Zinc(II)-Catalyzed Disproportionation in Rubber: The Mechanism of Sulfur Vulcanization Revisited

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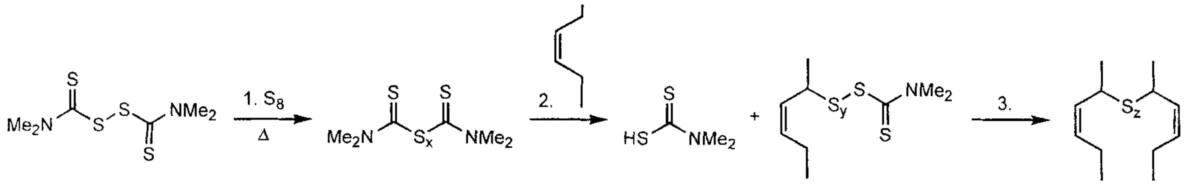
Abstract: Model studies have shown that cross-link precursors, that is, intermediates in the sulfur vulcanization of rubber, are transformed into cross-links by a nonsymmetric but regioselective disproportionation mechanism. Thus, two equivalents of the cross-link precursor of the type R–S–S–X are transformed into X–S–X and the actual cross-link R–S–S–S–R. Exchange of sulfur atoms is a prerequisite. A mechanism involving an S_Ni' reaction with an allylic moiety, suggested in the literature, has not been observed. The disproportionation reaction is catalyzed by rubber-soluble zinc–dithiocarbamate complexes, an important class of vulcanization accelerators. By virtue of ligand–functional-group exchange reactions these complexes serve to transport and exchange sulfur atoms.

Keywords

disproportionations · dithiocarbamate · homogeneous catalysis · vulcanization · zinc

Introduction

Sulfur vulcanization of rubber is the primary industrial process for the production of a large range of consumer and other products. Of these, rubber tires are the most important and well-known example. In general, vulcanization involves the heating of mixtures of sulfur, accelerators, and a polymer containing unsaturation.[1, 2] It is firmly established that this leads to the formation of sulfur bridges between rubber polymer molecules, so-called cross-links, which account for the elasticity and strength of the rubber. The cross-links are attached to allylic positions of the polymer and are formed according to the simplified route depicted in Scheme 1.[3]



Scheme 1. Generalized scheme for sulfur vulcanization accelerated by tetramethylthiuram disulfide (TMTD), adapted after Morrison and Porter [3].

Accelerated sulfur vulcanization is, however, a complex (physico)chemical process. It is not surprising, therefore, that important aspects of the chemistry of sulfur vulcanization are still not understood, despite extensive research efforts and large-scale industrial application over more than 60 years. One such matter concerns the transformation of cross-link precursors into cross-links, step 3 of Scheme 1. Cross-link precursors consist of a sulfur chain attached to a polymer molecule and are terminated by an accelerator residue, a dithiocarbamoyl group in the case of TMTD-accelerated vulcanization.[4] Despite considerable research effort,[5–9] it has remained unclear by what mechanism these precursors are transformed into cross-links. Consensus, however, has evolved[10, 11] that cross-links form either by disproportionation or by reaction of a precursor with the allylic moiety of a second polymer molecule (Scheme 2). The latter involves an S_Ni' reaction in which a hydrogen atom is removed with concomitant isomerization of a double bond of the substrate.[7] Until now neither of these mechanisms could be excluded or proven. This can be attributed to a plethora of difficulties, such as the incompatibility of conventional analytical techniques and vulcanized materials, and the low concentration of reactants and products during vulcanization. Moreover, in many studies the possibility that competing routes complicate

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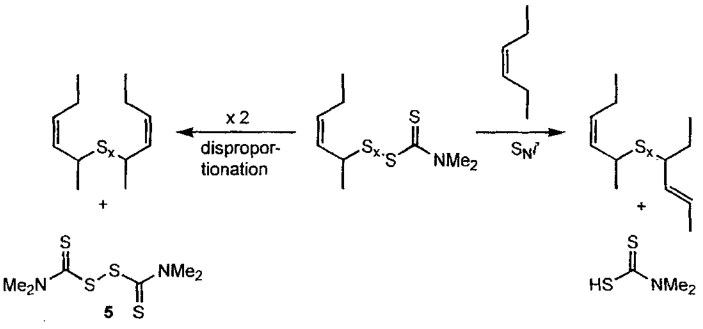


Scheme 2. Suggested mechanisms for cross-link formation from precursors.

the picture could not be excluded. Recently, McGill et al.[12] observed that for certain vulcanization recipes in which no zinc(II) is present, cross-link precursors are first deactivated and subsequently reactivated to yield a different type of precursor, apparently to react with an original precursor to form a cross-link. This route has been established in addition to the proposed disproportionation or S_Ni' pathways.

