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The Mechanism of Zinc(II)-Dithiocarbamate-Accelerated Vulcanization Uncovered; Theoretical and Experimental Evidence

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Abstract: The mechanism of cross-link formation in sulfur vulcanization mediated by bis(dimethyldithiocarbamato)zinc(II), ZDMC, has been uncovered, utilizing a combination of Density-Functional calculations and model experiments. These studies have revealed that, in a three-stage process, ZDMC exhibits a unique combination of catalytic activity: (1) It mediates the reaction between sulfur and rubber. This is achieved by incorporating sulfur atoms in the zinc-dithiocarbamate ring and inducing their insertion into an allylic C–H bond via an ene-like reaction. This ene reaction yields a rubber-bound polythiothiol and is only slightly endothermic, even though an activation energy of $\sim 90 \text{ kJ mol}^{-1}$ is required. (2) The resulting polythiothiols engage in equilibrated metathesis reactions to yield polysulfides, the initial sulfur cross-links. (3) In a hitherto unsuspected mechanistic step ZDMC has been found to shift the metathesis equilibrium to the side of cross-links by mediating desulfhydration of the polythiothiols, producing sulfides and H_2S . Thus, the combined results of theoretical and experimental work have allowed to put forward a novel mechanism for ZDMC-mediated sulfur cross-link formation that successively comprises (a) homogeneous catalysis of thiol formation from sulfur and rubber, (b) an equilibrium between polythiothiol intermediates and cross-links and (c) ZDMC-induced desulfhydration.

Introduction

Accelerated sulfur vulcanization is the key technology of an industry that prepares a wide range of useful rubber materials. The vulcanization process involves heating a mixture of sulfur, an *accelerator*, and a polymer containing unsaturation. This results in the formation of sulfur bridges or *cross-links* between polymer molecules (Scheme 1),^{1,2} which account for the rubber's elasticity and durability.

The particular properties of a vulcanized rubber are, among others, determined by the type of accelerator, of which there are many.³ They may be divided into purely organic accelerators, such as tetramethylthiuram disulfide (TMTD), and metal-based accelerators, of which bis(dimethyldithiocarbamato)zinc(II) (ZDMC) is the most important representative. Both types are interlinked because TMTD-accelerated vulcanization is often "activated" by ZnO, which results in the gradual formation of ZDMC during the course of vulcanization.² Both organic and metal-based accelerators produce sulfur cross-links, with the organic accelerators being mechanistically better understood. For example, in the case of TMTD-accelerated vulcanization it is well-known that cross-links become attached to the rubber as a result of reaction of a TMTD-based sulfurating agent with an allylic moiety (Scheme 1).^{1,2} This yields cross-link precur-

sors which, in turn, transform into sulfur cross-links.^{2,4} Similar schemes have been adopted to explain cross-link formation in ZDMC-accelerated sulfur vulcanization, even though evidence in this direction is incomplete and indirect.² Thus, the action of ZDMC has traditionally been thought to involve the formation of a *polythiocarbamato–zinc(II) complex* that reacts in a concerted fashion with rubber according to Scheme 2.¹

The involvement of polythiocarbamato–zinc complexes in vulcanization has been suggested as early as 1921,^{5,6} but only recently were we able to actually prove the existence of polythiocarbamato–zinc complexes.⁷ It has been established that sulfuration of ZDMC by two sulfur atoms, to yield bis-(trithiocarbamato)zinc(II), (3/3) ZDMC, is thermodynamically comparable to insertion of two sulfur atoms into bis(phenyldithiolato)zinc(II), yielding bis(phenyltrithiolato)zinc(II).⁷ The latter compound is stable at room temperature.⁸ Interestingly, nonsymmetric insertion of two sulfur atoms, providing (dithiocarbamato)(tetraethiocarbamato)zinc(II), (2/4) ZDMC, appeared to be slightly ($\sim 10 \text{ kJ mol}^{-1}$) more favorable than symmetric insertion (Scheme 3).⁷

Despite these encouraging findings, cross-link formation via polythio–zinc species has remained ill-understood. For example, the reaction proposed in Scheme 2 would seem feasible, as it

