The Limiting Value of ZDMC Formation: New Insight into the Reaction of ZnO and TMTD

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ABSTRACT: The reaction of ZnO and tetramethylthiuram disulfide (TMTD) was reinvestigated in detail. Under conditions where evaporation of volatiles is possible, TMTD and an excess of ZnO are found to produce bis(dimethyldithiocarbamato)zinc(II) (ZDMC) in limiting amounts close to 60 mol %, irrespective of the ratio between ZnO and TMTD. This result points to the operation of more than one route toward ZDMC. When ZnO and TMTD are reacted in closed vessels in inert atmosphere, a nucleophilic reaction of ZnO with TMTD was confirmed by GC–mass spectroscopy (MS) detection of COS and NMR observation of tetramethylthiourea (TMTU). This route is found to account for about 70 mol % of the total amount of ZDMC formed. A previously unrecognized redox reaction between ZnO, sulfur, and TMTD, furnishing ZnSO₄ and ZDMC, is responsible for approximately 15 mol % of the amount of ZDMC. Other products that were detected are CO₂, CS₂, and tetramethylurea, whereas ZnSO₃, ZnS, and dioxygen were absent. Based on the latter observation, the operation of a mechanism constituting radical reduction of water by TMTD, yielding dioxygen, was excluded. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1247–1257, 1999

Key words: ZnO; TMTD; ZDMC; mechanism; vulcanization

INTRODUCTION

It has been firmly established that tetramethylthiuram disulfide (TMTD) reacts with ZnO to form zinc dimethyldithiocarbamate (ZDMC).^{1,2} This reaction is considered to be an important route for the production of ZDMC during sulfur vulcanization of unsaturated elastomers.^{1,3–5} A second source of ZDMC in TMTD-accelerated vulcanization is the reaction of ZnO with dimethyldithiocarbamic acid (Hdmtc), which is produced when the active sulfurating agent tetramethylthiuram polysulfide (TMTP) reacts with the rubber unsaturation.² Whereas the latter reaction is well understood, the mechanism of the direct reaction between ZnO and TMTD has been the subject of ongoing scientific interest. As early as 1956, Scheele and Lorenz closely investigated ZDMC formation in ZnO/TMTD vulcanizates and found limiting yields of 66% with respect to TMTD.⁶ Unfortunately, this failed to account for other experimental observations,¹ and up until now the ZnO/TMTD reaction is far from completely understood.

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Products and Mechanisms

A variety of products were reported to form when ZnO/TMTD mixtures are heated at or above 140°C. Among the most important ones are ZDMC, Zn(dmtc)(dmmc) (dmtc, dimethyldithiocarbamate; dmmc, dimethylmonothiocarbamate), elemental sulfur, and carbonyl sulfide (COS).⁷⁻⁹ As minor products, CS₂, zinc sulfide (ZnS), tetramethylthiourea (TMTU), dimethylammonium dithiocarbamate (DMADC), and dimethylamine were demonstrated.⁷⁻¹⁰ Coleman et al. observed the formation of TMTP, ZDMC, and possibly Zn(dmtc)(dmmc) or Zn(dmmc)₂.¹¹ The formation of Zn(dmmc)₂ may be less likely, however, since carbamate salts are rather unstable. Savin et al.¹² showed that the ammonium salts of dmmc decompose to yield COS and the corresponding amines.

The ideas concerning the mechanism of the ZnO/TMTD reaction were recently summarized and discussed.² The traditional view constitutes a nucleophilic attack of the oxygen anion in ZnO on a thiocarbamoyl carbon atom of TMTD, furnishing dmmc anion and а trithioanion $[Me_2NC = S)S = S^{-1}$ (Scheme 1a). The so-formed reactive species is thought to induce homolysis of the S-S bond in TMTD, resulting in tetramethylthiuram trisulfide (TMTT) and a dmtc anion.⁴ As suggested by Watson,⁸ a combination of the dmtc and dmmc anions with the zinc cation would yield ZDMC, Zn(dmtc)(dmmc), and/or Zn(dmmc)₂, whereas degradation of dmmc ligands furnishes COS, accompanied by Me_2N^- . The latter species may react with TMTD to give TMTU and a (sulfurated) dmtc anion. Because TMTT may reform TMTD by splitting off elemental sulfur, eventually all TMTD will be transformed into ZDMC, COS, S_8 , and TMTU.

In an alternative reading, TMTT is not formed as a result of an anionic attack of sulfurated dmtc on TMTD, but due to incorporation of elemental sulfur into yet-unreacted TMTD (Scheme 1b). Elemental sulfur would be produced after reaction of the nucleophiles ZnO and Me_2N^- with TMTD, yielding ZDMC and TMTU, respectively. It was recently proposed that the reactions take place on the ZnO surface, during which adsorbed water molecules may play a facilitating role.²

In all readings, ZnO is inferred to act as a nucleophile, ultimately resulting in 1 equivalent of ZDMC and 1 equivalent of TMTU produced per 2 equivalents of TMTD reacted [eq. (1)]. In view of the detection of COS by previous workers,^{7,8} the

operation of this reaction was established beyond doubt.