An important method for the study of vulcanization concerns Model Compound Vulcanization, that is, vulcanization experiments in which a low molecular weight olefin is substituted for the rubber polymer.[13] Model Compound Vulcanization is especially suited for studying the vulcanization process, because the overall course of reaction is similar to that of real vulcanization experiments. More important, reactants, intermediates, and products are easily detected and studied. The degree of insight can even be improved by considering only one mechanistic step at a time. This approach, which we call Reaction Stage Modeling, is described in this paper for the stage of cross-link formation.

The present study employs synthetic models for cross-link precursors, of which the reactivity is studied under well-defined and controlled conditions. We now prove for the first time that cross-links are formed as a result of nonsymmetric regioselective disproportionation. These reactions are catalyzed by rubber-soluble zinc(II) complexes; this provides unique and unprecedented evidence that homogeneous catalysis plays an important role in rubber vulcanization.

Abstract in Dutch: *Model studies hebben aangetoond dat crosslink precursors, tussenproducten tijdens de zwavelvulkanisatie van rubber, worden omgezet in daadwerkelijke crosslinks via een niet-symmetrisch, doch regioselectief disproportioneringsmechanisme. Hierbij worden 2 equivalenten crosslink precursor van het type R–S–S–X omgezet in enerzijds X–S–X en anderzijds een crosslink R–S–S–S–R. Er vindt dus een uitwisseling van zwavelatomen plaats. Een mechanisme waarbij een S_Ni' reactie met een allylische functionaliteit is betrokken, gesuggereerd in de literatuur, is niet waargenomen. De disproportioneringsreactie blijkt te worden gekatalyseerd door in rubber oplosbare zink-dithiocarbamaat-complexen, een belangrijke klasse van vulkanisatieversnellers. Door de uitwisseling van liganden voor functionele groepen zorgen deze complexen voor het transport en de uitwisseling van zwavelatomen.*

Results and Discussion

Synthesis of starting materials: Suitable models for cross-link precursors **1**–**3**, depicted in Figure 1, were derived from 2,3-dimethyl-2-butene. This olefin has successfully been applied in Model Compound Vulcanization. From such reaction mixtures small amounts of the model cross-link precursors **1** and **2** were obtained and their X-ray structures were reported.[14, 15]

For the present study **1** was synthesized in high yield by the reaction of 1-bromo-2,3-dimethyl-2-butene with sodium dithiocarbamate, whereas **2** was obtained by oxidation of 2,3-dimethylbut-2-enethiol and sodium dimethyldithiocarbamate in the presence of iodine. A nonsymmetric substitution at SCl_2 using 2,3-dimethylbut-2-enethiol and sodium dimethyldithiocarbamate afforded **3** in 23% yield (Scheme 3). The propensity of S–Cl moieties to add to double bonds[16] was suppressed by performing the reaction at low temperature.

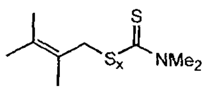
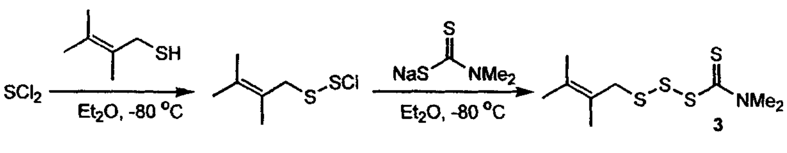


Figure 1. Synthetic model cross-link precursors used in this study.



Scheme 3. Synthesis of **3**.

The ^1H NMR spectrum of **3** is very similar to that of **1** and **2**, except that the signal of the allylic methylene hydrogen atoms is shifted slightly to lower field relative to that of **2**. Compound **3** is labile in acid and decomposes readily on silica, but could be purified by crystallization. Recrystallization from ethanol gave crystals suitable for X-ray analysis. The crystal structure in Figure 2 exemplifies the stability of this trisulfidic compound and is a rare example of a nonsymmetrically substituted trisulfide chain.[17] The observed bond lengths and angles are not unusual for polysulfidic species.[18] We have found that this compound is particularly active in reactions leading to cross-link formation.

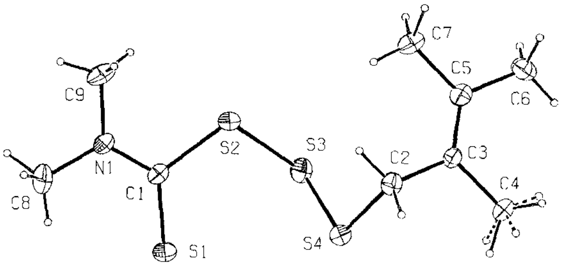
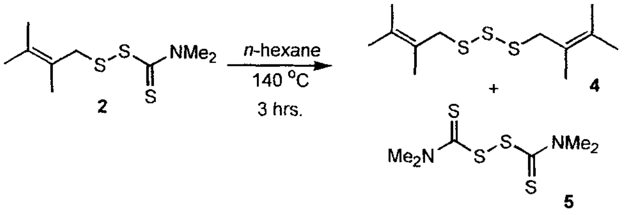


Figure 2. ORTEP diagram of **3** at the 50% probability level.