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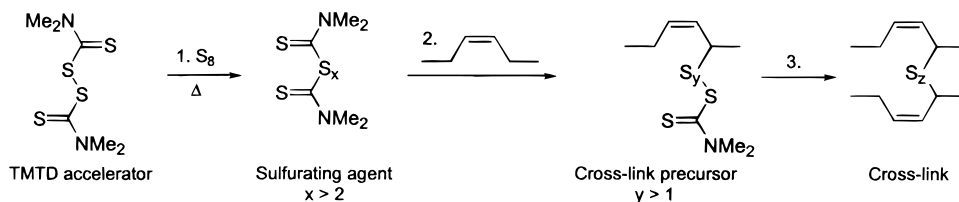
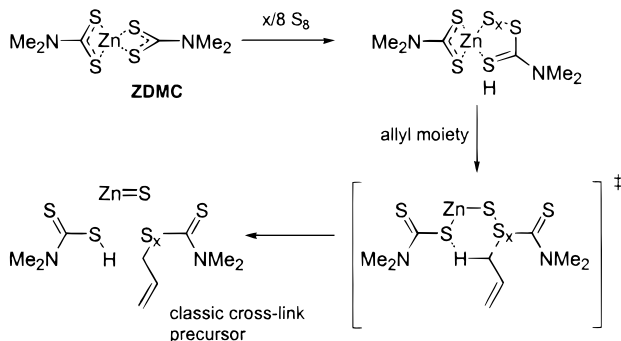
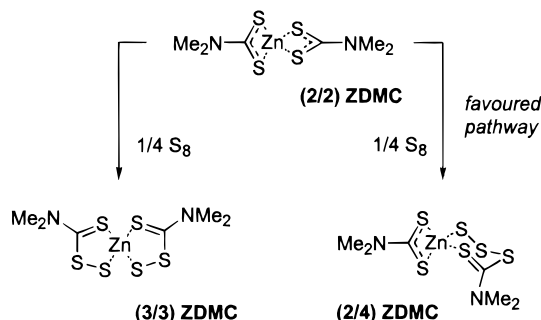
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Scheme 1. General Course of Tetramethylthiuram-Disulfide-Accelerated Sulfur Vulcanization^{1,2}**Scheme 2.** Inferred Formation of a Polythiocarbamate–Zinc Complex from ZDMC and Elemental Sulfur and Subsequent Reaction with Rubber¹**Scheme 3.** Modes of Sulfur Insertion into (2/2) ZDMC⁷

accounts for the production of TMTD-like cross-link precursors. It is known that such species disproportionate to yield sulfur cross-links, as well as thiuram sulfides.⁴ Nevertheless, this reaction path toward cross-links should be regarded with some hesitation, since these thiuram sulfides have not been observed in ZDMC-accelerated vulcanization. Furthermore, while Scheme 2 does account for ZnS formation, which is characteristic for this system, it cannot explain the equally important evolution of H_2S .⁹

To shed more light on this matter, and in view of the successful elucidation of the thermodynamics governing sulfuration of ZDMC,⁷ we have conducted an in-depth examination of the interaction between polythio-zinc and rubber by means of Density-Functional calculations. The present paper describes how state-of-the-art quantumchemical techniques were applied to investigate the reaction of a tetrathiocarbamate–zinc complex with propene, utilized as the model for the allylic moiety present in rubber. Subsequent model experiments provided additional insight, as a result of which the mechanism of ZDMC-accelerated sulfur vulcanization could be uncovered.

Experimental Section

Density-Functional Calculations. The calculations were carried out with use of the Amsterdam-Density-Functional (ADF) program

developed by Baerends *et al.*¹⁰ The MOs were expanded in an uncontracted set of Slater-type orbitals (STOs) containing diffuse functions. The basis sets of the main group atoms are of double- ζ quality and has been augmented with one set of polarization functions on each element (2p on H, 3d on C, N, S).^{11,12} The zinc basis set is of triple- ζ quality and has been augmented with a 4p polarization function. The 1s core shell of carbon and nitrogen and the 1s2s2p core shells of zinc and sulfur were treated by the frozen-core (FC) approximation.¹³ An auxiliary set of s, p, d, f, and g STOs, centered on all nuclei, was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle.¹⁴ The numerical integration was done with use of the scheme developed by te Velde *et al.*¹⁵ All calculations were performed at the NL-SCF level, using the local density approximation (LDA) in the Vosko-Wilk-Nusair parametrization¹⁶ with nonlocal corrections for exchange (Becke88)¹⁷ and correlation (Perdew86).¹⁸ Geometries were optimized by using the analytical gradient method implemented by Versluis¹⁹ and Ziegler.²⁰

