

Some Observations on the Mechanism of Action of Retarders in Rubber Vulcanization. A New Class of Retarder

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Synopsis

Attempts have been made to demonstrate the involvement of free radicals in the benzthiazolesulfenamide-accelerated vulcanization of natural rubber. Free radicals were only detected by ESR in reaction mixtures containing the retarder N-nitrosodiphenylamine (NDPA). In addition, NDPA was the only compound found, from the vulcanization accelerator and retarders tested, to affect the free-radical polymerization of methyl methacrylate. A purely ionic mechanism for sulfur vulcanization of natural rubber accelerated by benzthiazolesulfenamide derivatives has therefore been assumed and used to help in the design of new vulcanization retarders. A new class of retarder has been discovered, consisting of hydrocarbylthio derivatives of trisalkylsulfonyl methane. These retarders are believed to be the first vulcanization retarders to act by cleavage of a carbon-sulfur bond.

INTRODUCTION

Although the mechanism of sulfur vulcanization of natural rubber accelerated by sulfenamide derivatives of 2-mercaptobenzthiazole (MBT) has been extensively studied, it is still not clear whether the process involves radical intermediates, ions, or a combination of both. Most workers have proposed a radical mechanism,¹⁻⁶ whereas others⁷⁻⁹ have proposed a mechanism involving both free-radical and ionic intermediates. Bateman et al.^{10,11} have proposed an ionic mechanism. Recently, Manik and Banerjee^{12,13} have again proposed a mechanism involving both free-radical and ionic species. With the design of new vulcanization scorch retarders in mind, we have investigated the benzthiazole sulfenamide-accelerated vulcanization of natural rubber in an attempt to determine whether the main reactions in the vulcanization are free-radical or ionic processes.

A little work has been done on the mechanism of retardation of vulcanization by N-nitrosodiphenylamine (NDPA).¹⁴⁻¹⁷ As NDPA probably decomposes at vulcanization temperatures to give free radicals¹⁴⁻¹⁷ it was decided to examine some benzthiazole sulfenamide accelerators, both under vulcanization conditions and outside rubber, to see if they also gave rise to free radicals. Using the results from this and other work,^{9,18-23} it has been possible to design a new class of retarder.

EXPERIMENTAL

Materials

The natural rubber used was pale crepe SMR5. Vulcanization additives were obtained from ICI Organics Division, including MBT, dibenzthiazol-2-yl disulfide (MBTS), N-cyclohexylbenzthiazole-2-sulfenamide (CBS), 2-morpholinethiobenzthiazole (BSM), N-*tert*-butylbenzthiazole-2-sulfenamide (BSB), diphenyl chlorotriazine, N-nitrosodiphenylamine (NDPA), N-phenylthiomorpholine, N-phenylthiophthalimide, N-cyclohexylthiophthalimide (PVI), and active ZnO. The organic compounds were all recrystallized before use. Sulfur was sieved through a 100 mesh sieve. Stearic acid was "pure" from BDH. Methyl methacrylate was from ICI, Mond Division. Most other chemicals were from BDH, Koch-Light, or Ralph N. Emanuel Ltd.

Preparation of Compounds for Testing

N-Chlorodicyclohexylamine.²⁴ Dicyclohexylamine (18.1 g) was dissolved in methylene chloride (50 ml), stirred vigorously, and powdered N-chlorosuccinimide (13.35 g) was added. When the reaction mixture was neutral, the succinimide was removed by extraction with water, the methylene chloride solution was dried, and the solvent removed under reduced pressure. The product was recrystallized twice from methanol; mp, 22°–24°C (lit. 26°C).

Cyclohexanesulfonyl Chloride. Dicyclohexyldisulfide (11.5 g) was dissolved in carbon tetrachloride (70 ml), and redistilled sulfonyl chloride (6.7 g) was added dropwise with stirring at room temperature. The solution was heated to 55°C for 1 hr, and then N₂ was bubbled through the solution overnight at room temperature. The volume was adjusted to 100 ml by the addition of carbon tetrachloride. This solution was used without further purification.