Reactivity experiments: From several experiments in which model precursor **1** was heated for 3 h at 140 °C, a common vulcanization temperature,[19] it appeared to be completely unreactive. This observation is endorsed by the fact that functionalities similar to **1** have been found in rubber mixtures.[10, 14] They are regarded as desulfuration products of active—polysulfidic—precursors, leading to unreactive, so-called pendant groups.

When **2** is heated for 3 h at 140 °C in the inert solvent *n*-hexane, small amounts of the bis(alkenyl) trisulfide **4** and tetramethylthiuram disulfide **5** are formed (Scheme 4).



Scheme 4. Asymmetric disproportionation of **2**.

Table 1 contains details of reagents and conditions of the various experiments performed with **2**. To prevent any possible interference of dioxygen, such as oxidation or radical formation, all experiments reported were performed under an argon atmosphere. However, control experiments performed in the presence of dioxygen showed no alteration of the general course of the reaction.

Table 1. Disproportionation of **2** with or without Zn catalysis.

No	Initial conditions Solvent [a]	**2** (μmol)	$Zn(dmtc)_2$ (μmol)	**4** (μmol)	Product conversion (%)	Turnovers
1	*n*-hexane	278.0	–	1.449	0.52	–
2a	*n*-hexane	276.8	2.747	9.387	3.39	3.4
2b	*n*-hexane	283.5	2.747	8.487	3.00	3.1
3	toluene	278.3	–	2.615	0.94	
4	toluene	276.3	2.747	13.79	4.99	5.0
5a	2-dmb	277.5	–	3.834	1.38	–
5b	2-dmb	284.3	–	3.131	1.10	–
6a	2-dmb	281.3	2.747	8.307	2.95	3.0
6b	2-dmb	279.4	2.747	10.02	3.59	3.6
7	1-dmb	279.7	–	2.485	0.89	–
8	1-dmb	282.6	2.747	8.441	2.97	3.1

[a] 2-dmb = 2,3-dimethyl-2-butene; 1-dmb = 2,3-dimethyl-1-butene.

The formation of the trisulfide **4** from **2** is rather surprising, as straightforward disproportionation would provide a (bis)alkenyl disulfide as the expected product. Interestingly, the reaction is accelerated by a factor of 4–6 by the addition of a catalytic amount (≈1%) of bis(dimethyldithiocarbamate)zinc(II) ($Zn(dmtc)_2$). Although bis(dialkyldithiocarbamate)zinc(II) complexes are frequently added as an accelerator for vulcanization,[19] or form as a result of the (poorly understood) reaction of TMTD with zinc oxide[20] (added as a rubber filler and vulcanization activator), their role is rather obscure. They are known[1, 21] to induce precursor formation by a mechanism that is unknown; they have been attributed[22] a role in desulfurization of cross-links (cross-link shortening), and they have been suggested[1] to be stoichiometric reagents for the conversion of cross-link precursors into cross-links. The accelerated conversion of **2** into **4** now shows definitely that these complexes serve as homogeneous catalysts for the disproportionation reaction.

The RP-HPLC chromatograms of the zinc-catalyzed reaction of entry 2a in Table 1 are depicted in Figure 3. Although **5** is the initial product of disproportionation, it appears that tetramethylthiuram monosulfide **6** is formed in excess over **5** during the course of the reaction. It is of interest to note that the amounts of **6** and **4** increase almost linearly, whereas the amount of **5** present in the reaction mixture stabilizes at a certain level. Furthermore, the formation of **3** leads to the conclusion that **5** and the trisulfidic cross-link **4** originate from a nonsymmetric disproportionation of **2** and **3**. Two molecules of **2** apparently cannot engage in a symmetric disproportionation. Finally, the slow formation of the (bis)alkenyl tetrasulfide is assumed to be the result of disproportionation of two molecules of **3**. The catalyzed disproportionation proceeds in a similar fashion in other nonnucleophilic solvents such as toluene (entries 3 and 4 in Table 1), although the cross-link yields may vary. This is probably due to differences in solubility of the reagents and dielectric constants of the solvents, which influence the reactions.

