

# *N,N'*-Pentamethylenethiuram Disulfide- and *N,N'*-Pentamethylenethiuram Hexasulfide-Accelerated Sulfur Vulcanization. I. Interaction of Curatives in the Absence of Rubber

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**ABSTRACT:** *N,N'*-pentamethylenethiuram disulfide (CPTD), CPTD/sulfur, and *N,N'*-pentamethylenethiuram hexasulfide (CPTP6) were heated in a DSC at a programmed heating rate and isothermally at 140°C. Residual reactants and reaction products were analyzed by HPLC at various temperatures or reaction times. CPTD rapidly formed *N,N'*-pentamethylenethiuram monosulfide (CPTM) and *N,N'*-pentamethylenethiuram polysulfides (CPTP) of different sulfur rank, CPTP of higher sulfur rank forming sequentially, as reported earlier for tetramethylthiuram disulfide (TMTD). As with TMTD, the high concentration of the accelerator monosulfide that develops is attributed to an exchange between CPTD and sulfenyl radicals, produced on homolysis of CPTD. However, a different mechanism for CPTP formation to that suggested for TMTD is proposed. It is suggested that disulfenyl radicals, resulting from CPTM formation, exchange with CPTD and/or CPTP already formed, to give CPTP of higher sulfur rank. CPTD/sulfur and CPTP6 very rapidly form a similar product spectrum with CPTP of sulfur rank 1–14 being detectable. Unlike with TMTD/sulfur, polysulfides of high sulfur rank did not form sequentially when sulfur was present, CPTP of all sulfur rank being detected after 30 s. It is proposed that sulfur adds directly to thiuram sulfenyl radicals. Recombination with sulfenyl radicals, which would be the most plentiful in the system, would result in highly sulfurated unstable CPTP. CPTP of higher sulfur rank are less stable than are disulfides as persulfenyl radicals are stabilized by cyclization, and the rapid random dissociation of the highly sulfurated CPTP, followed by the rapid random recombination of the radicals, would result in the observed product spectrum. CPTP is thermally less stable than is TMTD and at 140°C decomposed rapidly to *N,N'*-pentamethylenethiourea (CPTU), sulfur, and CS<sub>2</sub>. At 120°C, little degradation was observed. The zinc complex, zinc bis(pentamethylenedithiocarbamate), did not form at vulcanization temperatures, although limited formation was observed above 170°C. ZnO inhibits degradation of CPTD to CPTU. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2718–2731, 2000

**Key words:** *N,N'*-pentamethylenethiuram disulfide; *N,N'*-pentamethylenethiuram hexasulfide; thiourea; accelerator polysulfides; zinc bis(pentamethylenedithiocarbamate)

## INTRODUCTION

Accelerator polysulfides play an important role in thiuram disulfide-accelerated sulfur vul-

canization.<sup>1–4</sup> Tetramethylthiuram monosulfide (TMTM) and tetramethylthiuram polysulfides (TMTP) form relatively fast on heating tetramethylthiuram disulfide (TMTD) to above its melting point (145°C).

Numerous researchers have suggested that TMTD and tetraethylthiuram disulfide decomposition reactions are radical in nature.<sup>2,5–9</sup> Coleman et al.<sup>1</sup> suggested that TMTP was formed

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via the symmetrical and unsymmetrical dissociation of TMTD, followed by radical recombination. Geysler and McGill<sup>6</sup> pointed out that, while recombination of radicals from the scission of tri- and tetrasulfides would lead to TMTP of higher sulfur rank, it would be difficult to explain the high concentrations of TMTM found, since this would require scission of the more stable C—S bond to be a frequent event. They suggested that the symmetrical dissociation of thiuram disulfides into thiuram sulfenyl radicals was followed by interaction of thiuram sulfenyl radicals with undissociated thiuram disulfide. Thiuram sulfenyl radicals would abstract sulfur atoms from undissociated TMTD, resulting in TMTM and thiuram disulfenyl radicals<sup>6,10</sup>:

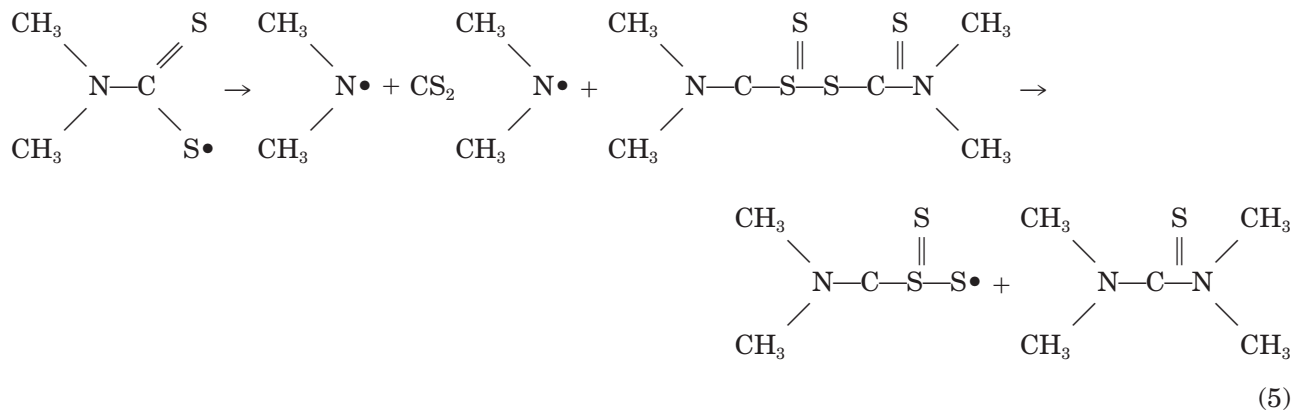


X is alkyldithiocarbonyl.

They further suggested that persulfenyl radicals of higher sulfur rank would also extract sulfur from undissociated TMTD, resulting in TMTM and trisulfenyl radicals:



Accelerator polysulfides of higher sulfur rank would then result from radical recombinations:



With 2-bisbenzothiazole-2,2'-disulfide (MBTS), it has been suggested that accelerator polysulfides of higher sulfur rank result from the exchange of disulfenyl radicals (BtSS•) with accelerator polysulfides, the result of the exchange being the insertion by disulfenyl radicals of a sulfur atom into the accelerator polysulfide<sup>13</sup>:



Persulfenyl radicals may be stabilized by cyclization<sup>11</sup> and Geysler and McGill<sup>6</sup> suggested that, in exchange reactions between sulfenyl radicals and TMTD or TMTP, radicals would abstract [eqs. (1b) and (2)] rather than add sulfur to TMTP. The dissociation of S—S bonds in polysulfides is more favorable than in disulfides, and other TMTP may also originate from exchange reactions following the symmetric dissociation of TMTP4 as suggested by Pickering et al.<sup>12</sup> for dimethyl disulfide:



Coleman et al.<sup>1</sup> also proposed the formation of TMTP via exchange reactions involving disulfenyl radicals, but disulfenyl radicals were suggested to be formed in the decomposition of disulfenyl radicals leading to tetramethylthiourea (TMTU):



Bt is benzothiazole.