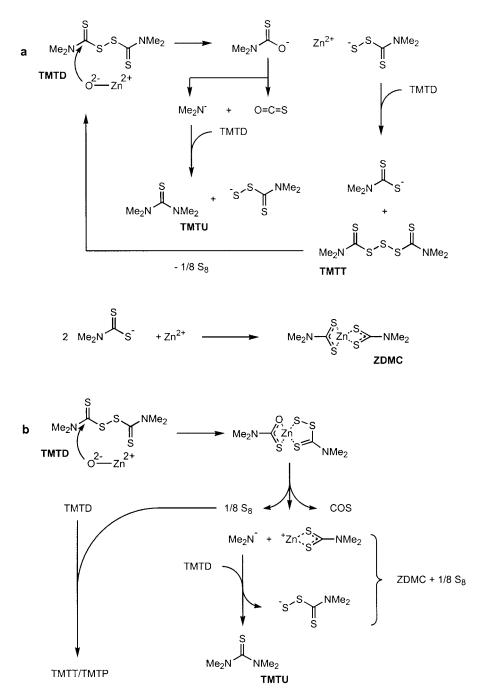
$$ZnO + 2 TMTD \rightarrow ZDMC$$

+ TMTU + COS + $\frac{1}{4}S_8$ (1)

A completely different mechanistic explanation for the formation of ZDMC from TMTD and ZnO was recently put forward by Geyser and McGill.¹³ They re-examined contradicting DSC experiments by Duchacek et al.,¹⁴ who found a strong exothermic reaction when heating a 1:1 mixture of ZnO and TMTD, and Kruger and McGill,^{9,15} who instead found a particular reluctance of ZnO and TMTD to react. It appeared¹³ that thoroughly dried ZnO hardly reacts with TMTD, and that the experimental discrepancies seem to be associated with an autocatalytic reaction initiated by H₂O. which is adsorbed onto the ZnO surface and is crucial for the reaction to proceed (Scheme 2). Geyser and McGill¹³ proposed that thiuram sulfenyl radicals, adsorbed onto the ZnO surface, react with water to form Hdmtc, which in turn reacts with ZnO to yield ZDMC and H₂O. Overall, a half equivalent of dioxygen is formed, according to eq. (2). Thus, in this mechanism, water is continuously used and reformed, and in fact, may be regarded as a catalyst. As yet, dioxygen was not detected among the reaction products of the ZnO/ TMTD reaction,

$$ZnO + TMTD \rightarrow ZDMC + \frac{1}{2}O_2$$
 (2)

Neither the correct stoichiometry nor the exact mechanism of the reaction between ZnO and TMTD was so far established. As part of the ongoing investigation of the products and mechanism of the ZnO/TMTD reaction, and in view of our own interest in the role of zinc dithiocarbamates in vulcanization,^{9,13,16–21} we embarked on a renewed investigation of the ZnO/TMTD reaction. Because the contradicting results that are reported in the literature² may in part be explained by small differences in experimental conditions, particular effort was put forth in establishing reliable experimental procedures. First, to limit the number of side reactions and by-products not resulting from the reactions of interest, only pure ZnO/TMTD samples were examined in the absence of rubber and after long reaction times (i.e., 16 h at 140°C). Second, small quantities of about 30 mg were studied, as this prevents a heat gra-



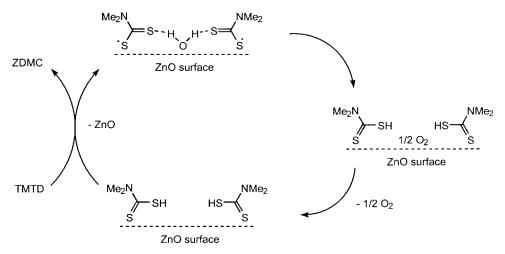
Scheme 1 Nucleophilic attack of ZnO on TMTD and subsequent reactions leading to ZDMC, ^{2,4,7,8,11}

dient to build up in the sample. The reaction products were characterized and quantified by various techniques, comprising mass spectrometry (MS), NMR, thermogravimetric (TG) analysis, and chromatography. By doing so, we observed limiting values for ZDMC formation, identified and excluded certain products beyond doubt, and were able to uncover a unique redox reaction by which ZDMC is produced (Table I).