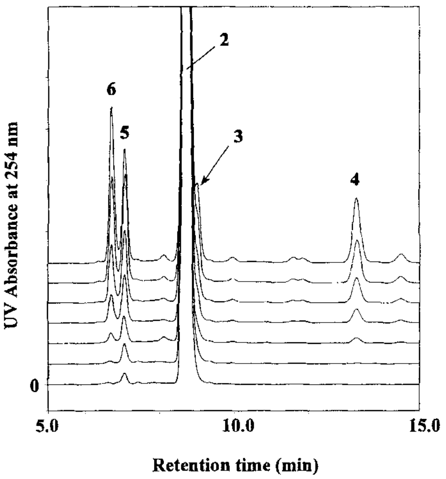


Figure 3. RP-HPLC chromatograms for the reaction of **2** in the presence of ≈1% $Zn(dmtc)_2$.

To probe whether cross-link precursors react with allylic moieties in rubber according to the suggested S_Ni' reaction, the model cross-link precursor **2** was heated for 3 h at 140 °C in the solvent 2,3-dimethyl-2-butene, both in the absence and presence of $Zn(dmtc)_2$ (entries 5 and 6 in Table 1, respectively). This olefin readily produces cross-links in TMTD-accelerated Model Compound Vulcanization.[13] Indeed cross-links are observed here as well, but only as a result of the aforementioned nonsymmetric disproportionation. The formation of allylically-rearranged monosulfides or dimethyldithiocarbamic acid, as shown in Scheme 2, can be excluded. With the objective of excluding the influence of steric hindrance at the double bond on the rate of the reaction, **2** was also heated with the isomeric olefin 2,3-dimethyl-1-butene, which possesses a terminal double bond (entries 7 and 8, respectively). Again, only nonsymmetric disproportionation takes place.

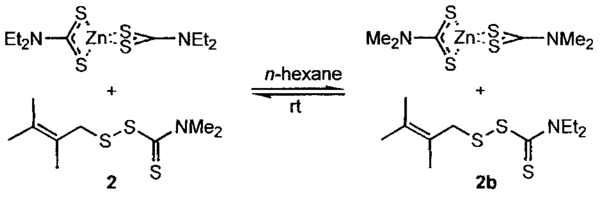
To obtain additional mechanistic understanding of the disproportionation, a mixture of **2** and 5 mol% of **3** was heated both in the absence and presence of the catalyst (entries 1 and 2, Table 2). Cross-link formation proceeds readily in both cases, but, in the absence of Zn(dmtc)$_2$, **5**, not **6**, is the main product. When Zn(dmtc)$_2$ is present, cross-link formation is abundant and formation of polysulfidic analogues of **3** takes place.

Table 2. Disproportionation of **2** with or without Zn catalysis in the presence of additives.

No	Initial conditions solvent	 **2** (μmol)	 Additive (μmol)	 Zn(dmtc)$_2$ (μmol)	 **4** (μmol)	Products Conversion [a] (%)	 turnovers
1	*n*-hexane	279.6	**3** (11.59)		8.814	3.15	–
2	*n*-hexane	278.2	**3** (12.82)	2.747	31.34	11.27	11.3
3	*n*-hexane	285.4	S_8 (37.35)	–	14.16	4.96	–
4	*n*-hexane	281.0	S_8 (37.15)	2.747	24.31	8.65	8.5

[a] Conversion based on **2**.

In order to study the interaction between catalyst and cross-link precursor, 4 mol% of bis(diethyldithiocarbamate)zinc(II) was added to a solution of **2** in *n*-hexane. As deduced from the immediate formation of **2b**, attributed to an equilibrium depicted in Scheme 5, it was that shown ligand–functional-group exchange between Zn(dmtc)$_2$ and **2** is very facile. ^{1}H NMR and HPLC analysis unambiguously indicated all four components to be present in the reaction mixture.