When sulfur is present, the accelerator will dissolve in the molten sulfur, and the very rapid formation of TMTP of higher sulfur rank is possible at lower temperatures, commensurate with

vulcanization temperatures.<sup>1,5-7,14</sup> In TMTD/sulfur systems, an induction period was observed before the formation of TMTP<sup>6</sup> and this was ascribed to the buildup of sulfenyl radicals in the symmetric dissociation of TMTD. TMTP of progressively higher sulfur rank formed sequentially and Geysler and McGill<sup>6</sup> proposed that sulfur atoms were abstracted from cyclic sulfur in a stepwise manner to produce presulfenyl radicals of increasing sulfur rank. Radical combination gave rise to more highly sulfurated TMTP. Extraction of sulfur from cyclic sulfur occurred in preference of sulfur abstraction from TMTD and little TMTM formed. Coleman et al.<sup>1</sup> favored a mechanism whereby persulfenyl radical formation involved the addition of S<sub>8</sub> to thiuram radicals, followed by radical recombination. Rapid random decomposition and radical recombination would follow.

TMTM is more stable than is TMTD but it does react with sulfur at 150°C and there have been a number of reports<sup>1,6,9,15</sup> of the rapid formation of TMTD and various TMTP on heating TMTM with sulfur. The decomposition of TMTD to TMTU at vulcanization temperatures has been reported,<sup>1,7,16</sup> although other authors<sup>5,6</sup> reported that it forms only at 190°C. Amines will catalyze TMTD degradation leading to TMTU and it has been suggested<sup>4</sup> in some studies that an amine impurity may have been trapped in the system, while in open systems, the amine may escape, preventing the catalytic degradation process. Dogadkin and Shershnev<sup>7</sup> and Craig<sup>16</sup> suggested that TMTM formed as an intermediate when TMTD broke down to TMTU, CS<sub>2</sub>, and sulfur.

Zinc perthiomercaptides are well known as ultra accelerators<sup>4,17,18</sup> and can be extracted from vulcanizates cured with alkylthiuram disulfide/sulfur/ZnO formulations. However, their formation in compounds prior to the onset of crosslinking is disputed,<sup>4</sup> and the role of an active sulfuring agent in vulcanizates with TMTD/sulfur/ZnO has been attributed to both the zinc perthiomercaptides<sup>4,19-22</sup> and to TMTP.<sup>1,23</sup> Kawaoka<sup>24</sup> reported a vigorous exothermic reaction between TMTD and ZnO. Duchacek et al.<sup>25</sup> also reported the formation of zinc bis(dimethyldithiocarbamate) (ZDMC) and kinetic studies by Scheele and Franck<sup>26</sup> provided evidence for a reaction between TMTD and ZnO as the first step in thiuram-based vulcanization. Coleman et al.,<sup>1</sup> using Raman spectroscopy, reported the formation to TMTP in addition to a number of zinc-containing species, including ZDMC, and possibly zinc (dimethylmonocarbamate–dimethyldithiocarbamate) and zinc bis(dimethylmonocarbamate),

as well as COS, as main products on heating TMTD/ZnO and TMTD/sulfur/ZnO at vulcanization temperatures. ZDMC only became prominent after 240 min. Moore et al.<sup>27</sup> suggested a nucleophilic reaction mechanism leading to ZDMC. By contrast, McGill and coworkers<sup>5,23</sup> found no evidence for a reaction between TMTD and ZnO at vulcanization temperatures, provided that the compounds had been dried. The formation of TMTP, obtained on heating TMTD or TMTD/sulfur mixes, was unaffected by the addition of ZnO to such mixes.<sup>5,23</sup> In the presence of moisture, limited ZDMC formation occurred, especially in closed tubes from which the escape of moisture on heating was prevented.<sup>23</sup> ZDMC forms rapidly at higher temperatures (>180°C) or slowly on prolonged heating (16 h) at vulcanization temperatures.<sup>28</sup>

*N,N'*-pentamethylenethiuram sulfides are commercially available both as a disulfide (CPTD) and a hexasulfide (CPTP6), and this article is the first in a series in which the reactions of these accelerators are compared to reactions in TMTD systems. The article reports on the formation of accelerator polysulfides in the absence of rubber and examines conditions for the interaction of the accelerator and its polysulfides with ZnO to form the zinc-accelerator complex, zinc bis(pentamethylenedithiocarbamate) (ZPD), in the absence of rubber.

## EXPERIMENTAL

### Materials

CPTD (Robac P.T.D) and CPTP6 (Robac P.25) (Robinson Brothers Ltd. (Bromwich, England), technical purity), TMTM (Vulcazit MS, Bayer, Leverkusen, Germany), TMTD (Orchem, Sasolburg, South Africa), TMTU (Fluka, Buchs, Switzerland), sulfur (Holpro Analytics (Johannesburg, South Africa), 99.94% purity), ZDMC (Vulcazit L, Bayer, Leverkusen, Germany), and ZnO (Zinc Process, Cape Town, South Africa) were used. The acronyms used are listed in Table I.

Curative mixtures (1:1 mol ratio) were ground together with a mortar and pestle and heated in a differential scanning calorimeter (DSC) or a thermogravimetric balance (TG) at 5°C/min or isothermally for various times. The experimental procedures, thermal analysis equipment, and HPLC analysis of the reactants and products have been described.<sup>6,29</sup> For HPLC analysis, a Waters  $\mu$ Bondapak<sup>TM</sup> C18 cartridge column (4.6

**Table I Acronyms Used**

Acronym	Name
CPTD	<i>N,N'</i> -Dipentamethylenethiuram disulfide
CPTM	<i>N,N'</i> -Dipentamethylenethiuram monosulfide
CPTP	<i>N,N'</i> -Dipentamethylenethiuram polysulfide
CPTP6	<i>N,N'</i> -Dipentamethylenethiuram hexasulfide
CPTS	<i>N</i> -Pentamethylenethiocarbamyl- <i>N'</i> - pentamethylenesulfenamide
CPTU	<i>N,N'</i> -Dipentamethylenethiourea
dma.dmtc	Dimethylammonium dimethyldithiocarbamate
Hdmtc	Dimethyldithiocarbamic acid
Hpmtc	Pentamethylenedithiocarbamic acid
MBT	2-Mercaptobenzothiazole
pip.pmtc	Pentamethylene ammonium pentamethylenedithiocarbamate
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TMTP	Tetramethylthiuram polysulfide
TMTU	Tetramethylthiourea
X in equations	Alkyldithiocarbonyl
ZDMC	Zinc bis(dimethyldithiocarbamate)
ZPD	Zinc bis(pentamethylenedithiocarbamate)
ZPD(pip)	Piperidine zinc bis( <i>N</i> -pentamethylenedithiocarbamate)