Reactivity of 2,3-Dimethyl-2-butenethiol. All experiments were carried out in argon atmosphere—using standard Schlenk techniques—in 30 mL tailor-made Schlenk-type reaction vessels, equipped with Teflon valves, screw caps having Teflon inserts, and a magnetic stirrer bar. 2,3-Dimethyl-2-butene-1-thiol²¹ (~0.75 mmol) was added to 2.00 mL of *n*-hexane (Baker, p.A.), the mixture was stirred, and a 50 μL aliquot was taken. To this were added either S_8 (~0.18 mmol) or ZDMC (~0.33 mmol), or both, and the mixture was stirred for 1 h at room temperature. Another 50 μL aliquot was taken, after which the valve was closed and the vessel was partly immersed in a thermostated oil bath of large volume, set at 140 $^\circ\text{C}$. After 10 min the vessel was taken out of the oil bath and the reaction was stopped by immediate cooling with liquid dinitrogen. When the vessel had reached room temperature a final sample was taken. All 50 μL aliquots were diluted with methanol to 5.00 mL, transferred to 1.5 mL plastic reaction tubes, and analyzed by means of Reversed-Phase HPLC. These analyses were performed 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 μL loop, an Alltech Nucleosil 100 C18 5 μm stainless steel RP-HPLC column thermostated at 30 $^\circ\text{C}$, and a Gynkotek HPLC UVD 320S photodiode-array detector. 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 Gynkosoftware chromatography data system installed on a PC. Products were identified by comparison of their RP-HPLC retention times and real-time UV spectra (200–356 nm) with reference compounds that

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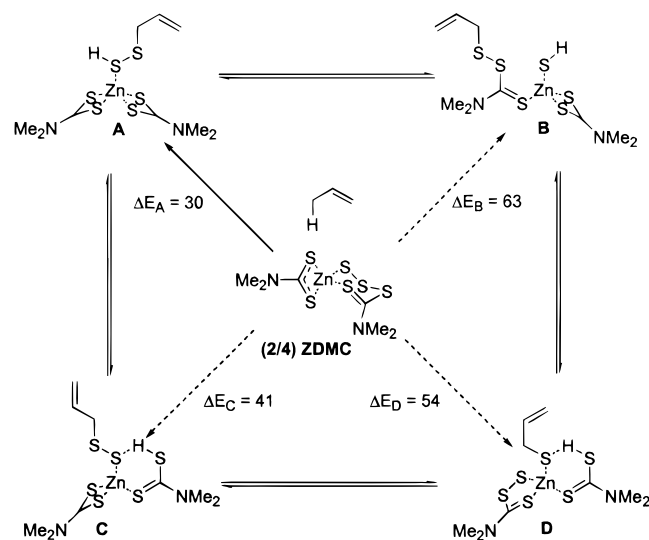
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Scheme 4. DF-Calculated Products **A–D** Resulting from the Reaction of Sulfurated (2/4) ZDMC with Propene (E in kJ mol⁻¹)

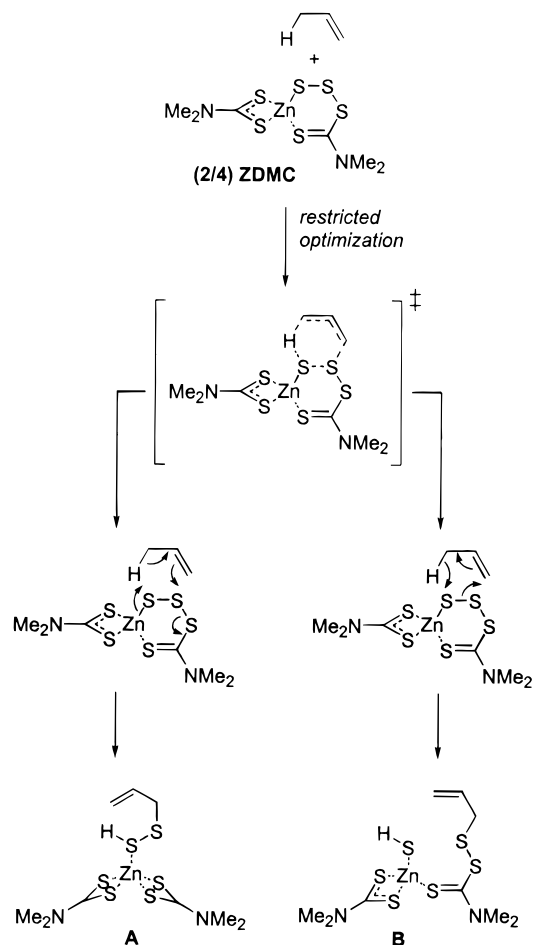
were obtained by standard ZDMC-accelerated sulfur vulcanization of the model olefin 2,3-dimethyl-2-butene.^{22,23}