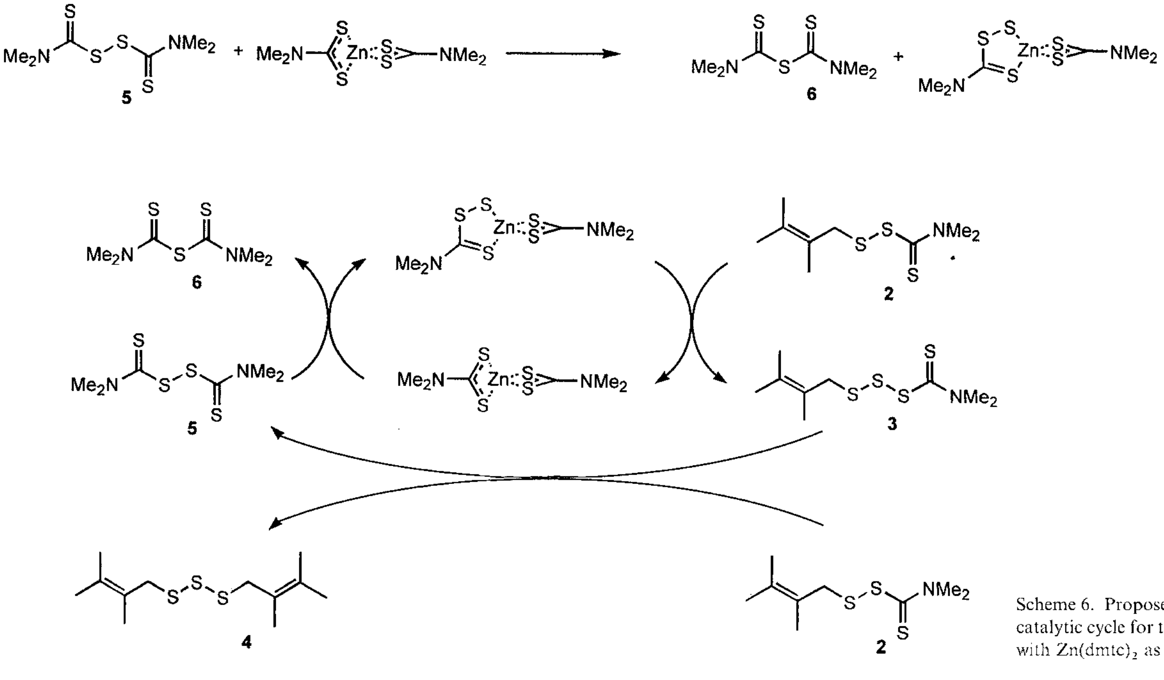


Scheme 5. Ligand-functional group exchange reactions between Zn(dmtc)$_2$ and **2**.

Finally, the addition of 16.6 mol% of S_8 to the reaction mixture (entries 3 and 4, respectively) leads to the formation of large amounts of polysulfidic analogues of **3**, the number of sulfur atoms ranging from 2 to 6, and, with a short delay, formation of polysulfidic cross-links (number of sulfur atoms in the chain varying from 3 to 6) with a clear preference for **4**.

Rationalization of the observations: The experiments performed in this study indicate that S_Ni' reactions do not occur. It can be concluded that cross-links do form in the absence of zinc(II), as long as they are sufficiently activated, for example, contain a sufficient number of sulfur atoms. However, for disproportionation to take place from **2**, **3** must be formed first, for which zinc(II) complexes are catalysts. A radical mechanism for the formation of **3** can be ruled out, as zinc(II) is known not to take part in chemistry involving changes of its oxidation state. Also, a mechanism involving the formation of cationic sulfur species can be excluded; such very electrophilic species would immediately react with olefins.[16] Instead the catalytic cycle shown in Scheme 6, which is in excellent agreement with the observations, is now proposed.

The cycle is initiated by a ligand–functional-group exchange reaction of Zn(dmtc)$_2$ with **5**, which is known to be present as an impurity in **2**. This results in the formation of a small amount of **6** and a so-called trithio–zinc(II) complex, in which a sulfur atom is incorporated in the zinc–dithiocarbamate ring. Ligand–functional-group exchange between **5** and bis(dialkyldithiocarbamate)zinc(II) has been reported to be very fast,[23, 24] a result similar to our observations for ligand–functional-group exchange between **2** and Zn(dmtc)$_2$. The trithiocarbamate ligand subsequently exchanges with the dithiocarbamoyl moiety of **2** in the first step of the cycle, affording **3**, now activated by the additional sulfur atom. This intermediate undergoes a nonsymmetric disproportionation with **2**, which is present in excess, explaining the initial formation of **4** and **5**. Because **5** is more readily desulfurized than **2**, as a result of a ligand exchange reaction with Zn(dmtc)$_2$, it will be transformed



Scheme 6. Proposed initiation reaction and catalytic cycle for the formation of **4** from **2** with Zn(dmtc)$_2$ as catalyst.

into **6** and the trithio–zinc(II) species, thereby completing the catalytic cycle. The net effect is that one sulfur atom is removed from **5** and inserted into a cross-link precursor. Thus, the exchange of a trithio ligand for a dithio functional group, and vice versa, is the basis of the observed catalytic reaction.