× 250 mm) with a mobile phase consisting of 80% (v/v) methanol and 20% (v/v) freshly distilled water was used. Compounds that were not available for qualitative and quantitative HPLC analysis were synthesized following the published procedures described below. The molar response factors of CPTD and CPTP6 were found to be identical and all CPTP were assigned the same molar response factor. In the figures and tables, the concentrations of reactants, intermediates, and products are expressed in terms of the initial concentration of the reactant.

Kaniwa<sup>30</sup> showed that zinc as well as sodium dithiocarbamates are easily quantified by HPLC, using a Nucleosil C18 column and methanol/water mixtures as the mobile phase, after their conversion into the respective cobalt(III) dithiocarbamates by shaking with CoCl<sub>2</sub>. Shaking ZDMC with CoCl<sub>2</sub>, where the CoCl<sub>2</sub>-to-ZDMC ratio was greater than 1.5:1, resulted in complete conversion to Co(dmtc)<sub>3</sub> after 10 min. The conversion of ZDMC to the corresponding cobalt(III) complex was essential as it was previously reported that ZDMC-containing solutions gave no peak on HPLC analysis.<sup>31</sup> Kruger and McGill<sup>29</sup> demonstrated that TMTD and CoCl<sub>2</sub> were unreactive toward each other, but the presence of TMTD in ZDMC mixtures interfered with the zinc-cobalt exchange process. In control experiments, analy-

sis of mixtures of TMTD and ZDMC gave TMTD values of up to 10% lower than those of prepared mixtures. HPLC analysis of ZPD yielded a single peak that exhibited extensive tailing. On HPLC analysis of a ZPD/CPTD mixture, a decrease in the concentrations of CPTD (16 mol %) and ZPD (10 mol %) were found, and an unidentified peak, eluting with a retention time longer than that for ZPD, was also detected. Analysis of curatives when both ZPD and CPTD were present presented more severe problems than reported with the corresponding ZDMC/TMTD mixtures.<sup>29</sup> HPLC analysis after conversion of ZPD to the corresponding cobalt(III) complex yielded a single symmetric peak when using dilute solutions, and care was taken not to overload the column. However, conversion of ZPD to the corresponding cobalt(III) complex in the presence of CPTD or CPTP resulted in a large decrease in the peak areas of CPTD and CPTP with a corresponding increase in the peak area of the cobalt(III) complex, rendering quantitative analysis unreliable. Thus, in CTPD-containing systems, where ZPD was added or formed during reaction, HPLC analysis is useful only in so far as changes in the curative concentrations can be taken as indicative of trends, that is, increases or decreases in the amounts of ZPD and/or CPTD and CPTP. The analysis of sulfur and of *N,N*,-pentamethyl-

**Table II** Analyses of Compounds Synthesized for HPLC Analysis

Compound	C (mass %)	H (mass %)	N (mass %)	S (mass %)	Melting Point (°C)
CPTU					
Calcd	62.22	9.49	13.19	15.10	57.5–58.5 <sup>32</sup>
Found	61.13	9.43	12.95	14.79	54.4
CPTM					
Calcd	49.94	6.99	9.71	33.34	116.5 <sup>33</sup>
Found	50.23	7.10	10.23	31.70	114.6
CPTD					
Calcd	44.96	6.29	8.74	40.01	128.5 <sup>33</sup>
Found	45.01	6.24	8.65	41.86	132.4
CPTS					
Calcd	—	—	—	23.1	100 <sup>32</sup>
Found	—	—	—	24.7	103.5
pip.pmtc					
Calcd	53.61	9.00	11.37	—	—
Found	52.89	8.92	11.10	—	—
ZPD					
Calcd	37.35	5.22	7.26	—	—
Found	41.56	5.37	6.64	—	—
ZPD(pip)					
Calcd	43.35	6.63	8.92	—	—
Found	44.33	6.63	8.82	—	—

enethiourea (CPTU) in these mixtures are not affected.

### Syntheses

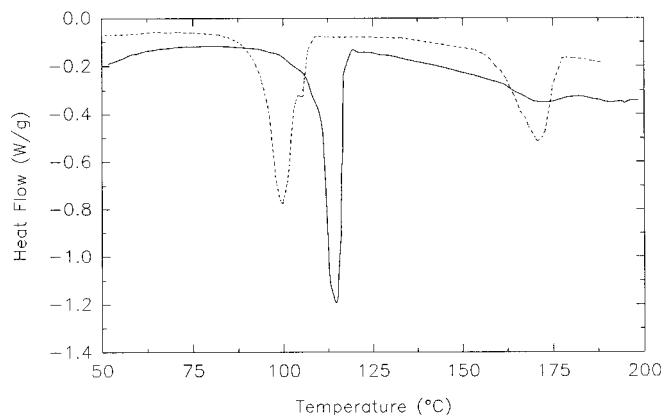
On heating CPTD for 1 h at 140°C, HPLC revealed only sulfur and one other compound. The latter was separated from sulfur by TLC, lifted from the plate, and recrystallized from dichloromethane, analyzed, and found to be *N,N'*-dipentamethylenethiourea (CPTU) (Table II). *N,N'*-pentamethylenethiuram monosulfide (CPTM), CPTD, and *N*-pentamethylenethiocarbamyl-*N'*-pentamethylenesulfenamide (CPTS) were prepared from piperidine and CS<sub>2</sub> following published procedures.<sup>33,34</sup> CHN analyses are shown in Table II. The method used to prepare the dimethylammonium salt (pip.pmtc) of dimethyldithiocarbamic acid (Hdmtc) was adapted to prepare the ammonium salt of pentamethylenedithiocarbamic acid (Hpmtc).<sup>35</sup> Sodium pentamethylenedithiocarbamate was prepared,<sup>33</sup> and Hpmtc was generated in solution by the addition of HCl. Hpmtc is unstable and on drying decomposes to pip.pmtc. A procedure previously described<sup>36</sup> for extracting Hpmtc from the buffered aqueous phase into an organic liquid proved unsuccessful, and for HPLC identification, the aqueous solution was injected directly into the column.

