

Kinetic Studies on the Vulcanization Reaction Accelerated with 2-Mercaptobenzothiazole

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Synopsis

Kinetic data for vulcanization of rubber with sulfur, accelerated with 2-mercaptobenzothiazole (MBT) are presented. The decrease in concentration of sulfur and MBT during vulcanization under various conditions of temperatures have been determined with a precise amperometric method developed by the authors. The order of reaction for disappearance of sulfur was found to be unity. The energy of activation and frequency factor were 28.8 kcal./mole and 4.0×10^{13} , respectively. The kinetics of disappearance of MBT was also first-order, and the rate of reaction, energy of activation, as well as frequency factor were much lower than those for the disappearance of sulfur. The consumption of sulfur proceeded as long as any free sulfur was present in the sample, indicating that the consumption of MBT is closely tied up with the disappearance of sulfur. It was found that about 133 atoms of sulfur were consumed for the disappearance of one molecule of MBT. The mechanism of ring opening involving an attack by the accelerator radical as proposed by Gordon is supported by the present investigation.

Introduction

In a previous communication¹ the authors presented a kinetic study of unaccelerated vulcanization with a precise amperometric method for the determination of sulfur. The present study is a continuation of this earlier work and is again based on the amperometric determination of both sulfur and the accelerator, 2-mercaptobenzothiazole (MBT).^{2,3} This method has many advantageous features which have been discussed earlier.³

The kinetics of the decrease of sulfur for accelerated vulcanization of natural rubber has been studied much less in the past than for unaccelerated vulcanization. In the particular case of the system accelerated with 2-mercaptobenzothiazole (MBT), all the earlier workers⁴⁻⁶ who studied the vulcanization process had directly chosen the system containing zinc oxide in addition to MBT, which is technically more important, without previously going into the details of the simpler system (rubber, sulfur, MBT) and getting background information which might serve as a basis for the mechanism for the more complex system.

The present investigation attempts to remove this discontinuity of

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knowledge by providing kinetic data on the system containing MBT in rubbersulfur vulcanization.

In order to see if any reaction takes place prior to vulcanization, estimation was carried out also during the stage of mixing the basic ingredients⁷ which showed that a part of the accelerator is consumed by the nonrubber ingredients, extractable with acetone, while no further reaction of the accelerator takes place in absence of sulfur even on prolonged heating with rubber at 140°C.

Experimental

The sample of smoked sheet used earlier¹ (RSS-1), was also used in the present investigation.

The other ingredients are as follows: sulfur, G.R. grade (E. Merck), m.p. 118°C.; 2-mercaptobenzothiazole, sp. gr. 1.42, m.p. 168°C., supplied by Naugatuck Chemical International Ltd.; acetone, A.R. grade.

For reasons discussed earlier,¹ a nonextracted rubber sample and 4.6 parts by weight of sulfur were used. The other conditions were also kept as similar as possible to those in the earlier work.¹

The sample for the determination of sulfur and the accelerator was ground to crumbs or converted to thin sheet and then extracted with acetone. The acetone extract was dissolved in an alcohol-benzene (2:3) mixture which was then divided into two parts. One part was dried and the residue was dissolved in alcohol in order to estimate mercaptobenzothiazole. The other portion was treated with potassium cyanide and the sulfocyanide so formed was dissolved in water and the free sulfur estimated. All estimations were performed by amperometric titration with a rotating platinum wire indicator electrode.^{2,3}

Results and Discussion

Figure 1 and Table I show the disappearance of sulfur with time of cure at different temperatures. It may be seen that at lower temperatures the curves show an inflection point in the earlier periods of vulcanization which could not be found at higher temperature as the rate was too quick. The inflection may be explained as due to an induction period before which formation of accelerator radicals in the system, in sufficient number, does not occur.

An induction period may also be inferred from the fact that the intercept (Fig. 2) is greater than two (corresponding to 100%). It is found that combination of rubber and sulfur is greatly accelerated in presence of MBT as compared to unaccelerated vulcanization, as shown by the plot in Figure 1 of the disappearance of sulfur at 140°C.

Figure 2 shows the first-order plot of disappearance of sulfur as reported in Table I. It is found that straight lines are obtained at all temperatures, showing that the reaction of rubber and sulfur which is 0.7th order in absence of the accelerator,¹ is first-order in its presence, so that it may be inferred that either the reaction in this case is not autocatalytic or that the

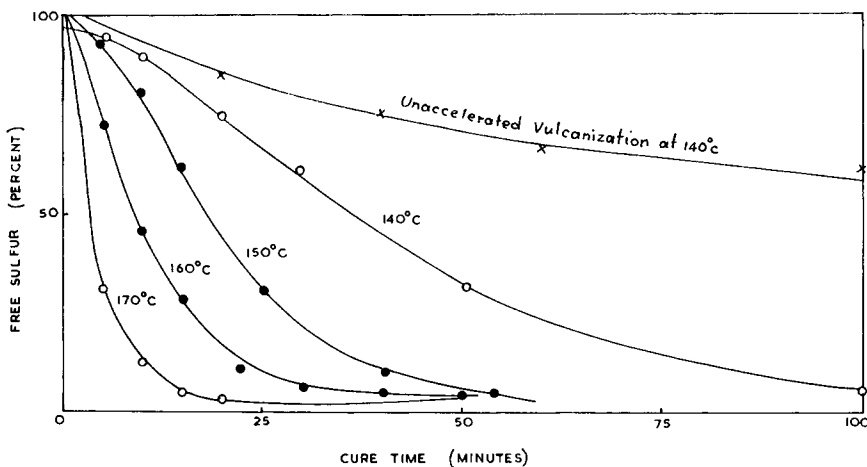


Fig. 1. Disappearance of sulfur with time. Stock: rubber, 100 parts; sulfur, 4.654 parts; MBT, 0.8896 part.