EXPERIMENTAL

General

Tetramethylthiuram monosulfide (TMTM; Bayer AG, Germany), TMTD (97%, Aldrich), tetraethylthiuram disulfide (TETD; >98%, Fluka, Switzerland), and ZDMC (Vulkacit L, Bayer) were recrystallized from chloroform and dried in a vacuum



Scheme 2 H₂O-catalyzed formation of ZDMC according to Geyser et al.¹³

prior to use. ZnO (99.72%, Zinc Process, South Africa, 0.2 μ), chloroform (Aldrich, p.a.), CoCl₂ · 6H₂O (Aldrich), TMTU (Purum, Fluka), thiourea (TMU; 99%, Acros, South Africa), Zn(OH)₂ (97%, Aldrich), and ZnS (Saarchem Pty. Ltd., USA) were used as received. The ratios of compound mixtures are in moles, whereas percentages refer to mol %, unless otherwise indicated.

Thermogravimetric Analyses

Thermogravimetric (TG) analyses were carried out using the TGA 2050 thermogravimetric analyzer of TA Instruments. Samples were heated from room temperature to 140° C at a rate of 2.5° C

 Table I
 Abbreviations Used in This Paper

$Co(dmtc)_3$	tris (dimethyl dithio carba mato) cobalt (III)
DMADC	Dimethylammonium
	dimethyldithiocarbamate,
	$[\mathrm{Me_2NH_2^+}\ ^-\mathrm{S_2CNMe_2}]$
dmmc	Dimethylmonothiocarbamate,
	$[Me_2NCOS]^-$
dmtc	Dimethyldithiocarbamate,
	$[Me_2NCS_2]^-$
MS	Mass spectrometry
NMR	Nuclear Magnetic Resonance
TG	Thermal Gravimetric Analysis
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TMTP	Tetramethylthiuram polysulfide
TMTT	Tetramethylthiuram trisulfide
TMTU	Tetramethylthiourea
TMU	Tetramethylurea
ZDMC	bis (dimethyl dithio carba mato) zinc (II)

 \min^{-1} , after which the temperature was kept constant for 700 min. In the last 50 min, the mass of the sample reached a constant value. During experimental runs, the apparatus was flushed with nitrogen containing 5 ppm of water, unless indicated otherwise. Samples were stored at room temperature before being analyzed.

Thermal Desorption AS-GC-MS

A mixture of 534 mg (6.6 mmol) of ZnO and 548 mg (2.3 mmol) of TMTD was brought into a 100-ml vessel, equipped with a septum and filled with helium. After closing, the vessel was heated for 1 h at 140°C. The gas head was analyzed by using a HP 5971A GC-mass spectroscopy (MS) system equipped with a 1.2- μ m CPSil 8 CB column (25 m × 0.25 mm). In a subsequent experiment, 66 mg (0.81 mmol) of ZnO and 65 mg (0.27 mmol) of TMTD were heated, after which HPLC-grade methanol was injected through the septum. The solid and gas phase were extracted by ultrasonification, after which the contents were analyzed by GC-MS.

ZDMC Quantification

TG samples (10–30 mg) were quantitatively transferred to a volumetric flask using ~ 5 mL of dichloromethane. The suspension was ultrasonificated for 15 min to allow ZDMC to dissolve.²² Methanol and an appropriate amount of a 2-mM solution of CoCl₂ in methanol, containing approximately 1 equivalent of HCl, was added, after which the flask was shaken in air for 30 min, resulting in a green solution. The calibration

curve for ZDMC, transformed into $Co(dmtc)_3$ according to this procedure, was linear. Reversedphase high-performance liquid chromatography (RP-HPLC) was performed using a Waters 510 HPLC pump equipped with a Rheodyne injector, an Alltech Nucleosil 100A C18 7 μ m stainless steel column, and a Waters 484 Tunable Absorbance Detector, set at 280 nm. An ultrasonificated 45 : 55 mixture of water and methanol was used as the mobile phase at a volumetric flow rate of 1.0 mL min⁻¹. Data were acquired and processed with the baseline package installed on a PC.

Experiments Performed in Inert Atmosphere

All experiments were performed in argon atmosphere in 30-mL tailor-made Schlenk-type reaction vessels (23×125 -mm diameter), equipped with airtight Teflon valves and screw caps with Teflon inserts. In a typical experiment, the reaction vessel was treated with concentrated HCl. thoroughly rinsed, and dried overnight in a 150°C stove. Immediately before reaction, the vessel was removed from the stove and cooled under a stream of argon. The vessel was charged with a known amount of a 2 : 1 ZnO/TMTD mixture, evacuated three times, and filled with argon. The valve was closed and the vessel was partly immersed for 16 h in a thermostated oil bath of large volume, set at 140°C. After cooling to room temperature, the argon pressure was reinstalled, $\sim 10 \text{ mL}$ chloroform was added, and the suspension was ultrasonificated for 20 min. After sedimentation, chloroform was pipetted off and transferred to a round bottom flask over a membrane filter. This procedure was repeated two times, and the third time, the insoluble residue was quantitatively transferred to the filter and weighed after drying. The residue was analyzed for the presence of ZnS, $ZnSO_3$, and $ZnSO_4$. The filtrate was evaporated under reduced pressure and analyzed by NMR to characterize and quantify the soluble products. The amount of S_8 was determined by RP-HPLC analysis, whereas EDTA titration furnished the amount of ZDMC.