ZPD precipitated immediately on addition of a zinc acetate solution to an aqueous solution of sodium pentamethylenedithiocarbamate and the product was filtered, washed, and dried before recrystallization from boiling benzene. On heating to 400°C on a thermobalance, the 20.8 mass % residue compared favorably with the 25.2 mass % ZnS expected on decomposition. TG analysis is reported to give masses that corresponded to within 3–4 % of that required for ZnS.<sup>37</sup> CHN analysis is in Table II. ZPD(pip) was prepared from ZPD and piperidine.<sup>38</sup> On cooling of the resulting solution, the product crystallized and was washed and dried. Analysis shown in Table II.

## RESULTS

### CPTM

A DSC scan of CPTM at 5°C/min revealed two endothermic events (Fig. 1). The first endotherm, with a peak maximum at 115°C, was attributed to the melting of crystalline CPTM, and a second, broader endotherm (150–180°C), accompanied by a mass loss, to CPTU formation (Fig. 1 and Table III). (The magnitude of the latter endotherm varies and is dependent on how readily volatiles can escape from DSC pans.) Complete decomposition



**Figure 1** DSC scan of CPTM and CPTM/sulfur (1.0:1.0 mol ratio) at 5°C/min: (—) CPTM; (---) CPTM/sulfur.

of CPTM to CPTU and  $\text{CS}_2$  would result in a  $\text{CS}_2$  mass loss of 26.4%, which corresponds well with the 28.0% mass loss observed at 190°C. Small amounts of CPTU could also evaporate from closed DSC pans at these temperatures. Small amounts of CPTS were observed. Isothermal experiments on CPTM at 140°C resulted in an identical product spectrum as was observed for CPTM heated at 5°C/min.

#### CPTM/Sulfur (1.0:1.0 Mol Ratio)

A DSC scan of CPTM/sulfur at 5°C/min revealed a double endotherm below vulcanization temperatures (95–110°C) and a broad endotherm at 150–175°C (Fig. 1). The endotherms at 95–110°C were due to sulfur phase transitions and the mutual solubilization of sulfur and CPTM. Similar endothermic events were reported in study of TMTM/sulfur.<sup>15</sup> The second endotherm (150–175°C) was accompanied by a mass loss (Table IV). Complete degradation of CPTM to CPTU and  $\text{CS}_2$  would result in a  $\text{CS}_2$  mass loss of 13.97%, whereas mass losses of 17.70 and 21.70% observed at 170 and

180°C would account for lost  $\text{CS}_2$  and some CPTU. On heating, CPTU was found to evaporate above 100°C and only 64 mol % remained at 180°C. Small amounts of CPTS were also formed during the reaction of CPTM with sulfur (Table IV). Isothermal experiments at 140°C revealed an identical product spectrum.

#### CPTD and CPTD/ZnO (1.0:1.0 Mol Ratio)

A DSC scan of CPTD at 5°C/min (Fig. 2) resulted in a sharp endotherm with a peak maximum at 132°C, attributed to the melting of crystalline CPTD followed by the formation, at 155°C, of 25 mol % CPTM. A second endotherm (160–185°C), was accompanied by a mass loss and CPTU and sulfur production. Complete decomposition of CPTD to CPTU, sulfur, and  $\text{CS}_2$  would result in a  $\text{CS}_2$  mass loss of 23.75%. The 36.60% mass loss observed at 185°C would, in part, account for the 21 mol % CPTU not detected.

The DSC scan of CPTD/ZnO at 5°C/min revealed the melting of crystalline CPTD at 123°C, earlier than found in the absence of ZnO

**Table III** Mass Loss and HPLC Analysis of Reaction Products Formed on Heating CPTM at 5°C/Min

Temperature (°C)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTS (mol %)	Sulfur (mol %)
25	0	0	102	0	0	0
120	1.1	0	87	1	0	0
140	2.7	0	87	2	Trace	0
150	4	3	78	3	3	0
160	6.7	14	63	5	6	0
170	11.4	41	45	3	4	0
180	21.3	68	16	3	5	0
190	28	78	0	0	0	0

**Table IV** Mass Loss and HPLC Analysis of Reaction Products Formed on Heating CPTM/Sulfur (1.0 : 1.0 Mol Ratio) at 5°C/Min

Temperature (°C)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTP (mol %)	CPTS (mol %)	Sulfur (mol %)
25	0	0	100	0	0	0	104
130	0	0	53	8	23	0	86
150	4.1	16	5	14	36	5	75
160	7.5	39	1	18	21	5	93
170	17.7	62	0	0	0	6	99
180	21.7	64	0	0	0	0	95

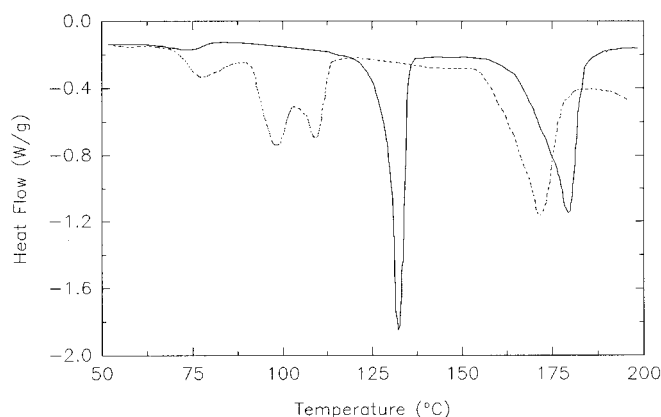
(132°C), while the endotherm at 150–180°C, found in the absence of ZnO and attributed to the evolution of CS<sub>2</sub> accompanying the formation of CPTU, was absent. No CPTU formation was detected on heating CPTD/ZnO at 5°C/min (Table V), although CPTD decomposed entirely to CPTU and sulfur when heated in the absence of ZnO. Since CS<sub>2</sub>, which accompanies CPTU formation, was not evolved, a negligible mass loss was recorded. As in the case of TMTD/ZnO mixtures,<sup>5,23</sup> a zinc-accelerator complex did not form at vulcanization temperatures. An exotherm commencing at 165°C was attributed to the interaction of CPTD with ZnO, and by 170°C, HPLC analysis revealed the formation of 5 mol % ZPD (Table V).

Isothermal studies at 140°C showed the complete decomposition of CPTD to CPTU, sulfur, and CS<sub>2</sub> (Figs. 3 and 4). CPTD is considerably less stable than is TMTD where decomposition to TMTU at vulcanization temperatures (150°C) has never been detected in this laboratory,<sup>5,6</sup> although reported in the literature.<sup>1,4,7</sup> As with TMTD, the rapid formation of accelerator mono- and polysulfides was observed.