Density-Functional-Calculation Results

1. Sulfuration of Rubber by Polythiocarbamate–Zinc(II) Complexes. To investigate the reaction of allylic moieties (i.e. the reactive moieties present in unvulcanized rubber) with polythiocarbamate–zinc complexes, the nonsymmetric disulfurated complex (2/4) ZDMC was chosen, since the formation of this complex is thermodynamically favored over its symmetric analogue, (3/3) ZDMC.⁷ Because quantumchemical calculations cannot cope with very large molecules such as rubber, propene was chosen as a small model. This compound does contain the essential rubber features, namely a double bond and an allylic position, but it should be realized that it cannot sufficiently account for conformational restraints which are normally encountered in polymeric systems.

The present quantumchemical study of the reaction of propene with (2/4) ZDMC was carried out by exploring possible courses of the reaction, starting from a number of relevant initial structures and carrying out constrained and unconstrained geometry optimizations. By doing so, four likely and energetically feasible reaction products **A–D** were identified and are displayed in Scheme 4. As will appear, the essential aspects that govern the chemistry of ZDMC-mediated sulfur vulcanization are adequately described by these four products.

2. Reaction of (2/4) ZDMC with Propene. Traditionally it has been assumed that TMTD-like precursors also form in ZDMC-accelerated sulfur vulcanization, according to Scheme 2, even though they have not been observed. The first approach was therefore to attempt to react propene with (2/4) ZDMC and induce formation of a TMTD-like cross-link precursor.² However, reaction according to Scheme 2 was not feasible: to attain the required transition state, zinc has to go from a regular four-coordinated situation to an unlikely coordinatively unsaturated situation (2 coordination). As a result, this reaction path is energetically unfavorable. The only reaction pathway in which a TMTD-like cross-link precursor arises is the one in which

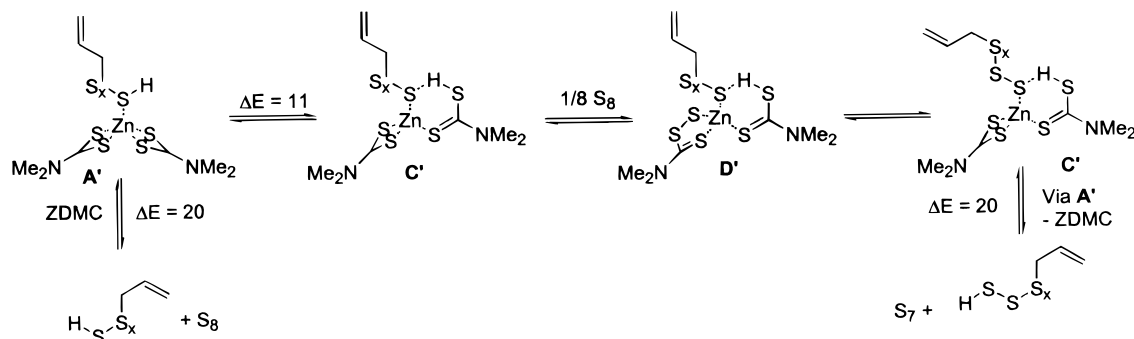
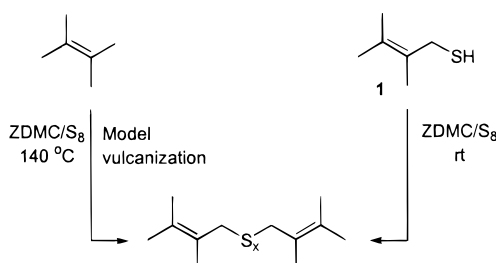
Scheme 5. Transition States for the Formation of Intermediate **A** and **B** from Propene and (2/4) ZDMC