Cyclohexylthiobisethylsulfonyl Methylsulfonylmethane. Methylsulfonylbisethylsulfonylmethane²⁵ (2.78 g) and 1N NaOH (10 ml) were added to toluene (100 ml). The system was heated to reflux, and most of the water was removed using a Dean Stark head. Final traces of water were removed by refluxing the toluene over calcium hydride in a Soxhlet. Cyclohexanesulfonyl chloride (20 ml solution from the above preparation) was added at room temperature, and the system was stirred and heated under reflux for 1 hr and then filtered hot. The product crystallized out on cooling and was recrystallized from ether. Yield 1.4 g (36%); mp 141°–144°C.

ANAL. Calcd: C, 36.7%; H, 6.2%; S, 32.6%. Found: C, 37.1%; H, 7.0%; S, 32.2%.

Phenylthiobisethylsulfonyl Methylsulfonylmethane. Methylsulfonylbisethylsulfonylmethane (4 g) was dissolved in ethanolic sodium ethoxide (made from 0.32 g sodium and 50 ml ethanol), and the solution was heated

under reflux for 45 min. The solvent was removed under reduced pressure, toluene (250 ml) was added, and any remaining ethanol removed by distilling off half the toluene. Phenylsulfenyl chloride (2.1 g) was added and the system was heated under reflux for 3¹/₂ hr. The system was evaporated to dryness under reduced pressure, and the residue was suspended in toluene (100 ml). The solution was filtered and poured into petroleum ether (150 ml). The product precipitated out. Yield 2.1 g (39%); mp 118.5°C.

The NMR spectrum in CDCl₃ at 220 MHz was consistent with the proposed structure; there were peaks at 2.0 τ (doublet), approximately 2.55 τ (multiplet), 6.25 τ (quartet), 6.65 τ (singlet), and 8.5 τ (triplet).

Investigation of Involvement of Free Radicals in Vulcanization

The ESR measurements were made on a Varian V4500-10A spectrometer. Solutions of the accelerators and retarders which had been refluxed in *n*-decane were examined for decomposition products by TLC on silica gel. The methyl methacrylate polymerization experiments were conducted by heating 1 ml of the monomer, with and without the various additives, at 90°C. The times taken for the different mixtures to solidify were compared.

Testing of Potential Retarders in Rubber

The standard mixture used for testing potential retarders was: Pale Crepe (SMR5), 300 g; CBS, 1.5 g; stearic acid (pure), 1.5 g; active zinc oxide, 4.5 g; potential retarder, 6 m mole; and sulfur (≤ 100 mesh), 7.5 g.

The rubber was milled on a Planters Mill at 70°C, the ingredients being added in the above order, except when the retarder was a liquid, in which case it was mixed in with the zinc oxide. The speeds of the rollers were: front, 13 rpm; rear, 17 rpm. A standard milling procedure was adopted so that results would be reproducible. The rubber was tested the following day.

Both the elastic and inelastic moduli of the rubber were followed on a Weissenberg rheogoniometer under nitrogen. The inelastic modulus fell as vulcanization proceeded, but the change was often small. Scorch delay and total cure times were measured at 130° and 153°C, respectively, using only the elastic modulus.

Some retarders were tested on a Mooney plastometer at 120°C and a Monsanto rheometer at 150°C (see Table IV), the standard mix used in these cases was: smoked sheet, 100; CBS, 0.5; ZnO, 3.5; stearic acid, 3.0; sulfur, 2.5; carbon black (Cosmos 60), 45; and Dutrex R, 3.5.

RESULTS

Thermal Stability of Accelerators and Retarders

When the benzthiazolesulfenamides derived from morpholine and *tert*-butylamine, and the retarders NDPA and PVI, were heated separately in

decane under reflux (174°C) for 0.5 hr, only NDPA decomposed, giving off brown fumes and forming diphenylamine. The sulfenamides and PVI were unchanged after this treatment, indicating that they do not break down unimolecularly at this temperature to produce free radicals.