From the experiments with elemental sulfur added to the mixture, Zn(dmtc)$_2$ appears to be able to incorporate purely inorganic sulfur as well, which must occur by another mechanism that that described above. Indeed, the solubility of sulfur in benzene has been reported to increase proportionally with the amount of zinc(II).[25] Obviously, under practical vulcanizing conditions where large amounts of sulfur are present, the latter will be the primary mode of incorporation of sulfur atoms in the zinc–dithiocarbamate ring. This aspect is currently under investigation. At this stage, it can already be noted that the sulfur atoms are inserted into the precursor one by one, and not as an octatomic cluster. This presumably reflects the fact that not more than one sulfur atom at a time can be accomodated in the zinc–dithiocarbamate ring; this would agree with a suggestion by Fackler et al. for the related zinc–dithiolate complexes.[26] The latter class of complexes constitutes more evidence for the involvement of trithio–zinc complexes in rubber vulcanization; bis(trithiolate)zinc complexes have been synthesized and characterized by means of X-ray crystallography.[27, 28] However, incorporation of more than one sulfur atom in the zinc–dithiolate ring could not be achieved, presumably due to the opposing effects of chelate ring size and resonance stabilization.[26]

It must be added here that until now it has not been possible to isolate trithiocarbamate–zinc complexes, nor to observe them by any spectroscopic technique.[2] This must be due to their extreme instability and low concentration. Trithiocarbamate–zinc complexes are, however, regarded important intermediates in TMTD-accelerated vulcanization.[1, 2] The existence of the related trithiolate–zinc complexes and the observations presented in this paper clearly support this postulate.

The turnover numbers for the zinc-catalyzed disproportionations are quite moderate, even when it is taken into account that these are somewhat obscured by the fact that the disproportionation product **4** is monitored, and not the primary product of ligand–functional-group exchange **3**. However, in rubber vulcanization, the molar ratio of elemental sulfur vs. accelerator usually is about 3:1.[19] Overall this would result in a 1:1 ratio of catalyst and cross-link precursor, so the presence of a large amount of catalyst will compensate for its low activity. The ratio of 100:1 employed in the present study was chosen to enable careful determination of the reactivity of cross-link precursors and the role of the catalyst.

Conclusion

The study described in this paper allows for a balanced appraisal of the reactivity of cross-link precursors and the role of zinc–dithiocarbamate complexes in the stage of cross-link formation during the vulcanization process. Based on the olefin 2,3-dimethyl-2-butene, which is known to be a realistic model for rubber in Model Compound Vulcanization experiments, model compounds for cross-link precursors were synthesized. From reactivity studies it can be concluded that the primary route for cross-linking during accelerated sulfur vulcanization of rubber most likely involves disproportionation of two polysulfidic dithiocarbamoyl groups (or cross-link precursors). An S$_N$i′ mechanism, in which a precursor directly reacts with an allylic moiety, has not been observed, and it is therefore assumed that such a mechanism is unlikely to operate during rubber vulcanization. For the disproportionation reaction, Zn(dmtc)$_2$ serves as a homogeneous catalyst, inducing sulfur exchange and sulfur transport via (trithio)ligand–functional-group exchange reactions. The complex is able to incorporate sulfur atoms from TMTD, polysulfidic cross-link precursors, and elemental sulfur.

Experimental Section

General: Sodium dimethyldithiocarbamate (Aldrich) was dried by heating for 6 h in vacuo at 60 °C and was stored under argon. 2,3-Dimethyl-1-but-2-enethiol was synthesized by bromination of 2,3-dimethyl-2-butene with NBS, followed by treatment with thiourea and base after Goodrow and Musker.[29] SCl$_2$ (80%) was obtained from Aldrich and used without further purification. Analytical-grade diethyl ether (Baker) for syntheses was freshly distilled from LiAlH$_4$ before use. Pyridine (Baker) was used as provided. Bis(dimethyldithiocarbamate)zinc(II) was purchased from Aldrich and recrystallized from chloroform. Zn(dmtc)$_2$ solutions were prepared using p.a.-grade dichloromethane (Aldrich). 2,3-Dimethyl-2-butene (98%) and 2,3-dimethyl-1-butene (98%) were obtained from Aldrich, distilled prior to use, and stored over activated 4 Å molecular sieve, as was p.a.-grade *n*-hexane (Baker). Molecular sieves were shown not to catalyze the reaction.

^{1}H NMR spectra were recorded in CDCl$_3$ on a Bruker WM-300 spectrometer (300.13 MHz). ^{13}C NMR spectra were recorded at 75.47 MHz. Chemical shifts (δ) are given relative to tetramethylsilane as an internal standard for ^{1}H NMR data and relative to CDCl$_3$ for ^{13}C NMR data. Mass-spectrometric analyses were performed on a Finnigan MAT900 equipped with a direct insertion probe, kept under vacuum at 40 °C. Spectra were collected in electron impact (EI) mode at 70 eV. Exact measurements were performed using a peak matching procedure with perfluorokerosine as internal calibrant. Elemental analyses were performed at the Microanalytical Laboratory of University College Dublin, Ireland. Reversed-phase HPLC analyses were performed using a Gynkotek M480 ternary gradient pump equipped with Gastorr model GT-103 on-line degassing device, Marathon XT autoinjector, Alltech Nucleosil 100 C18 5 μm stainless steel RP-HPLC column, maintained at 30 °C, and Gynkotek HPLC UVD 320S photodiode-array detector. Methanol 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. Column chromatography was performed using Merck Kieselgel 60 (0.040–0.063 mm). Petroleum ether (40/60) and diethyl ether used for chromatography were of technical grade and distilled prior to use.