(2/4) ZDMC and propene react according to an ene-like reaction, resulting in intermediate **B**, in which the TMTD-like cross-link precursor is coordinated to zinc(II) (Scheme 5). This structure was calculated to have an energy of 63 kJ mol⁻¹ relative to (2/4) ZDMC and propene. Due to the large number of degrees of freedom in this system it was not practically feasible to calculate the height of the activation barrier of the ene-like reaction by a full transition state search. Instead, an activation barrier of about 90 kJ mol⁻¹ could be estimated by partial and manual optimization of plausible structures for the transition state. At common vulcanization temperatures of 140 °C such a barrier is certainly surmountable.

Interestingly, going downhill in completely unconstrained geometry optimization from a structures close to the transition-state region does not result in intermediate **B**. Instead, an allylic hydrogen atom is transferred to sulfur with concomitant double-bond rearrangement and addition of sulfur. At the same time the regenerated dithiocarbamate ligand resumes its original position (Scheme 5). The net effect is insertion of two sulfur atoms in an allylic C–H bond with double-bond isomerization, providing intermediate **A** (Scheme 4, solid arrow). This intermediate consists of a perthiol coordinated to ZDMC and has an energy relative to (2/4) ZDMC of only 30 kJ mol⁻¹. The formation of a coordinated perthiol is striking, since such species are not known to be produced during vulcanization. Although intermediate **A** is a stable complex, it was calculated that dissociation of the allylic perthiol, which regenerates the catalyst, is exothermic by 20 kJ mol⁻¹. This is explained in part by a relatively weak coordinative bond between ZDMC and perthiol, which requires a small dissociation only. In

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Scheme 6. Proposed Mechanism of ZDMC-Catalyzed Polythiothiol (De)sulfuration (E in kJ mol^{-1})**Scheme 7.** Formation of Bis(2,3-dimethyl-2-buten-1-yl) Polysulfides by Vulcanization of 2,3-Dimethyl-2-butene²³ or by Room Temperature Reaction of 2,3-Dimethyl-2-buten-1-thiol in the Presence of ZDMC and Sulfur

addition, the catalyst can lower its energy, upon dissociation of the perthiol, by a favorable reconfiguration from a pyramidal to a distorted tetrahedral configuration sphere around zinc. Due to the exothermic dissociation of the perthiol, the whole process of sulfuration of an allylic moiety by (2/4) ZDMC is endothermic by a negligible 10 kJ mol^{-1} .

Because dithiocarbamic acid, in the form of dimethylammonium dithiocarbamate, is a (side-) product of ZDMC/sulfur vulcanization,²³ intermediates **C** and **D** were constructed. In these complexes the proton is bound to one of the dithiocarbamate ligands (Scheme 4). Dissociation would explain the formation of dithiocarbamic acid in ZDMC/sulfur vulcanization. The energies of intermediates **C** and **D** were found to lie between those of **A** and **B**, namely 41 and 54 kJ mol^{-1} , respectively. In view of this, the high relative energy of **B** is striking, but may be explained by the absence of hydrogen bridging as observed in **C** and **D**. Geometry optimization of a structure analogous to **B**, but in which an intramolecular hydrogen bond was induced by directing the hydrogen atom of hydrogen sulfide toward the coordinated cross-link precursor, also gave intermediate **B** as the lowest-energy conformation, thus showing that a hydrogen bond is energetically unfavorable.

Intermediates **A–D** have been obtained from computer-simulated reactions of propene with disulfurated (2/4) ZDMC, but it is reasonable to assume that the results will be similar in case more sulfur atoms are incorporated in the zinc–dithiocarbamate ring. Thus, polythiocarbamate–zinc will react with propene to yield a (polythio)thiol as the preferred product.