NMR Analysis

¹H-NMR and ¹³C{¹H}-NMR spectra were recorded in CDCl₃ on a Bruker WM-300 (300.13/75.47 MHz) spectrometer. Compounds were identified by comparing their ¹H-NMR and, if possible, ¹³C-NMR chemical shifts to those of reference compounds. The amounts of ZDMC, TMTD, TMTU, and TMU for the experiments performed in argon were determined by integration of the ¹H-NMR signals. Such an approach is allowed when it is ascertained that the excited ¹H nuclei have sufficient time to relax to an equilibrium state after NMR signal acquisition. The required delay time is derived from the T_1 time by multiplication with a factor of five. T_1 was determined for TMTU (2.465 s) and ZDMC (2.665 s) and assumed to be similar for other thiuram species. Consequently, D_1 was set at 15 s.

Quantification of Elemental Sulfur

The amount of sulfur was quantified by RP-HPLC using a Gynkotek M480 ternary gradient pump equipped with a Gastorr GT-103 on-line degassing device, a Marathon XT autoinjector equipped with a 20- μ L loop, an Alltech Nucleosil 100 C18 5 μ stainless steel RP-HPLC column thermostated at 30°C, and a Gynkotek HPLC UVD 320S photodiode-array detector. HPLC-grade methanol (100%) was used as the mobile phase at a volumetric flow rate of 0.45 mL min⁻¹. Data acquisition and management were performed with the Gynkosoft chromatography data system installed on a PC.

Head-Space Analysis

A reaction vessel was equipped with a screw cap and an all-Teflon Mininert syringe valve. After reaction, 100 μ L of the gas head was injected on a Fisons Tri 1000-GC8165, equipped with a 5- μ m DB-1 column (30 m \times 0.32 mm) and set up for identification of low molecular weight gases. Spectra were collected in electron impact mode.

Elemental Analysis

Samples were checked for the presence of TMTU by ¹H-NMR. Ensuing analyses for ZnS were performed at the Tun Abdul Razak Research Laboratory, Brickendonbury, United Kingdom. The amount of extracted ZDMC was determined by standard EDTA titration of zinc(II) after careful destruction.

Ion Chromatography

The four samples obtained after chloroform extraction were completely dissolved in concentrated hydrochloric acid. Note that the solutions obtained from samples 1 and 2 displayed more H_2S evolution (as detected by smell) than the solutions obtained from samples 3 and 4. The content of ZnSO_3 and ZnSO_4 in the solutions was determined by ion chromatography using a Dionex AS9 low-capacity anion exchanger. An aqueous solution of 200 mg/L NaHCO₃ and 200 mg/L Na₂CO₃ was used as the mobile phase at a volumetric flow rate of 2 mL min⁻¹, and the (suppressed) conductivity was monitored.

RESULTS AND DISCUSSION

Influence of Adsorbed Water

To examine the stoichiometry of the reaction between ZnO and TMTD, TG analysis was performed on ZnO/TMTD samples. During reaction, volatiles are produced and as a result, the sample mass decreases. The decrease is initially fast but ceases afterward for as long as 10 h. The amount of ZDMC is subsequently determined by means of RP-HPLC, as ZDMC itself is not volatile at the applied reaction temperature of 140°C.

Geyser and McGill¹³ noted that at short reaction times water strongly influences the amount of ZDMC that is formed, and it was proposed that water acts as a catalyst for ZDMC formation.¹³ Therefore, the influence of water on ZDMC production on complete reaction was examined. First, the amount of water adsorbed onto undried ZnO was established by TG at 0.15 wt %. The adsorbed water evaporates while warming up to 140°C, and no additional mass loss occurs upon heating for another 7 h. Also, heating ZnO at 900°C for several hours does not result in any subsequent mass loss. The observed values are in line with Karl–Fischer titration of undried ZnO, revealing the presence of 0.075(5) wt % of water.