Heating CPTD/ZnO mixtures isothermally at 140°C for various times led to the formation of equilibrium amounts of CPTM (36 mol %), CPTD (45 mol %), and CPTP (22 mol %) after an induction period of 3 min; CPTP3 (13 mol %), CPTP4 (7 mol %), and CPTP5 (2 mol %) were detected in higher concentrations when compared to their formation (prior to degradation) in the absence of ZnO (cf. Fig. 4). No ZPD was detected after 25 min, in accord with the absence of ZDMC in TMTD/ZnO mixtures studied at vulcanization temperatures.<sup>5,23</sup> At vulcanization temperatures, in the absence of ZnO, CPTD ultimately decomposed to CPTU and sulfur, whereas when heated to vulcanization temperatures in the presence of ZnO, it did not decompose into CPTU or was any mass loss detected. Equilibrium concentrations of CPTP formed, as is the case with TMTD systems, where decomposition to the corresponding thio-urea does not occur.<sup>5,6,23</sup>

#### CPTD/Sulfur (1.0:1.0 Mol Ratio) and CPTD/Sulfur/ZnO (1.0:1.0:1.0 Mol Ratio)

The DSC scan of CPTD/sulfur at 5°C/min revealed four endotherms (Fig. 2). The first, small



**Figure 2** DSC scan of CPTD and CPTD/sulfur (1.0:1.0 mol ratio) at 5°C/min: (—) CPTD; (---) CPTD/sulfur.

**Table V Mass Loss and HPLC Analysis of Curatives Formed on Heating CPTD/ZnO (1.0 : 1.0 Mol Ratio) at 5°C/Min**

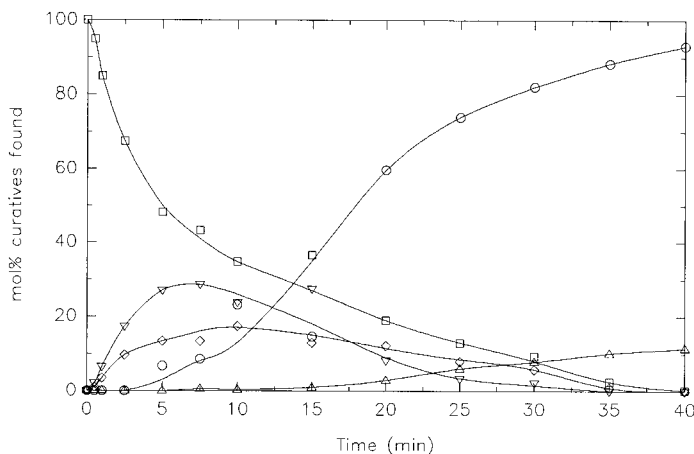
Temperature (°C)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTP (mol %)	ZPD (mol %)	Sulfur (mol %)
120	0.11	0	1	98	0	0	0
140	0.28	0	33	50	2	0	0
150	0.45	0	36	45	22	0	0
160	0.3	0	36	44	25	0	0
170	0.21	0	35	43	25	5	0

endothermic event took place at around 75°C and HPLC analysis at 85°C revealed that reaction had occurred between CPTD and sulfur in the solid state, forming CPTP6. The consumption of 45 mol % CPTD and the formation of 48 mol % CPTP were recorded on programmed heating to 85°C. Isothermal studies at 75°C confirmed a slow solid-state reaction between CPTD and sulfur, with the consumption of 54 mol % CPTD and 30 mol percent; sulfur, to form 44 mol % CPTP6 and 4 mol % of other CPTP after 7.5 min. After 15 min, the amount of CPTP6 increased to 57 mol %. A similar endotherm was not found below 100°C in TMTD/sulfur, and on holding the mix at 80°C for 30 min, analysis revealed no change in the components.

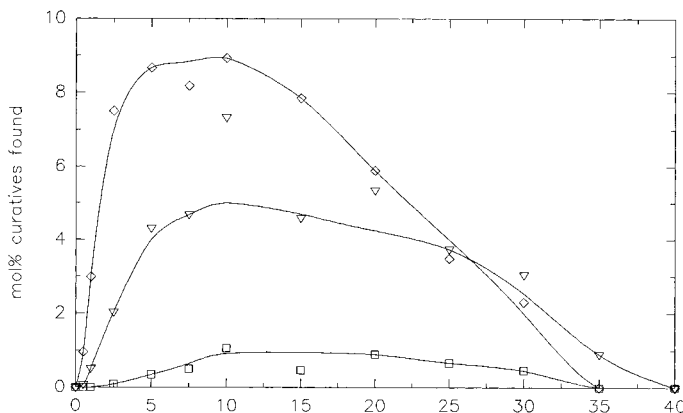
The two endotherms in the 90–120°C region were interpreted as sulfur phase transitions and the mutual solubilization of sulfur and CPTD. These transitions (the sulfur melt in particular) did not occur at as sharply defined temperatures as similar thermal events found on heating TMTD/sulfur (1.0:1.0 mol ratio),<sup>5</sup> possibly because of the presence of CPTP6 and the ready

interaction between sulfur and CPTD that occurs even prior to solubilization. Once solubilized, polysulfides of various sulfur rank (CPTP3–CPTP14) formed from an interaction of CPTP6 and residual CPTD with sulfur. Decomposition of CPTD and CPTP to CPTU and sulfur, giving rise to the fourth endotherm (160–180°C), was accompanied by a mass loss. Complete degradation of CPTD to CPTU, sulfur, and CS<sub>2</sub> would result in a CS<sub>2</sub> mass loss of 13.19%, whereas a 17.10% mass loss observed includes the escape of some CPTU from DSC pans. All the sulfur was regenerated as S<sub>8</sub>.

The DSC scan of CPTD/sulfur/ZnO at 5°C/min revealed a single endotherm above 100°C, indicating that the sulfur transitions and the dissolution of CPTD in the molten sulfur had merged. The endotherm, observed in CPTD/sulfur at 75°C due to the interaction of unmolten CPTD with sulfur to preferentially form CPTP6, was absent. An explanation may be found in reduced interfacial contact between CPTD and sulfur in the presence of ZnO. By 165°C, 5 mol % CPTM and 49 mol % CPTP formed, but no CPTU, and the mass loss

**Figure 3** HPLC analysis of curatives and reaction products found in the reaction of CPTD at 140°C: (○) CPTU; (▽) CPTM; (□) CPTD; (◇) CPTP; (△) sulfur.