Polythiothiols may also be formed from perthiols via a different pathway, which does involve ZDMC in the form of intermediates (analogous to **A**, **C**, and **D**). This is shown in Scheme 6. After coordination of the thiol to ZDMC, conversion into intermediate **C'** may occur, in which the hydrogen atom is bound to a dithiocarbamate ligand. Elemental sulfur may subsequently be incorporated as in intermediate **D'**, after which it can be inserted into the zinc–thiol(ate) bond. Ensuing

dissociation yields a polythiothiol that is enriched with one sulfur atom. The interconversion of the intermediates requires only small structural changes, which, according to Hammond's postulate,²⁴ infer only small activation-energy barriers. The number of sulfur atoms ultimately present is determined by the relative energies of a sulfur atom in elemental sulfur and in a polythiothiol.

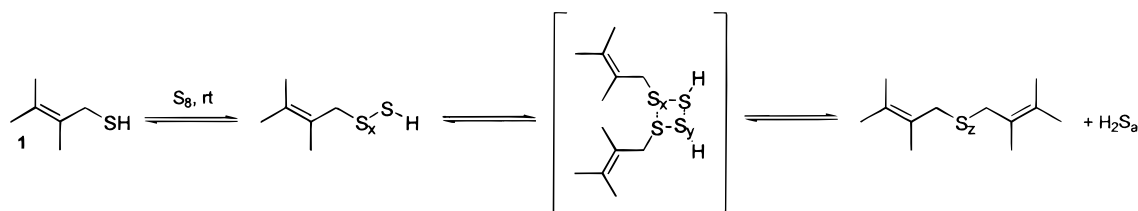
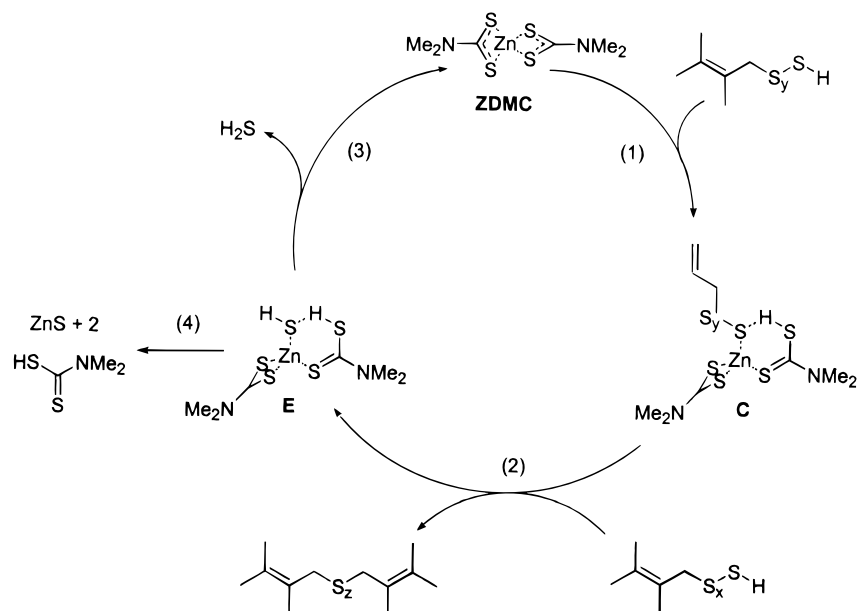
In conclusion, the reaction of propene with (2/4) ZDMC yields intermediate **A** as the preferred initial product. The transition-state energy barrier toward **A** amounts to $\sim 90 \text{ kJ mol}^{-1}$, whereas dissociation of a perthiol yields 20 kJ mol^{-1} . In addition, three other intermediates **B–D** were constructed, in view of their potential involvement in the cross-linking process brought about by ZDMC. The DF-calculated reaction energies of each of the products firmly suggest that (polythio)thiols are intermediates in cross-link formation. However, as such these results explain neither the formation of cross-links, ZnS, and dithiocarbamic acid nor the evolution of H_2S . These products are obtained when (a model for) rubber is vulcanized with ZDMC and sulfur.²³ A reaction mechanism involving the production of TMTD-like cross-link precursors, through intermediate **B**, may still be envisaged, but the finding that this reaction path requires substantially higher energies is a strong argument against its involvement. Moreover, the fact that so far thiuram sulfides have not been detected among the products of ZDMC-accelerated vulcanization⁴ constitutes evidence against TMTD-like cross-link precursors and in that sense corroborates the present quantumchemical findings. Thus a cross-linking mechanism appears to be operative which involves polythiothiols as cross-link intermediates. To confirm this hypothesis, as well as to examine how polythiothiols may be transformed into cross-links, the reactions of allylic thiols in the presence of sulfur and ZDMC were investigated experimentally.