From TG experiments performed with Zn(OH)₂ and samples of ZnO to which water was added, it was demonstrated that ZnO reacts readily with H_2O to form $Zn(OH)_2$. Upon heating a ZnO/H_2O mixture, at temperatures around 40°C, it first loses water that is only adsorbed to the $Zn(OH)_2$ surface. Subsequently, Zn(OH)₂ discharges most of its (coordinated) H₂O up to 80°C, furnishing ZnO, after which the mass loss is negligible. Because Zn(OH)₂ dehydrates so readily, it was concluded that at normal vulcanization temperatures, the amount of water coordinated to ZnO must be minimal. More importantly, drying or wetting neither influences the total mass loss from a ZnO/TMTD mixture when it is heated nor the amount of ZDMC that is formed. Because the

dinitrogen, which was used to purge the TG analyzer, also contains 5 ppm of water, in one experiment the dinitrogen was predried by leading it through concentrated sulfuric acid and a phosphorus pentoxide column. Again, the TG curve and the amount of ZDMC were found unaltered. Thus, although H_2O was shown to facilitate the reaction between ZnO and TMTD during warming up¹³ (i.e., while it was not evaporated), for complete reaction, it was not found to be essential.

TG Experiments and RP-HPLC Analysis of ZDMC

Different batches of ZnO and TMTD in molar ratios of 8 : 1, 4 : 1, and 2 : 1 were prepared and heated for 10 h. An excess of ZnO was chosen to determine the stoichiometry in TMTD. After heating, the TG samples were analyzed by RP-HPLC to determine the final ZDMC content.

Direct quantitative determination of the amount of ZDMC and other zinc(II) dithiocarbamate complexes by RP-HPLC is problematic; zinc dithiocarbamates exhibit extensive tailing upon conventional RP-HPLC analysis using C18 columns, attributed to strong interaction with the silica support. It was found that the use of columns with double endcapping effectively eliminates the observed tailing, but the equilibrium between mono- and dinuclear ZDMC in methanol, resulting in a double peak in the HPLC chromatogram, still prevents proper quantification.

To overcome these difficulties, Kaniwa²² devised a method in which zinc dithiocarbamates are transformed into their respective cobalt(III) complexes by reaction with cobalt(II) chloride. Cobalt(III) dithiocarbamate complexes are quantified by RP-HPLC without noticeable problems. Nevertheless, this method has its own drawbacks, as it involves ligand transfer from ZDMC to cobalt(II) and oxidation to cobalt(III). It was reported that when ZDMC is reacted with cobalt(II) in the presence of thiuram compounds such as TMTD and TMTM, an increase of the intensity of the Co(dmtc)₃ signal is observed.²³ In the present study, significant amounts of TMTD and TMTM indeed disappeared after treatment with Co^{II}Cl₂ \cdot H₂O and clearly added to the signal attributed to $Co^{III}(dmtc)_3$. When either TMTD or TMTM is shaken with a Co^{II} solution in methanol, no reaction takes place, eliminating the possibility that Co^{II} and TMTD together act as a redox couple, forming Co^{III}(dmtc)₃. This observation is explained by the fact that in the absence of suitable

ZnO/TMTD Ratio	TMTD Loading (µmol)	ZDMC Formed (µmol)	ZDMC Formed ^a (%)	
8:1	26.20	15.56	59.4	
	28.37	16.74	59.0	
	30.80	17.69	58.4	
4:1	33.03	19.36	58.6	
	37.60	23.83	63.4	
	46.91	18.79	59.9	
2:1	52.54	32.53	61.9	
	61.26	39.69	64.8	
	67.26	42.63	63.4	

Table II ZDMC Formation in ZnO/TMTD TG Samples at 140°C

^a µmol of ZDMC formed versus µmol of TMTD loaded.

complexing agents, oxidation of Co^{II} to Co^{III} is known to be very unfavorable.²⁴ The observed signal increase in the presence of TMTD is therefore attributed to reduction of TMTD by Co^{II} $(\text{dmtc})_2$ or $[\text{Co}^{\text{II}}(\text{dmtc})_3]^-$, obtained after ligand transfer from ZDMC to Co^{II} . When TMTD is not available, $\text{Co}^{\text{II}}(\text{dmtc})_2$ or $[\text{Co}^{\text{II}}(\text{dmtc})_3]^-$ is oxidized by atmospheric dioxygen. It was found that elemental sulfur does not influence the reactions.

Clearly, quantitative determination of zinc dithiocarbamate salts by transforming them into $Co(dmtc)_3$ salts is only viable in the absence of thiuram species such as TMTM and TMTD. For the present study, the TG samples were heated until mass loss ceased, meaning that any unreacted or produced thiuram compound would have evaporated. HPLC analysis immediately after reaction revealed only ZDMC to be present, and for all TG samples, the amount of ZDMC was determined by RP-HPLC. The data are listed in Table II.