**Figure 4** HPLC analysis of lower sulfur rank polysulfides found in the reaction of CPTD at 140°C: ( $\diamond$ ) CPTP3; ( $\nabla$ ) CPTP4; ( $\square$ ) CPTP5.

(0.7 %) was negligible. Some ZPD (17 mol %) formed at 195°C, well above vulcanization temperatures.

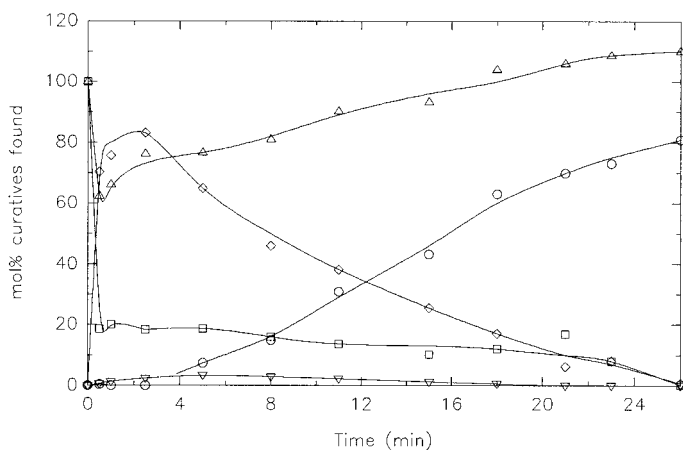
Interaction of CPTD with sulfur at 140°C resulted in the rapid formation of 70 mol % CPTP (Fig. 5). Using pure methanol as the mobile phase for HPLC analysis, CPTP3–CPTP14 were detected (Fig. 6). CPTP4 was the most abundant polysulfide, with CPTP3 and CPTP5 detected in lesser amounts and CPTP of higher sulfur rank formed in progressively lower amounts. The sulfur concentration decreased rapidly to 62 mol %, increasing once again with increased reaction time. CPTM, like TMTM formation in TMTD/sulfur (1.0:1.0 mol ratio),<sup>5</sup> formed in low concentrations (<3 mol %) in the presence of sulfur. At 140°C, complete degradation of CPTD to CPTU occurred (Fig. 5), although when held at 120°C,

the accelerator did not degrade as rapidly, and equilibrium concentrations of CPTP were obtained after 2 min (Figs. 7 and 8).

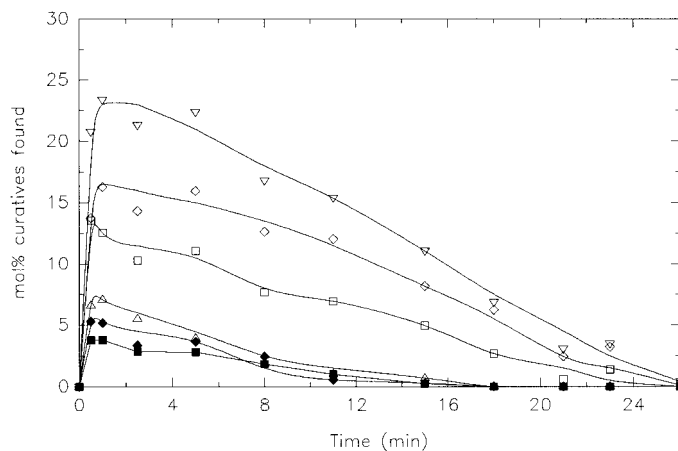
Holding CPTD/sulfur/ZnO at 140°C resulted in the rapid formation of equilibrium amounts of 7 mol % CPTM, 19 mol % CPTD, and 78 mol % CPTP after 2 min. No ZPD or CPTU formation was observed, which was consistent with lack of ZDMC and TMTU formation in TMTD/sulfur/ZnO (1.0:1.0:1.0 mol ratio).<sup>5,23</sup> At 120°C, the rate of CPTP formation was much slower than in the absence of ZnO and can be attributed to dilution of the mixture by ZnO. A similar effect was observed with TMTD/sulfur/ZnO mixes.<sup>23</sup>

#### CPTP6 and CPTP6/ZnO (1.0:1.0 Mol Ratio)

The DSC scan of CPTP6 at 5°C/min (Fig. 9) revealed two endotherms and is essentially similar



**Figure 5** HPLC analysis of curatives and reaction products found in the reaction of CPTD/sulfur (1.0:1.0 mol ratio) at 140°C: ( $\circ$ ) CPTU; ( $\nabla$ ) CPTM; ( $\square$ ) CPTD; ( $\diamond$ ) CPTP; ( $\Delta$ ) sulfur.



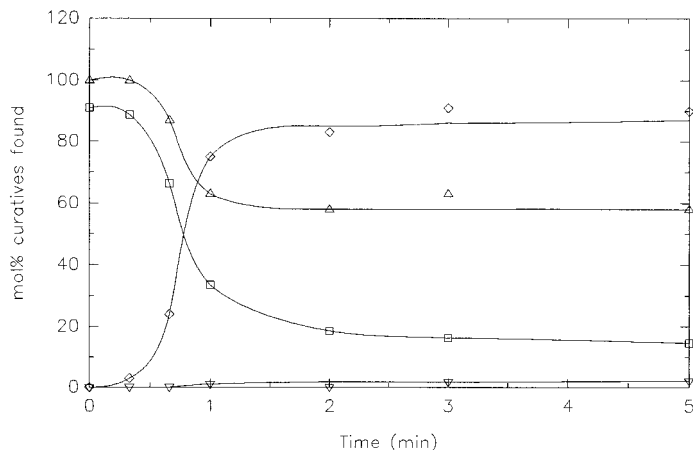
**Figure 6** HPLC analysis of lower sulfur rank polysulfides found in the reaction of CPTD/sulfur (1.0:1.0 mol ratio) at 140°C: ( $\diamond$ ) CPTP3; ( $\nabla$ ) CPTP4; ( $\square$ ) CPTP5; ( $\diamond$ ) CPTP6; ( $\blacklozenge$ ) CPTP7; ( $\blacksquare$ ) CPTP8.

to that for CPTD. Crystalline CPTP6 melted at 135°C, and by 156°C, 7 mol % CPTM and 24 mol % CPTD had formed with the liberation of 17 mol % sulfur. The broad endotherm at 160–180°C was accompanied by a mass loss and CPTU and sulfur formation on decomposition of CPTD and CPTP. Complete degradation of CPTP6 to CPTU, sulfur, and CS<sub>2</sub> would result in a CS<sub>2</sub> mass loss of 16.96%; the observed 23.2% mass loss observed at 180°C therefore included the escape of some CPTU.

