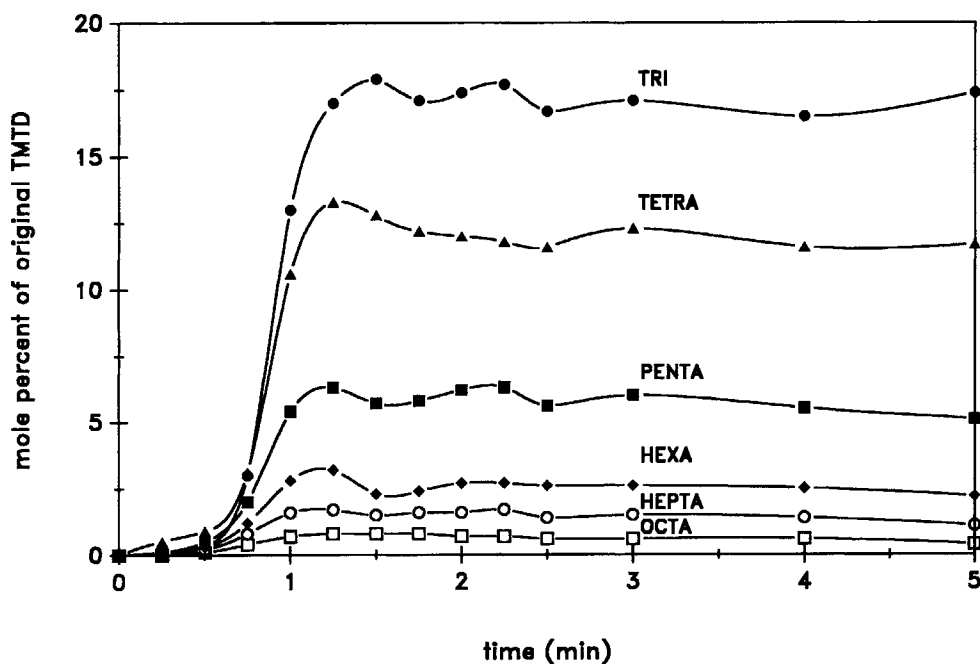


Figure 6 Formation of thiuram polysulfides from the reaction of TMTD and sulfur (1:0.25 mol ratio) as a function of time at 130°C. Thiuram sulfide concentrations are expressed as a percentage of TMTD originally present.

Induction Period

An induction period before the rapid formation of products is observed both in the presence and absence of sulfur. The decomposition of TMTD is relatively slow (k_d (100°C) = $5.5 \times 10^{-6} \text{ s}^{-1}$),¹⁴ and there would be a low concentration of XS radicals during the early stages of reaction. Consequently, the rate of formation of TMTM would be limited. TMTM formation (reactions 4 and 5) is accompanied by the regeneration of persulfenyl radicals that could combine with XS radicals to form TMTPs, but as the XS concentration is low, limited recombination will occur. Instead, these radicals would participate in further sulfur extraction (reaction 5).

Blokh²⁰ noted that the rate controlling step in sulfur exchange reactions involving disulfides was their decomposition into RS radicals. The energy for the decomposition of TMTD is 150 kJ/mol, although sulfur exchange is rapid with an activation energy of only 90 kJ/mol. The activation energy of sulfur exchange in various accelerators is closely similar (MBTS = 96, MBT = 100, TMTD = 90 kJ/mol).²⁰ Thus, the bulk of TMTD decomposition would result from radical extraction rather than from homolysis. The total number of radicals will increase progressively as a result of the continued homolysis of TMTD and the regeneration of radicals already present (reactions 4, 5, and 9). At some point this accumulation of radicals will result in the rapid formation of TMTM (induction period 15 to 60 s). The increasing radical concentration will at the same time result in the recombination of radicals to yield TMTPs. The shorter induction period observed in the presence of higher sulfur ratios in the TMTD/sulfur mix suggests that sulfur exchange with cyclic sulfur occurs more rapidly than with TMTD. The higher the cyclic sulfur concentration, the more readily will thiuram persulfenyl radicals with higher sulfur rank form.

As the concentration of the various product and radical species increases, the reverse reactions become more important, i.e., sulfuration of thiuram sulfides of lower sulfur rank becomes more important while the desulfuration of polysulfides of higher sulfur rank increases.

The C—S bond is considerably more stable than the S—S bond in TMTD, and TMTM is expected to be less reactive than TMTD. Yet, at 130°C, both react with sulfur with virtually identical induction periods (cf., Figs. 1 and 5). This behavior would be expected if sulfur exchange (reaction 9) is more rapid than the homolysis of TMTM or TMTD (reactions 4 and 5), i.e., the rapid reaction and regen-

eration of the few radicals formed by homolysis accounts for most of the product formation.

CONCLUSIONS

These studies confirm (1) the formation of thiuram sulfide species of sulfur rank 1 and upwards on heating TMTM/sulfur, TMTD, and TMTD/sulfur mixes, the formation of larger amounts of TMTPs of higher sulfur rank being associated with higher sulfur loadings, and (2) the existence of an induction period prior to rapid reaction. New findings are that the induction period is a function of the sulfur concentration, higher loadings shortening the induction period. It is also shown that equilibrium concentrations of the various species is rapidly established (< 2 min). Furthermore, in the absence of sulfur or at low sulfur loadings, the concentration of TMTM increases more rapidly than that of any other thiuram sulfide species. Most importantly, the formation of thiuram trisulfide is faster than that of thiuram polysulfides of higher sulfur rank. This shows that sulfur atoms are sequentially added to the thiuram sulfides; polysulfides of higher rank do not form by the addition of S₈ to TMTD or a thiuram disulfide radical, which species then desulfurates. Although, based on Raman spectra, Coleman et al.⁴ reported the slow formation of TMTU and the absence of TMTM, this study points to the ready formation of TMTM. Little TMTU formed below 200°C. The latter findings are consistent with an earlier study by Kruger and McGill.⁸

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