Table II shows that the ZDMC yield, irrespective of the initial ZnO : TMTD ratio, always totals approximately 60% (with respect to the amount of TMTD that was loaded). Since some TMTD will have evaporated during reaction, the real yield will be even higher. The current outcome is not readily explained by nucleophilic attack of ZnO onto TMTD, according to the mechanisms in Scheme 1, as it would result in a yield of at most 50 mol %. Thus, in addition, a second, high-yielding route should be operative to explain the observed yield of 60%. Geyser's mechanism (Scheme 2) seems a likely candidate, as it predicts a yield of 100%.¹³ The operation of this mechanism would be proven by the detection of dioxygen. Consequently, the formation of volatile products from the ZnO/TMTD reaction was monitored by

TDAS-GCMS. This resulted in the detection of TMTU, tetramethylurea (TMU), and CS_2 only. COS, dimethylamine, and O_2 were not present in detectable amounts. This result, in particular, the inability to detect COS in this experiment, was unexpected in view of previous work,^{7,8} but might be explained by the fact that the TDAS-GCMS technique is less sensitive to low molecular mass gases, evolving in small amounts only. Thus, detection of gases such as O_2 and COS, as well as of other products than ZDMC, required a different experimental setup.

Characterization of Reaction Products of ZnO/TMTD Reaction

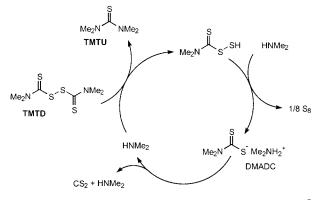
To allow detection of dioxygen, subsequent reactions were carried out in 30-mL closed vessels in argon atmosphere. At the same time, this excludes a possible influence of dioxygen on the reaction. A 2 : 1 mixture of ZnO/TMTD was heated overnight in a closed vessel in argon atmosphere, after which the evolved gases were analyzed by means of GC-MS. Table III lists the observed products. The amount of CS_2 is rather

Table IIIGC-MS Gas-Head Analysis of HeatingZnO/TMTD (2:1) for 16 h in a Closed Vessel^a

Component ^b	Blank Level	Sample Level		
Argon	466	396		
CO_2	< 0.01	9		
COS	< 0.01	198		
CS_2	< 0.01	407		

^a Arbitrary units.

^b No other gases detected.



Scheme 3 HNMe₂-catalyzed degradation of TMTD.²

high, yet it should be realized that sample levels do not relate to relative amounts only, but also reflect the ionizability of a particular compound in the mass spectrometer. The formation of CS_2 from TMTD in closed vessels was explained by (aminecatalyzed) degradation of TMTD as depicted in Scheme 3.² When pure TMTD is treated under similar conditions as the ZnO/TMTD mixtures, it is found, after 16 h at 140°C, to degrade almost quantitatively into TMTU with concomitant evolution of CS_2 , leaving only traces of TMTD.

The GC–MS technique is sufficiently sensitive and selective, to allow the conclusion that COS, CS_2 , and a small amount of CO_2 are the only gaseous products resulting from heating. Production of O_2 and HNMe₂ may thus be ruled out. However, in the presence of CS_2 , the amine may also be present as the ammonium salt DMADC.^{2,25} To characterize nongaseous products such as ZDMC and S₈, the solid residue of the reaction was carefully extracted with chloroform. This extract was analyzed by ¹H-NMR, proving ZDMC and TMTU to be the major compounds present, as well as over 20 other products, among which TMTD and TMU could be clearly identified. DMADC was below the detection limit. The formation of ZDMC and TMTU was additionally corroborated by ¹³C-NMR analysis.

Extraction by means of chloroform leaves an insoluble residue containing unreacted ZnO and potentially other zinc salts. This residue was analyzed for ZnS, ZnSO₃, and ZnSO₄. ZnS was not observed (detection limit, 0.5 wt %). Of the other salts, ZnSO₄ was the only one detected and found in amounts close to 2 wt %. Since detection of ZnSO₄ in ZnO/TMTD reaction mixtures is unprecedented and rather surprising, unreacted ZnO was also checked for the presence of ZnSO₄. This revealed that at most 0.02 wt % of ZnSO₄ is present in ZnO, indicating that the sulfate salt is indeed produced during the ZnO/TMTD reaction and should be regarded with interest.

Quantitative Determination of Reaction Products

To obtain more insight in the quantities of the main reaction products, and as such in the stoichiometry of the reaction, four identical 2:1ZnO/TMTD samples were heated for 16 h in argon in a closed vessel, after which the products were analyzed by NMR and chromatography. By equaling the integral of all signals in the NMR spectrum to the initial molar amount of TMTD loaded, the exact molar amounts could be determined for ZDMC, TMTD, TMTU, and TMU. These quantitative data are listed in Table IV. To validate the approach, ZDMC was also quantified by conventional EDTA titration, which provided ZDMC contents within an average 5.5% margin of the NMR data. Nonidentified products were found to total at most 16%. In addition, the amounts of free