Synthesis of 1-dimethyldithiocarbamoyl-2,3-dimethyl-but-2-ene (1): A 250 mL flask was charged with 2,3-dimethyl-2-buten-1-yl-thiuronium bromide (3.00 g, 12.6 mmol), sodium dimethyldithiocarbamate (1.70 g, 12.6 mmol) and water (150 mL). The mixture was stirred for 1.5 h at 80 °C and tested for the absence of thiuronium bromide with picrinic acid. The solution was then extracted twice with dichloromethane, the organic layers were dried on Na$_2$SO$_4$, filtered, and concentrated in vacuo. Column chromatography by elution with a 4:1 mixture of petroleum ether/diethyl ether gave **1** as a white solid (1.32 g, 6.50 mmol; yield: 52%). ^{1}H NMR: $\delta = 1.70$ (s, 3H), 1.75 (s, 6H), 3.36 (s, 3H), 3.55 (s, 3H), 3.94 (s, 2H); ^{13}C NMR: $\delta = 18.19$, 20.39, 20.66, 41.16, 43.43, 44.79, 120.62, 131.26, 198.02; MS: 203 (41) [M^+], 120 (17) [Me$_2$NC(S)S$^+$], 88 (100) [Me$_2$NC(S)$^+$], 83 (49) [C$_6$H$_{11}^+$]; exact mass: calcd 203.08024; found 203.07902; anal. calcd for C$_9$H$_{17}$NS$_2$ (202.36) C, 53.16; H, 8.43; N 6.89; found: C, 53.43; H, 8.52; N, 6.86.

(2,3-Dimethyl-2-butene-1-yl)(dimethyldithiocarbamato)sulfide (2): A solution of I$_2$ (1.09 g, 4.3 mmol) in pyridine (20 mL) was added dropwise to a solution of 2,3-dimethyl-2-butenethiol (0.50 g, 4.3 mmol) and sodium dimethyldithiocarbamate (0.62 g, 4.3 mmol) in pyridine (20 mL), during which the reaction slowly turned brown. The mixture was stirred for 2 h, after which pyridine was removed in vacuo. The residue was extracted with diethyl ether (3 × 30 mL) and filtered. The diethyl ether was evaporated in vacuo, the crude product dissolved in dichloromethane, and purified by column chromatography. Initial elution with petroleum ether, followed by a 4:1 mixture of petroleum ether and diethyl ether gave **2** as a solution in the eluent, from which the product was obtained as white crystals by repeated crystallization. Total yield: 50% (0.51 g, 2.17 mmol). ^{1}H NMR: $\delta = 1.70$ (s, 3H), 1.79 (s, 3H), 1.81 (s, 3H), 3.43 (s, 3H), 3.59 (s, 3H), 3.60 (s, 2H); ^{13}C NMR: $\delta = 18.18$, 20.71, 20.78, 41.40, 43.00, 46.93, 121.73, 132.33, 197.63; MS: 120 (7) [$Me_2NC(S)S^+$], 115 (24) [$C_6H_{11}S^+$], 88 (100) [$Me_2NC(S)^+$]; exact mass: calcd 235.05232; found 235.05305; anal. calcd for $C_9H_{17}NS_3$ (235.42): C, 45.90; H, 7.22; N, 5.95; found: C, 46.10; H, 7.33; N, 5.99.

(2,3-Dimethyl-2-butene-1-yl)(dimethyldithiocarbamato)disulfide (**3**): A solution of sulfur dichloride (0.24 g, 2.37 mmol) in freshly-distilled diethyl ether (10 mL) was cooled to −80 °C. A solution of 2,3-dimethyl-2-butenethiol (0.25 g, 2.15 mmol) in diethyl ether (10 mL) was added slowly and the temperature was allowed to rise to −50 °C. The solution was then cooled again to −80 °C and sodium dimethyldithiocarbamate (0.31 g, 2.15 mmol) was added as a solid, while stirring vigorously. The reaction mixture was then allowed to rise to room temperature and the solvent was removed in vacuo. The residue was crystallized from petroleum ether, affording a yellow–white solid (0.13 g, 0.49 mmol; 23% yield). Recrystallization from ethanol gave crystals suitable for X-ray crystal structure analysis. ^{1}H NMR: $\delta = 1.69$ (s, 3H), 1.76 (s, 6H), 3.43 (s, 3H), 3.60 (s, 3H), 3.76 (s, 2H, CH_2); MS: 184 (14) [$Me_2NC(S)S_3^+$], 153 (15) [$Me_2NC(S)S_2^+$], 120 (17) [$Me_2NC(S)S^+$], 115 (13) [$C_6H_{11}S^+$], 88 (100) [$Me_2NC(S)^+$], 83 (26) [$C_6H_{11}^+$]; exact mass: calcd 267.0244; found 267.0232; anal. calcd for $C_9H_{17}NS_4$ (267.48): C, 40.45; H, 6.42; N, 5.24; found C, 40.58; H, 6.49; N, 5.35.