Effects of CBS, PVI, and NDPA on the Polymerization of Methyl Methacrylate

The presence of 0.5% of the accelerator CBS, or of the retarder PVI, in methyl methacrylate, neither inhibited nor accelerated the polymerization at 90°C. Addition of 0.05% azobisisobutyronitrile (AIBN), a known radical initiator, to either of these systems effected rapid polymerization of the methyl methacrylate. NDPA, however, was found to inhibit the AIBN catalyzed polymerization of methyl methacrylate in agreement with earlier work.¹⁷ These polymerization experiments suggest, therefore, that PVI and the sulfenamide accelerator do not form free radicals, nor do they react with free radicals. There is, however, further confirmation that radicals are readily generated from NDPA or react readily with it.

ESR Study of Rubber Containing Various Additives

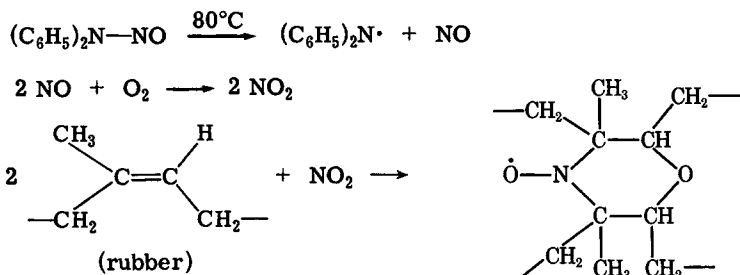
Samples of natural rubber containing various vulcanization additives were heated at 135°C in the ESR cavity for 45 min. The details of these experiments are summarized in Table I.

Free radicals were only detected when NDPA was one of the compounds added to the rubber, and no evidence was found to support the proposed thermal dissociation of benzthiazolesulfenamides into radicals.^{7,13} The identity of the radical formed in the presence of NDPA is not certain, but the same ESR signal was obtained whatever other compounds were present in the rubber. In natural rubber, the free radical was formed at temperatures as low as 80°C, whereas heating NDPA in *p*-xylene at 80°C did not produce a free-radical signal. On addition of a small quantity of natural

TABLE I
Effect of Heating Various Rubber Samples in ESR Instrument

Additives present						Results
2.5% Sulfur	0.5% BSB	0.5% PVI	1.5% ZnO	0.5% Stearic acid	0.5% N-Nitro- sodiphenyl- amine	
+	-	-	-	-	-	no ESR signal
+	+	-	-	-	-	no ESR signal
+	+	+	-	-	-	no ESR signal
+	-	-	+	+	-	no ESR signal
+	+	+	+	+	-	no ESR signal
+	+	-	+	+	-	no ESR signal
+	+	-	-	-	+	ESR signal
+	+	-	+	+	+	ESR signal

rubber to this solution, an ESR signal was obtained. In every case the ESR signal consisted of a nitrogen triplet with a splitting of approximately 15 gauss. This splitting, and the stability of the radical, are characteristic of nitroxide radicals which have no α -hydrogen atoms. The most probable explanation of these observations can be summarized by the following equations:



The above reactions may account for some of the harmful side effects from the use of NDPA. Similar reactions between nitric oxide and simple unsaturated aliphatic compounds have been reported.²⁶ The diphenyl nitrogen radical formed would be too short-lived to be detected, therefore in *p*-xylene no radical is observed. Earlier attempts to observe the diphenyl nitrogen radical in solution by ESR have been unsuccessful.^{27,28}

The absence of an ESR signal in systems containing the sulfenamide or PVI does not preclude the involvement of short-lived radicals whose concentration is never sufficiently high to be detected. (The lower limit of detection is approximately 2×10^{11} spins/g for a line width of 1 gauss, i.e., of the order of 3×10^{-13} moles.) Nevertheless, there is no evidence in the above reactions to suggest that the sulfenamide accelerators or the retarder PVI either react with radicals or themselves produce free radicals. Radicals were only found when NDPA was used; and, of course, even in this case the formation of free radicals may not explain the retarding action of NDPA.