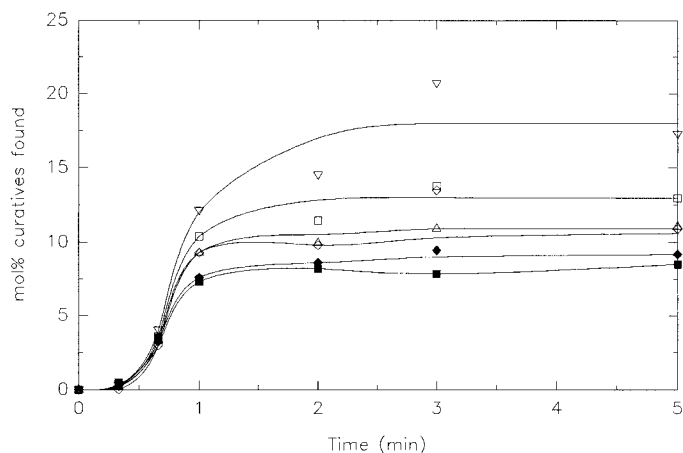
The DSC scan of CPTP6/ZnO, heated at 5°C/min, showed the melting of CPTP6 commencing at 125°C and an exotherm commencing at 190°C due to ZPD formation. The partial dissociation of CPTP6 took place once it was molten, but no decomposition to CPTU was detected.

Holding CPTP6 and CPTD/sulfur at 140°C for 1 min resulted in a similar product spectrum (cf. Figs. 5 and 6 with Figs. 10 and 11). CPTP6 decomposed to 2 mol % CPTM, 20 mol % CPTD, 64 mol % CPTP, and 22 mol % sulfur, whereas interaction of CPTD with sulfur at 140°C resulted in 1 mol % CPTM, 19 mol % CPTD, 70 mol % CPTP, and 62 mol % sulfur. Approximately 38 mol % sulfur was consumed to form the 70 mol % CPTP observed in CPTD/sulfur, whereas sulfur atoms corresponding to 42 mol % sulfur was calculated to be incorporated in CPTP formed from CPTP6 (CPTP6 corresponds to a 1.0:0.5 mol ratio CPTD/sulfur mixture; an additional 11 mol % sulfur was detected in CPTP6 as an impurity).

Heating of CPTP6/ZnO at 140°C resulted in the formation within 2 min of 5 mol % CPTM, 18



**Figure 7** HPLC analysis of curatives and reaction products found in the reaction of CPTD/sulfur (1.0:1.0 mol ratio) at 120°C: ( $\nabla$ ) CPTM; ( $\square$ ) CPTD; ( $\diamond$ ) CPTP; ( $\triangle$ ) sulfur.



**Figure 8** HPLC analysis of lower sulfur rank polysulfides found in the reaction of CPTD/sulfur (1.0:1.0 mol ratio) at 120°C: ( $\diamond$ ) CPTP3; ( $\nabla$ ) CPTP4; ( $\square$ ) CPTP5; ( $\diamond$ ) CPTP6; ( $\blacklozenge$ ) CPTP7; ( $\blacksquare$ ) CPTP8.

mol % CPTD, and 75 mol % CPTP, after which amounts of curatives and reaction products remained constant. CPTP3–CPTP14 formed, with CPTP4 detected in highest concentrations, followed by CPTP3 and CPTP5. CPTPs of high sulfur rank were detected in progressively lower concentrations. No ZPD or CPTU was found after 25 min at 140°C.

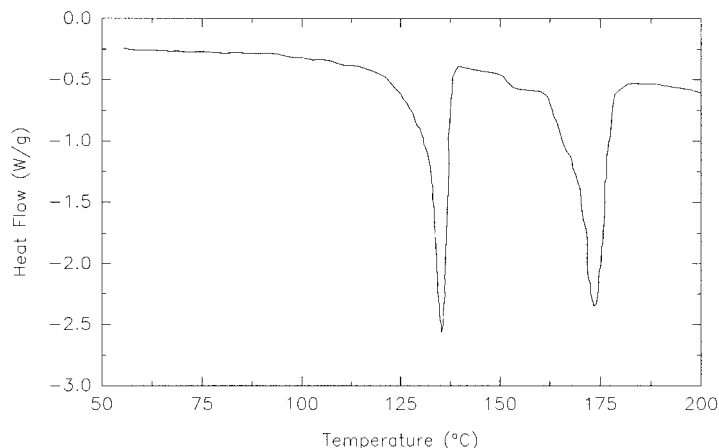
## DISCUSSION

### CPTP Formation

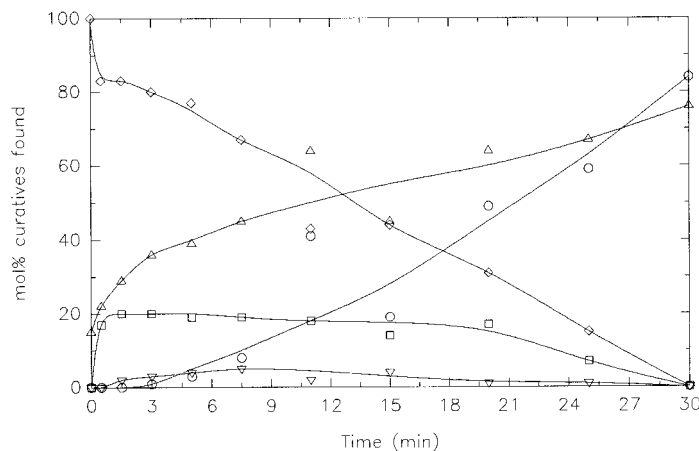
CPTD could be expected to undergo homolytic dissociation similar to TMTD, resulting in CPTM and CPTP. The large amounts of CPTM formed (Fig. 3) support the contention<sup>5</sup> that CPTM formation occurs predominately by extraction of sul-

fur atoms by thiuram sulfenyl radicals from undissociated CPTD. It is suggested that the sequential formation of CPTP of higher sulfur rank (Fig. 4) results largely via exchange reactions involving disulfenyl radicals [as in eq. (6)] rather than by the recombination of persulfenyl radicals formed on the addition of sulfur to sulfenyl radicals or lower sulfur rank as previously suggested for TMTD. Reactions (1b) and (4), in concert, constitute a chain process and is a more plausible scenario than is radical recombination to explain the formation of high concentrations of CPTM, together with CPTP of sequentially higher sulfur rank.