Results of Model Experiments

1. Reactivity of Allylic Thiols. To test the suggestion that during some stage of ZDMC-mediated vulcanization free per- or polythiothiols are produced, it was crucial to prepare polythiothiols of various sulfur ranks under controlled conditions. Standard procedures are not available, but given the nucleophilicity of thiols,²⁵ and the fact that many nucleophiles yield polysulfur species when reacted with elemental sulfur, it was anticipated that polythiothiols would be obtained upon reaction of elemental sulfur with a suitable thiol. For this purpose 2,3-dimethyl-2-butenethiol **1** was used, since possible polysulfidic products derived from **1** would be similar to the model cross-links that are reported to form upon regular

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Scheme 8. Formation of Polysulfides from Polythiothiols via Metathesis Reactions ($z = x + y + 1$)**Scheme 9.** ZDMC-Mediated Cross-Link Formation and Catalyst Degradation ($z = x + y + 1$)

vulcanization of 2,3-dimethyl-2-butene (Scheme 7),²³ allowing easy comparison.

Reaction of **1** with ZDMC in *n*-hexane left the thiol unaffected, showing that an unsulfurated thiol is not reactive. Instead, stirring the thiol **1** with S₈ in *n*-hexane at room temperature, but in the absence of ZDMC, resulted in smooth formation of polysulfidic analogues of **1**, i.e. in model cross-links having sulfur rank 3–9. The RP-HPLC chromatogram obtained from this reaction mixture displays the same products as those produced upon standard vulcanization of 2,3-dimethyl-2-butene (DMB),²³ except that in addition some unreacted **1** is present. Although the formation of polysulfides may initially seem surprising, it is readily explained by (a) reaction of nucleophilic thiol with elemental sulfur yielding polythiothiols and (b) metathesis reactions between polythiothiols. Since all reactions were carried out in an argon atmosphere, a pathway involving the oxidation of thiols could safely be excluded. The metathesis reaction is accompanied by production of polysulfanes H₂S_x,²⁶ but not by H₂S formation. Similar transformations occur when cross-links are produced from TMTD-model cross-link precursors.⁴

Quite surprisingly, the seemingly simple reactions of Scheme 8 are not well documented at all, although in some of the older literature an analogous reaction is mentioned in which potassium thiolates react with sulfur to yield alkyl disulfides and potassium (poly)sulfides.²⁷ Also, heating alkyl-perthiols and alkyltrithiols has been reported to yield polysulfides,²⁸ but here polysulfide formation is accompanied by evolution of hydrogen sulfide. Irrespective of the precise mechanistic details, the

formation of polysulfides—model cross-links—from thiol **1** and elemental sulfur is unambiguous and essential for a proper evaluation of the vulcanization mechanism under investigation. This result is in good agreement with the Density-Functional calculations, which had indicated that polythiothiols are cross-link intermediates in ZDMC-mediated vulcanization. Moreover it reveals that heating is only necessary to overcome the activation-energy barrier of approximately 90 kJ mol⁻¹, required for sulfur insertion. After formation of the polythiothiols, cross-linking proceeds readily and smoothly.

2. Catalyzed Desulfhydration of Polythiothiols. Interestingly, the production of cross-links from **1** and elemental sulfur in the absence of ZDMC is not accompanied by evolution of H₂S. This is readily deduced from the absence of a characteristic smell. H₂S is not even observed when the mixture is heated for 10 min at 140 °C, a common vulcanization temperature. This observation contrasts with previous work done on polythiothiols,²⁸ but may be attributed to the sole operation of metathesis reactions, which do not result in H₂S evolution. The operation of metathesis reactions without H₂S formation implies that an equilibrium exists between **1** and polythio **1** on one side, and polysulfides, as well as polysulfanes, H₂S_n, on the other. The presence of unreacted **1**, as well as the fact that the ratio between **1** and polysulfides does not change in time, and even not upon heating, endorses this assumption. In contrast, in standard (model) vulcanization experiments thiols are not observed and H₂S is prominent.²³ In such experiments ZDMC is present, suggesting that this complex is involved not only in the initial production of polythiothiols but also in their subsequent transformation into polysulfides, during which H₂S is emitted. Indeed, addition of ZDMC to a mixture of **1** and polysulfides, followed by heating at 140 °C for as short as 10

