The Isolation and X-Ray Structure Determination of an Active Intermediate in the Accelerated Sulfur Vulcanization of Alkenes

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In the sulfur vulcanization reaction of 2,3-dimethylbut-2-ene (C_6H_{12}), in the presence of S_8, ZnO and organic accelerators, intermediate products are formed, which consist of an alkene bound by sulfur to an accelerator fragment: C_6H_{11}–S_n–S(S)$CNMe_2$, where $n \geqslant 0$; the isolation, characterisation and vulcanization activity of 2,3-dimethylbut-2-en-1-yl dimethyltrithiopercarbamate [C_6H_{11}–S–S(S)$CNMe_2$] is described.

Vulcanization with sulfur systems is the most important commercial method for crosslinking unsaturated rubbers.[1] Vulcanization studies using low molecular mass alkenes as models for unsaturated rubbers appeared to be very useful and provided detailed knowledge of the crosslink structure.[2,3] Besides giving structural information, model vulcanizations may also provide information on the influence of changes in vulcanization conditions, as reported by Lautenschlaeger,[4] and on the vulcanization mechanism.

A new model alkene has now been used in which only equivalent allylic positions are present: 2,3-dimethylbut-2-ene (tetramethylethylene; C_6H_{12}).[5] Vulcanization of this alkene leads to a relatively simple product mixture and is expected to simplify the study of the mechanism of the vulcanization reaction.

The mechanism of the accelerated sulfur vulcanization is still not completely understood. There is still a lot of discussion, especially about the role of the different accelerators, the identity of crosslink precursors and the question whether the predominant reaction is of a polar or a free radical nature. It is quite likely that owing to the complexity of the vulcanization systems both polar and free radical reactions may occur.

Our studies are involved with the S_8–ZnO–tetramethylthiuram disulfide [$Me_2NC(S)S$–S(S)$CNMe_2$] curing system. Vulcanization is carried out at 140 °C for a period of one hour using the model alkene as solvent. It is commonly accepted that in these systems intermediates are formed which consist of an accelerator fragment bound to the rubber, or the model alkene.[6] By varying the reaction conditions, *i.e.* shortening of the reaction time or lowering the temperature, we have been able to isolate and consequently to characterize these intermediates by using HPLC and NMR spectroscopy.[5]

Separation of the reaction mixtures by column chromatography results in two main fractions. The first consists of the final vulcanization products, bis(2,3-dimethylbut-2-en-1-yl)

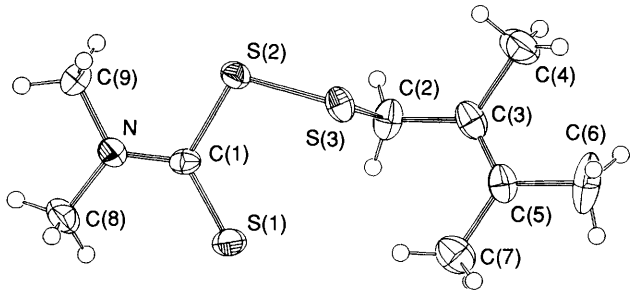

Fig. 1 ORTEP drawing (50% probability level) of C_6H_{11}–S–S(S)$CNMe_2$. The alkene part is disordered over two conformations. The structure of the major conformer is shown. Selected bond lengths (in Å) are: S(1)–C(1) 1.667(4), S(2)–C(1) 1.804(4), S(2)–S(3) 2.0172(13), S(3)–C(2) 1.822(4), N–C(1) 1.315(5), N–C(8) 1.470(6), N–C(9) 1.483(6), C(3)–C(2) 1.535(1), C(3)–C(4) 1.588(12), C(3)–C(5) 1.291(18), C(5)–C(6) 1.551(11) and C(5)–C(7) 1.47(11). Selected valence angles (°) are: S(3)–S(2)–C(1) 105.28(12), S(2)–S(3)–C(2) 105.01(14), C(1)–N–C(8) 120.6(4), C(1)–N–C(9) 123.2(4), C(8)–N–C(9) 116.3(3), S(1)–C(1)–S(2) 122.0(2), S(1)–C(1)–N 125.1(3), S(2)–C(1)–N 112.9(3), S(3)–C(2)–C(3) 105.5(4), C(2)–C(3)–C(4) 122.6(9), C(2)–C(3)–C(5) 118.8(9), C(4)–C(3)–C(5) 118.6(8), C(3)–C(5)–C(6) 117.9(9), C(3)–C(5)–C(7) 118.9(8) and C(6)–C(5)–C(7) 123.2(8).