The symmetrical dissociation of CPTD by scission of the S—S bond will be energetically favored compared to scission of the more stable C—S bond, yet the formation, at 120–130°C, of small



**Figure 9** DSC scan of CPTP6 at 5°C/min.

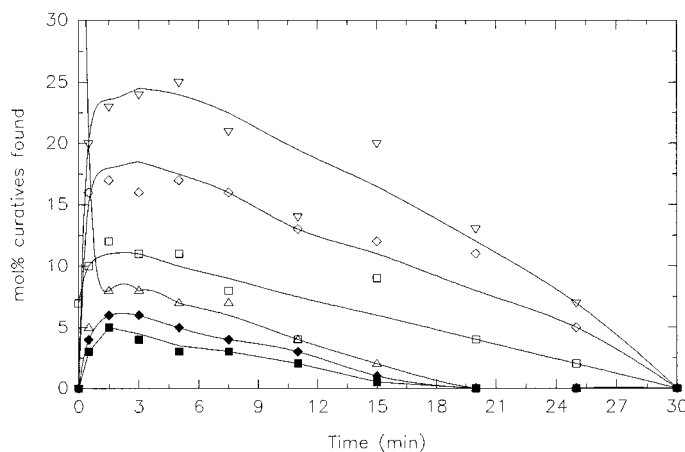


**Figure 10** HPLC analysis of curatives and reaction products found in the reaction of CPTP6 at 140°C: (○) CPTU; (▽) CPTM; (□) CPTD; (◇) CPTP; (△) sulfur.

amounts of CPTD on heating CPTM (Table III), shows that the C—S bond can dissociate at these temperatures. An exchange with CPTM may yield CPTD. Trace amounts of CPTS and possibly other undetected products also result. CPTM is less stable than is TMTM, which decomposes very slowly at 125°C.<sup>39</sup> On heating, CPTU was detected at 150°C (Tables III and IV), while no reaction was observed when TMTM was held at 140°C for 5 min, and only at 220°C did it decompose to TMTU.<sup>5</sup> TMTU and CS<sub>2</sub> have been reported<sup>1</sup> on heating TMTM to 140°C for 120 min.

At 150°C, CPTD/sulfur very rapidly formed CPTP (Figs. 5 and 6), but at 120°C, an induction period, similar to that in TMTD/sulfur,<sup>6</sup> can be observed (Figs. 7 and 8) and can be attributed to the buildup of sulfenyl radicals on the symmetric

dissociation of CPTD. In the absence of cyclic sulfur, CPTP of higher sulfur rank clearly form after those of lower sulfur rank (Fig. 4). The same does not apply when sulfur is present (Figs. 6 and 8), CPTP of all sulfur ranks being detected after 30–40 s. Indeed, the concentration of CPTP4 is greater than that of CPTP3. The reaction mechanism, in the presence of sulfur, clearly differs from that suggested for TMTD.<sup>5</sup> On heating, CPTP6 formed a similar product spectrum to CPTD/sulfur (cf. Figs. 5 and 6 with Figs. 10 and 11), the concentration of CPTP4 again being greater than that of CPTP3. Kende et al.<sup>40</sup> noted that alkyl persulfenyl radicals were stabilized to a larger extent than were alkyl sulfenyl radicals and suggested that alkyl polysulfides, therefore, decomposed into radicals much faster than did



**Figure 11** HPLC analysis of lower sulfur rank polysulfides found in the reaction of CPTP6 at 140°C: (◇) CPTP3; (▽) CPTP4; (□) CPTP5; (△) CPTP6; (◆) CPTP7; (■) CPTP8.

the corresponding alkyl disulfides. Following Kende et al., it is suggested that thiuram persulfenyl radicals, with their added stability, would permit the rapid dissociation of CPTP6 into persulfenyl radicals. Various persulfenyl radicals would form, recombine, and dissociate at random into persulfenyl radicals, rapidly resulting in polysulfides of various sulfur rank (CPTP3–CPTP14). Little CPTM forms as radicals react with sulfur in preference to CPTD. The dissociation energy of TMTD is reported as 150 kJ/mol, while the activation energy of sulfur exchange is 90 kJ/mol.<sup>8</sup> The data support the proposals of Coleman et al.<sup>1</sup> who suggested the addition of S<sub>8</sub> to sulfenyl radicals. The rapid random decomposition of CPTP, as suggested by Kende et al.,<sup>40</sup> and the random recombination of radicals produced would account for the CPTD/sulfur product spectrum being very similar to that found with CPTP6 (cf. Figs. 5 and 6 with Figs. 10 and 11).

A solid-state reaction between CPTD and cyclic sulfur at 75°C led to CPTP6, but an analogous reaction was not observed with TMTD/sulfur. The mechanism of the reaction is not known, but the formation of a single polysulfide, CPTP6, and the absence of a similar reaction in TMTD may suggest the molecular conformation of CPTD (in the crystal) may be important. A concerted rather than a radical reaction may be involved; for example, the interaction of two thione sulfurs of CPTD and the sulfur ring could lead to CPTP6. The possibility of a similar reaction occurring in the melt at higher temperatures (120 and 150°C) leading to CPTP6, which would then disproportionate as found on heating CPTP6, cannot be excluded. It has been reported<sup>39</sup> that the reaction product of CPTD/sulfur systems (1:2–1:6 mol ratios), boiled in toluene for 2 h, always contained the same amount sulfur as that of the hexasulfide. After recrystallization, the melting point of the reaction product corresponded to that of the hexasulfide.

#### Effect of ZnO

CPTP formation was in no way altered by the inclusion of ZnO, but the decomposition to CPTU was prevented, thus allowing equilibrium concentrations between the various CPTP to be established. In the case of TMTD also, ZnO did not affect TMTD formation.<sup>23</sup> In line with the low reactivity of TMTD toward ZnO at vulcanization temperatures,<sup>5,23</sup> no evidence was found for the reaction of CPTD, or its polysulfides, with ZnO at vulcanization temperatures. ZPD did form above 170°C.

#### CPTU Formation

CPTU formation will be discussed in article 2 of this series where the thermal stability of CPTD and TMTD will be contrasted with respect to thio-urea formation.

#### CONCLUSIONS

CPTD and its polysulfides are thermally less stable than is TMTD and rapidly decompose to CPTU, sulfur, and CS<sub>2</sub> at 140°C, although little degradation occurs at 120°C. CPTP of different sulfur rank form rapidly, and a reaction between sulfur and alkyl sulfenyl radicals that gives highly sulfurated species, which immediately dissociate at random and recombine to give CPTP of different sulfur rank, is suggested. CPTP6 likewise rapidly forms CPTP of different sulfur rank. As with TMTD/ZnO, CPTD and ZnO do not interact at vulcanization temperatures, which implies that, on vulcanization, the zinc-accelerator complex (ZPD) is not available to initiate reaction and must be formed during the reaction as a by-product of the vulcanization process, initiated by CPTP. ZnO inhibits CPTU formation.

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