Entry No.	TMTD Loading (µmol)	${ m TMTD^a} \ { m Residual} \ (\mu { m mol})$	ZDMC ^a (µmol)	ZDMC ^b (%)	TMTU ^a (µmol)	TMU ^a (µmol)	${ m S^c}\ (\mu { m mol})$	${ m ZnSO_4}^{ m d}$ (μ mol)	ZDMC ^e (µmol)
1	75.56	6.13	36.05	51.2	20.51	0.90	38.4	1.52	35.24
2	75.56	8.20	30.73	45.6	23.78	0.95	40.3	1.31	34.98
3	73.54	7.21	30.43	45.9	20.69	2.49	25.3	1.79	32.60
4	76.41	7.05	33.43	48.2	20.89	2.44	26.3	1.90	35.05

Table IV Products of Heating ZnO/TMTD (2:1) for 16 h in Argon Atmosphere at 140°C

^{a 1}H-NMR analysis.

 $^{\rm b}\,\mu mol$ ZDMC formed versus μmol TMTD reacted.

^c RP-HPLC analysis as S₈.

^d Ion-chromatography.

^e EDTA titration.

sulfur and $ZnSO_4$ were determined by RP-HPLC and ion chromatography, respectively.

A first striking feature about these experiments, performed in quadruplicate, is the fact that the product quantities display a large variation. For example, the amount of the main product ZDMC, as determined by NMR, varies as much as 20%. This may have to do with the fact that the reaction between ZnO and TMTD does not take place in the homogeneous phase (e.g., in solution), but on the surface of ZnO particles. Nevertheless, the four experiments do give a fair indication of the obtained product yields.

A second interesting feature is the lower ZDMC yield compared to reaction in the TG analyzer. Excluding unreacted TMTD, an average value of only 48% is found in closed vessels, whereas Table II shows values of around 60%. This discrepancy is presumably associated with amine-catalyzed TMTD degradation. It was suggested² that in closed vessels, HNMe₂ catalyzes TMTD breakdown into CS₂ and TMTU according to Scheme 3. The CS₂ that is detected by gas analysis supports this hypothesis.

Finally, an inverse relationship appears between the amounts of TMU and elemental sulfur. More TMU is accompanied by less sulfur. On the other hand, when less sulfur is formed, significantly more ZnSO_4 is obtained. Unfortunately, it is not possible to determine whether these observations are mechanistically relevant.

Summarizing, the above-described results provide closer insight in the products of ZnO/TMTD reaction, yet at the same time point out that this reaction, even under carefully maintained conditions, remains a very complicated system to investigate.

Reactivities of ZnS and TMTM

To obtain information about the reactivity of ZnS and TMTM, possible by-products of the ZnO/ TMTD reaction, ZDMC formation from 2:1 ZnO/ TMTM, and 2:1 ZnS/TMTD samples were investigated by TG. When a ZnO/TMTM mixture was heated until mass loss discontinued, requiring 38 h at 140°C, the sample was shown to contain as much as 30% of ZDMC, relative to the initial amount of TMTM present. This contradicts earlier statements that ZnO and TMTM do not react,^{26,27} but, in view of the long reaction times, it is not excluded that degradation of TMTM would have furnished the required elemental sulfur to produce reactive TMTD. Irrespective of the course of action, the ability of TMTM to yield ZDMC in the presence of ZnO should not be ruled out. Also, ZnS was found to react with TMTD, but the reaction is rather sluggish; when a 2 : 1 ZnS/TMTD mixture is heated at 140°C for 10 h, only about 15 mol % ZDMC is produced.

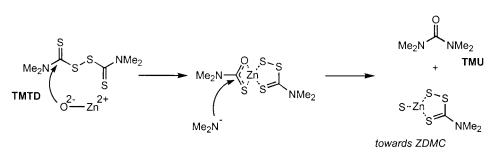
Mechanistic Pathways Toward ZDMC

The present study differs from previous ones as it attempts to quantify the products in the ZnO/ TMTD reaction mixture after complete reaction. This determines the reaction stoichiometry and discriminates between the mechanisms that were proposed for the production of ZDMC during ZnO/ TMTD reaction.

The detection of COS, in conjunction with substantial amounts of TMTU that are observed, again confirms the operation of a mechanism in which ZnO performs a nucleophilic attack onto TMTD (cf. Scheme 1). Contrary to earlier reports,⁷ in the present setup, the reaction between ZnO and TMTD does not result in the production of detectable amounts of dimethylamine or DMADC. In fact, the absence of amines among the products is not unexpected at all, since no suitable proton source is available that could account for the production of amines.