Effect of PVI on Vulcanization Systems Containing MBT and MBTS

In order to obtain a clearer understanding of the mechanism of retardation by PVI, the effect of PVI on systems containing MBT and MBTS has been examined. The details and results of these experiments are summarized in Table II.

The results for systems containing zinc oxide and stearic acid show that at 130°C PVI inhibits MBT-accelerated vulcanizations more than those accelerated by MBTS. The results for MBT can be understood by assuming that all the PVI has reacted with the MBT to give compound I, leaving

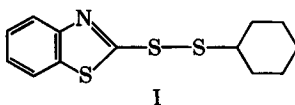


TABLE II
Effect of PVI on MBT and MBTS Accelerated Vulcanizations

Reagents present					Scorch delay at 130°C, min	Vulcanization at 153°C, min		
0.32% MBT	0.32% MBTS	0.52% PVI	1.5% ZnO	0.5% Stearic acid		T_5	T_{95}	ΔT
-	+	-	+	+	15.0	3.25	15.5	12.25
-	+	+	+	+	27.0	5.75	21.75	16.0
+	-	-	+	+	3.75	1.25	18.75	17.5
+	-	-	-	-	5.0	1.0	>40.0	>40.0
+	-	+	+	+	40.0	5.0	16.25	11.25
+	-	+	-	-	≥60.0	-	-	-

approximately 0.017% free MBT. This amount of MBT will cure the rubber very slowly, and if compound I is a very safe accelerator, vulcanization will be very slow. At 153°C, it appears that PVI in the mixture increases the rate of cure once vulcanization has started, it is possible that T_{95} is critically dependent on the amounts of MBT and PVI used, in which case the experimental error will be large. The results show that compound I is not a very safe accelerator at 153°C and so explains why PVI has little or no effect on the rate of cure with sulfenamide accelerators.

Examination of Potential Retarders in Gum Stock Test System

To obtain a better understanding of the types of compounds that will retard CBS-accelerated vulcanizations, several compounds were tested in a simple gum stock. The compounds chosen for these tests were those which would be expected to react with a nucleophile such as MBT. The details of the tests used are given in the experimental section. The results are given in Table III. Failure of the compound tested to react, or instability of the resultant adduct, may explain the poor retarding effect of some of the compounds.

Comparison of New Retarders with Phthalimide Derivatives

Details of the test method are in the experimental section. The results are given in Table IV.

DISCUSSION

The sulfur vulcanization of natural rubber accelerated by benzthiazole-sulfenamides involves a complex series of reactions. The aims of the present work were (a) to determine whether the main reactions in the process are ionic and/or free radical in nature, and (b) to use this information in the design of a new type of scorch retarder which would delay the onset of

TABLE III
Examination of Potential Retarders in Gum Stock Test System

Retarder (2 mmoles/100 g rubber)	Scorch delay at 130°C, min	Vulcanization at 153°C, min			
		T_5	T_{95}	T_{100}	ΔT
None	21.75	4.0	8.25	11.0	4.25
NDPA	35.25	5.5	10.0	13.5	4.5
N-Phenylthiomorpholine	49.5	8.25	12.0	14.0	3.75
PVI	87.0	11.25	18.0	21.0	6.75
2,4-Dinitrochlorobenzene (II)	23.0	5.0	9.75	13.0	4.75
2,4-Dinitrofluorobenzene (III)	41.25	4.75	10.0	16.0	5.25
2,4,6-Trinitrochlorobenzene (IV)	49.5	9.5	17.25	22.0	7.75
1,3,5-Trichlorotriazine (V)	73.5	11.75	21.75	29.0	10.0
3,5-Diphenyl-1-chlorotriazine (VI)	29.0	5.5	11.0	17.0	5.5
2-Chloropyrazine (VII)	31.75	4.25	9.0	12.5	4.75
Diphenyl carbamylchloride (VIII)	28.25	4.5	10.0	12.5	5.5
N-Chlorodicyclohexylamine (IX)	35.25	6.5	13.5	15.5	7.0
Phenylthiobisethylsulfonyl methyl- sulfonylmethane* (X)	54.4	7.0	13.25	19.0	6.25