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min, resulted in unambiguous evolution of H_2S , whereas complete depletion of **1** was observed. Since zinc(II) does not readily change its oxidation state, it is highly unlikely that radical reactions would account for the observed formation of polysulfides and H_2S . Instead, the type of activity exhibited by ZDMC in this reaction is strikingly similar to that displayed by the enzyme *cysteine desulfhydrase*,²⁹ which catabolyses (per)thiols by transforming them into disulfides and H_2S . In a similar fashion ZDMC apparently effects desulfhydration of polythiothiols, and by doing so it draws the thiol–polysulfide equilibrium to completion. Thus, ZDMC may be regarded as a homogeneous catalyst for the production of polysulfides and H_2S .

The desulfhydration reaction was furthermore found to be accompanied by extensive production of dimethylammonium dithiocarbamate, indicative of formation of dithiocarbamic acid. This latter observation is of interest, since it indicates that ZDMC does not induce desulfhydration by simply acting as a Lewis acid or base, but that the action takes place within the coordination sphere of zinc(II) and involves the ZDMC ligands. A catalytic cycle explaining the observations can now be put forward (Scheme 9).

It is proposed that in step (1) ZDMC and a polythiothiol combine to form intermediate **C**. In this intermediate, the polythiothiol is rendered more nucleophilic by labilization of the S–H bond through interaction with one of the dithiocarbamate ligands. This allows the polythiothiolate in intermediate **C** to react efficiently with a second polythiothiol in step (2) of the cycle, yielding a polysulfide, and a new intermediate, **E**, which formally has H_2S coordinated to zinc(II). The catalyst is reformed in step (3) by expelling H_2S , thus completing the catalytic cycle. However, intermediate **E** may also degrade according to step (4), which would explain the formation of ZnS and dithiocarbamic acid during the desulfhydration reaction. The degradation is likely to be heat induced. Early observations that ZDMC decomposes into ZnS in the presence of H_2S provide further evidence for the involvement of intermediate **E** in desulfhydration.^{6,30}

In conclusion, the present experiments show that ZDMC may bring about transformation of polythiothiols into polysulfides by catalyzing their desulfhydration. Efficient desulfhydration activity involves reformation of the catalyst with concomitant evolution of H_2S , but undesired degradation into ZnS and dithiocarbamic acid may occur as well. This indicates that, in contrast to what has been assumed traditionally (Scheme 1), ZnS is not the inevitable byproduct of precursor formation, but rather the result of a derailment of catalytic (desulfhydration) activity. In fact, this insight now allows, for the first time, for

the screening of vulcanization catalysts for this undesired characteristic, as well as for the development of vulcanization catalysts with better performance.

Discussion and Conclusions

The theoretical and experimental studies reported in the current paper have provided unprecedented and detailed new insight into the reactions governing ZDMC-accelerated sulfur vulcanization. These reactions differ substantially from those observed in the case of organic accelerators, such as TMTD, and a new mechanism for cross-link formation during ZDMC-accelerated sulfur vulcanization has been proposed. Three discrete mechanistic stages may be distinguished, each in agreement with all presently available observations. The first step in ZDMC-accelerated vulcanization is sulfuration of the rubber backbone. ZDMC incorporates sulfur atoms in the zinc–dithiocarbamate ring and brings about their insertion into an allylic C–H bond. The resulting polythiothiols may be regarded as cross-link intermediates, which, in a second step of the cross-linking mechanism, readily yield polysulfides, i.e. cross-links, via metathesis reactions. The metathesis reactions are, however, equilibria which are not drawn to completion other than by ZDMC; in the third and final stage of vulcanization ZDMC induces H_2S formation, by inducing desulfhydration of polythiothiols. Overall, this study constitutes an exceptional case in which a theoretical study first hinted at the operation of a mechanism that had not been conceived before, whereas ensuing experimental work provided the additional evidence that allowed a new and improved mechanism to be put forward in which ZDMC acts as a “true” two-way homogeneous catalyst for cross-link formation.

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