sulfides, whereas the second consists of the intermediate products, C_6H_{11}-S_n-S(S)$CNMe_2$. It has been possible to obtain crystals of one of these intermediates by evaporation of the eluent of the second fraction, redissolving it in ethanol and slowly cooling to −15 °C. The ^1H NMR spectrum of these white crystals (m.p. 94 °C)† differs from that of C_6H_{11}–S(S)$CNMe_2$ obtained from the vulcanization mixture under standard conditions.[5] It seems that the new crystals contain an additional sulfur atom. This is confirmed by the crystal structure determination.‡

The crystallographically independent unit consists of a tetramethylethylene–S–dimethyldithiocarbamate molecule. It is made up from an accelerator fragment coupled to an alkene at the allylic position through one sulfur atom. The double bond moiety of the alkene is found disordered: either *cis* relative to the accelerator fragment, or, as a result of rotation around the S(3)–C(2) bond, *trans*.

The accelerator fragments in both orientations are identical. An ORTEP drawing of the major conformation (58%) is given in Fig. 1. It is possible that the molecule has a large vibrational freedom around the C=C double bond, explaining the deviant bond lengths. The disorder is also likely to influence the accuracy of the determination of the different bond lengths in the unsaturated fragments.§

Experiments with mixtures of the earlier obtained C_6H_{11}–S(S)$CNMe_2$ and sulfur show no reaction under vulcanization conditions. However, reaction of C_6H_{11}–S–S(S)$CNMe_2$ with free alkene in the presence of sulfur and zinc dimethyldithiocarbamate[7] at 140 °C shows the formation of C_6H_{11}–S_n–C_6H_{11}. The HPLC peak of C_6H_{11}–S–S(S)$CNMe_2$ decreases whereas new peaks that may be ascribed to C_6H_{11}–S_n–C_6H_{11} increase. These reactions are in agreement with the reactions of model crosslink precursors as described by Morrison[8] and they confirm the conclusion that C_6H_{11}–S–S(S)$CNMe_2$ is indeed an active intermediate in the accelerated sulfur vulcanization process of 2,3-dimethylbut-2-ene.

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† ^1H NMR spectra of C_6H_{11}–S–S(S)$CNMe_2$ and C_6H_{11}–S(S)$CNMe_2$ were recorded on a Bruker 300 MHz spectrometer, using $CDCl_3$ as solvent and $SiMe_4$ as external standard. The chemical shifts for C_6H_{11}–S–S(S)$CNMe_2$ are: δ 1.70, 1.78, 1.80 and 3.59 for the alkene fragment and δ 3.43 and 3.60 for the accelerator fragment. The chemical shifts for C_6H_{11}–S(S)$CNMe_2$ are δ 1.68, 1.74, 1.74 and 3.93; δ 3.53 and 3.35.

‡ *Crystal data* for C_6H_{11}–S–S(S)$CNMe_2$: $C_9H_{17}NS_3$, M = 235.44, orthorhombic, space group $Pna2_1$, with a = 16.9668(3), b = 10.6142(5), c = 6.8438(8) Å, V = 1232.5(2) Å^3, Z = 4, D_c = 1.269 g cm^{-3}, $F(000)$ = 504, μ(Mo-Kα) = 5.4 cm^{-1}, colourless transparent crystal, 0.10 × 0.12 × 0.60 mm; 3321 reflections ($\theta < 27.5°$; ω–2θ scan; T = 150 K) were measured on an Enraf-Nonius CAD4T/rotating anode diffractometer (monochromated Mo-Kα; λ = 0.71073 Å). The data were corrected for Lorentz–polarization and absorption (DIFABS: correction range 0.87–1.17) and averaged (R_{av} = 0.03). The structure was solved with DIRDIF and refined by full-matrix least-squares (SHELX76) to a final R = 0.034 [R_w = 0.032, $w^{-1} = \sigma^2(F) + 0.000162F^2$] for 1239 reflections with $I > 2.5\sigma(I)$ and 154 parameters. H atoms in calculated positions. The C(3),C(5) moiety is disordered (58 : 42). $|\Delta\rho| < 0.26$ e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The S(1)–C(1) bond [1.667(4) Å] is short because of its double bond character. The S(2)–S(3) bond [2.0172(13) Å] behaves as a normal S–S bond as also found in elemental sulfur and S_2Cl_2. The C(3)–C(5) double bond [1.29(2) Å] is remarkably shorter than a normal C–C double bond. Most of the C–C single bonds are as expected; however, the C(3)–C(4) [1.589(12) Å] bond is longer than a normal single bond. Because of the disorder around the C–C double bond, conclusions based on the various bond lengths should be regarded with care.