Since TMTU, S₈, and ZDMC are the products of nucleophilic reaction [eq. (1)], the average amount of TMTU detected in the reaction mixtures is indicative for the share of ZDMC that is formed via nucleophilic attack. This was established at 66%, (i.e., the average amount TMTU formed divided by the average amount of ZDMC present). Interestingly, in addition to TMTU, small quantities of TMU are produced. TMU is not observed when TMTU and ZnO are heated together, nor on heating TMTD as such. This suggests that TMU somehow forms in a step following a nucleophilic attack of ZnO onto TMTD. A possible explanation is visualized in Scheme 4, which depicts a nucleophilic attack of a dimethylamide ion on Zn(dmmc). The amount of TMU, therefore, adds another, average, 5% to the total share of ZDMC formed via the nucleophilic reaction.

A nucleophilic attack thus explains at most 70% of the ZDMC that is found, provided that (amine-catalyzed) degradation of TMTD is negligible. The amount of S_8 that is detected correlates reasonably with this figure. Nevertheless, this leaves unexplained at least 30% of the ZDMC that is produced. Radical oxidation of H_2O at the ZnO surface seemed likely,¹³ but had to be rejected in



Scheme 4 Possible mechanism for the formation of TMU from ZnO and TMTD (Me_2N^- is produced in the first steps of the reaction, see Scheme 1).

view of the inability to detect dioxygen among the reaction products (*vide supra*). A second alternative would be the reaction of ZnS with TMTD (Scheme 5). This reaction is similar to the reaction of ZnO with TMTD, but no COS is produced.

As discussed above, the reaction between ZnS and TMTD is slow and yields only 15% of ZDMC. The fact that, after ZnO/TMTD reaction, the insoluble remainder does not contain detectable ZnS, constitutes strong evidence against formation of ZnS and subsequent reaction with TMTD. In an environment where ZnO is in large excess, TMTD will react with ZnO rather than with ZnS. It is, therefore, concluded that direct reaction between ZnS and TMTD does not contribute significantly to ZDMC formation.

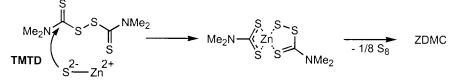
Interestingly, the chloroform-insoluble ZnO/ TMTD residue was consistently found to contain as much as 2 wt % of ZnSO₄. Since the reaction was performed in inert atmosphere, the oxidation of elemental sulfur by atmospheric dioxygen could be excluded, and instead ZnO must be the source for ZnSO₄. In view of this, the redox reaction of Scheme 6 is proposed, in which TMTD acts as the oxidant. The observation of this redox reaction is unprecedented, yet provides an intriguing additional route by which ZDMC may be produced during ZnO/TMTD reaction. The amounts of ZnSO₄ established account for as much as 15% of the ZDMC produced. It is not excluded that this value may increase in the presence of additional S₈.

Although Kawaoka⁷ mentioned the production of ZnSO₃ during ZnO/TMTD reaction, ZnSO₃ is not observed in the present case. Also, SO_2 is not identified among the gaseous reaction products, yet $ZnSO_3$ and SO_2 must be intermediate products toward $ZnSO_4$. This suggests that such species, once formed, are rapidly transformed into $ZnSO_4$. It may be speculated that in ambient atmosphere, where dioxygen might bring about oxidation of elemental sulfur to SO_2 , the share of this reaction may even be higher.

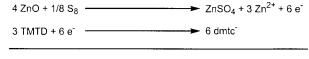
In summary, nucleophilic attack and sulfur oxidation explain about 85% of the ZDMC found in these experiments, leaving 15% unaccounted for. This is probably explained by the 15% of unidentified products that were shown to be present by NMR. Although further characterization of these products and the related mechanistic routes is desirable, the present investigation established the mechanistic origin of the larger part of ZDMC produced as a result of two reactions between ZnO and TMTD.

CONCLUSIONS

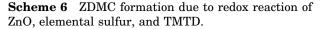
The reaction between ZnO and TMTD posed many scientific problems, and it is rather surprising that this important and seemingly simple transformation always evaded (and still does) proper understanding. The current paper reports the first detailed investigation of the stoichiometry of the ZnO/TMTD reaction. Two routes furnishing ZDMC from ZnO and TMTD were estab-



Scheme 5 Formation of ZDMC from ZnS and TMTD.







lished. The traditionally-proposed nucleophilic attack of ZnO on TMTD was corroborated by GC-MS detection of COS and ¹H-NMR identification of TMTU. Together with TMU, and neglecting possible TMTD degradation for which CS_2 detection is indicative, this reaction accounts for about 70% of the ZDMC obtained after reaction. Reduction of TMTD by H₂O on the ZnO surface was excluded in view of the absence of dioxygen in the gas mixture produced upon reaction. The detection of ZnSO₄ suggests that a redox reaction of ZnO, elemental sulfur, and TMTD accounts for about 15 mol % of the ZDMC observed. Thus, although 15% still remains unaccounted for, most of the ZDMC produced was now explained by nucleophilic attack of ZnO on TMTD and a unique and previously unrecognized redox reaction.

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