* Only 1 $\frac{2}{3}$ mmoles/100 g rubber used.

TABLE IV
Comparison of New Retarders with Phthalimide Derivatives

Retarder added (0.25%)	Mooney scorch (min + 10) at 120°C, min	Rheometer at 150°C		
		T_2 , min	Time to peak, min	Peak torque
None	25	7.7	29.2	64
Phenylthiobisethylsulfonyl methyl- sulfonylmethane (X)	33	9.1	31.4	64
Cyclohexylthiobisethylsulfonyl methyl- sulfonylmethane (XI)	35	8.7	31.0*	63
N-Phenylthiophthalimide (XII)	41	—	—	—
PVI	47	11.4	32.6	64

* Time to reach 95% maximum torque (T_{95}).

vulcanization without significantly affecting the rate of cure once vulcanization had started.

The results of the experiments designed to detect the presence of free radicals suggest that the key reactions in the sulfenamide-accelerated, PVI-retarded vulcanization of natural rubber involve ionic intermediates. It seems probable, therefore, that PVI reacts with a nucleophile to effect retardation.

While this work was in progress, other workers proposed²² that MBT was an autocatalyst in this type of vulcanization and that PVI acted by react-

ing with MBT to give a relatively inert product. Once the PVI has been expended, the vulcanization proceeds at approximately its unretarded rate.

It is to be expected that compounds other than phthalimide derivatives will remove MBT and similar nucleophiles from the system, and so delay the onset of vulcanization. The results (Table III) of experiments using compounds which might be expected to scavenge MBT confirm this point.

Using the information from these last experiments, it was possible to design a new class of retarder. The hypothesis used was that a good retarder should react specifically and rapidly with MBT (presumably at the sulfhydryl group), to give a product which would take little part in the subsequent vulcanization.

MBT will react readily with sulfur(II) derivatives because mercaptides, being soft bases²⁹ react most readily with soft acids. As the reaction of PVI with MBT involves the cleavage of a sulfur-nitrogen bond, the possibility of designing new retarders based on cleavage of the sulfur-carbon bond was investigated.

Because the sulfur-carbon bond is stronger than the sulfur-nitrogen bond,³⁰ it appeared probable that the leaving group should be derived from a stronger acid than phthalimide. Derivatives of the type RSC(SO₂R')₃, where HC(SO₂R')₃ will have a pK_a of approximately zero,³¹ were therefore made and tested as retarders. The results in Table III confirm that compound X is a good retarder and hence suggest that the hypothesis used is correct.

Examples of the new class of retarder were tested in a more realistic rubber stock on a Mooney plastometer at 120°C and a Monsanto rheometer at 150°C. (See experimental section.) The results, given in Table IV, confirm that compounds X and XI are good retarders when tested in a more scorchy rubber stock. They have no adverse effect on the efficiency of vulcanization, as shown by the peak torque level. On a molar basis, compound X is 76% as effective a retarder as XII, and XI is 68% as effective as PVI. Within the limits of experimental error, these two figures are the same. Thus it seems probable that these two pairs of retarder differ only in the rate at which they react with MBT, the sulfur-carbon bond being cleaved slightly less readily than the sulfur-nitrogen bond. It is likely that compounds of the type XIII, where R is an alkyl or aryl group

RSCXYZ

XIII

and X, Y, and Z are chosen so that HCXYZ is a fairly strong acid, will be retarders for the vulcanization of rubbers.

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