Reaction of 2 with Zn(detc)$_2$: The reaction mixture obtained after following the product formation from reaction of **2** (65.45 mg, 278 µmol) and Zn(detc)$_2$ (14.16 µmol) was transferred to a flask, the solvent evaporated under reduced pressure, the residue dissolved in dichloromethane, and purified by column chromatography with petroleum ether. (2,3-Dimethyl-2-butene-1-yl)(diethyldithiocarbamato) sulfide (**2b**, 4 mg, 15 µmol) was obtained as a colorless liquid (53%). ^{1}H NMR: $\delta = 1.29$ (t, 6H), 1.70 (s, 3H), 1.77 (s, 3H), 1.80 (s, 3H), 3.60 (s, 2H), 3.80 (q, 2H), 4.06 (q, 2H); MS: 180 (7) [$Et_2NC(S)S_2^+$], 148 (7) [$Et_2NC(S)S^+$], 116 (100) [$Et_2NC(S)^+$], 83 (9) [$C_6H_{11}^+$]; exact mass: calcd for $C_{11}H_{21}NS_3$ 263.08362; found 263.08304.

Reactivity experiments: All reactivity experiments were carried out under an argon atmosphere in 30 mL tailor-made Schlenk-type reaction vessels equipped with Teflon valves and screw caps with Teflon inserts. To preclude cross-contamination of catalyst, the reaction vessels were treated before use with concentrated hydrochloric acid, thoroughly rinsed, and dried overnight in a stove at 150 °C. In a typical experiment, a vessel was charged with 2.00 mL of a 1.373 mM solution of Zn(dmtc)$_2$ in dichloromethane. A magnetic stirrer bar was added, the solvent was evaporated in vacuo, and a precise amount (≈65 mg) of **2** was weighed into the vessel. The vessel was then evacuated three times and filled with argon, after which 2.00 mL *n*-hexane was added under outstream of argon. A 50 µL sample was taken for HPLC analysis and the vessel was closed, the valve closed, and the vessel partly immersed at 140.0 °C in an oil bath equipped for magnetic stirring. For 3 h, every 30 min the vessel was removed from the oil bath and the reaction stopped by immediate cooling in liquid dinitrogen. When the vessel had reached room temperature, the argon pressure was reinstated, the screw cap was removed, and a sample (50 µL) taken under outstream of argon. The vessel was then closed again. Pressure effects due to the decrease in liquid volume were neglected. The 50 µL samples were diluted with methanol to 5.00 mL and analyzed using RP-HPLC within a period of 6 h, or—in view of the inherent instability of polysulfanes—stored at −20 °C and analyzed within 12 h. Products were identified by comparison of their HPLC retention times and real-time UV spectra (200–350 nm) with those of reference compounds. Yields were determined using an RP-HPLC calibration curve for bis(2,3-dimethyl-2-buten-1-yl)trisulfide (**4**) at 254 nm.

Crystallographic data for 3: $C_9NS_4H_{17}$, $M_r = 267.50$, colorless, transparent, cut to size (0.18 × 0.38 × 0.45 mm), monoclinic, space group $P2_1/c$, with $a = 22.937(3)$, $b = 7.4918(8)$, $c = 7.650(3)$ Å, $\beta = 90.481(11)^\circ$, $V = 1314.5(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.352$ g cm^{-3}, $F(000) = 568$, $\mu(Mo_{K\alpha}) = 6.9$ cm^{-1}, 6461 reflections measured, 2995 independent ($R_{av} = 0.07$), $\theta < 27.5^\circ$, $T = 150$ K, $Mo_{K\alpha}$, graphite monochromator, $\lambda = 0.71073$ Å, Enraf Nonius CAD4T on rotating anode. The structure was solved by Patterson techniques (DIRDIF96) and refined on F^2 by full-matrix least-squares methods(SHELXL96). Hydrogen atoms were located from a difference map and their positions refined with U(iso) related to the U(eq) of the atom they are attached to. A disorder model was refined for the hydrogens on C4 (60:40). Convergence was reached at $R_1 = 0.048$ [for 2170 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.116$ ($\sigma = 1.006$, 188 parameters). Final residual density was in the range $-0.39 < \Delta\rho < 0.60$ e Å^{-3}.

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