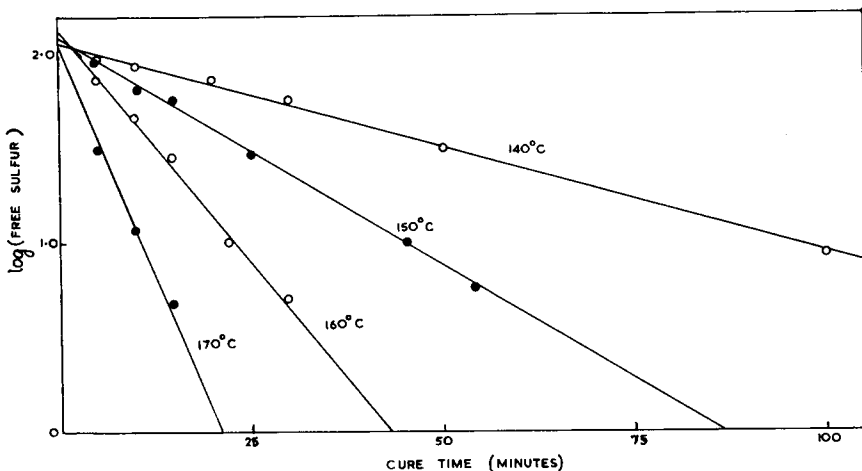


Fig. 2. First-order kinetic plot of disappearance of sulfur. Stock; rubber, 100 parts; sulfur, 4.654 parts; MBT, 0.8896 part.

autocatalytic effect is not predominant because of the enormous acceleration of the primary reaction. The first-order rate constants obtained from Figure 2 are given in Table II.

The speeding up of the reaction by the accelerator must involve the acceleration of the governing step of the vulcanization, i.e., the opening of the S_8 ring, as has been put forward by Gordon.⁸ This can occur by decrease in the energy of activation or increase in the frequency factor or both. However, there is little scope for increasing the vibrational frequency of the S—S bond but considerable scope for decrease in energy of activation. In the present investigation the energy of activation calculated

TABLE I
Disappearance of Sulfur with Time at Different Temperatures^a

Cure temperature, °C.	Cure time, min.	Free sulfur, %
140	5	94.22
	10	90.00
	20	75.17
	30	61.29
	50	31.54
	100	5.52
	150	1.12
150	5	94.04
	10	80.00
	15	62.11
	25	30.00
	40	10.10
	54	5.77
	100	3.21
160	207	2.93
	5	72.88
	10	46.49
	15	28.80
	22	10.05
	30	5.32
	40	5.30
170	50	4.88
	100	5.99
	5	30.59
	10	12.38
	15	5.00
	20	3.74
	50	4.15

^a Composition of the stock: rubber, 100 parts by weight; sulfur, 4.654 parts; MBT, 0.8896 parts.

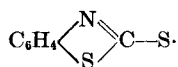
from the Arrhenius plot (Fig. 5) is 28.8 kcal., which is much lower than that obtained for unaccelerated vulcanization¹ (35.6 kcal.). The Arrhenius frequency factor was found to be 4.0×10^{13} compared to 7.4×10^{16} in the case of unaccelerated vulcanization.

TABLE II
Arrhenius Parameters for Reaction of Sulfur with Natural Rubber^a

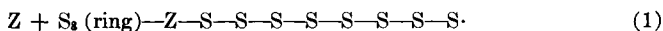
Cure temperature, °C.	Rate constants $K_s \times 10^2, \text{min.}^{-1}$	Energy of activation, kcal./mole	Frequency factor
140	2.512	28.8	4.0×10^{13}
150	5.062		
160	11.52		
170	23.03		

^a Composition of the stock: rubber, 100 parts by weight; sulfur, 4.654 parts; MBT, 0.8896 parts.

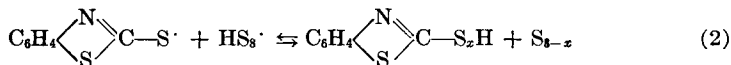
In fact the accelerator used here (MBT), is known to form the radical



at the vulcanizing temperature, and sulfur is very prone to attack by a radical. In view of these facts the mechanism as proposed by Gordon⁸ involving an attack of an accelerator Z on the sulfur ring seems to be a plausible key to the problem of accelerated vulcanization. The actual reaction, however, is not considered to be so simple, because of interference by secondary reaction products, but this may serve as a basis for the kinetic considerations.



This mechanism is in contradiction to that put forward recently by Scheele and co-workers⁹ in which an equilibrium is supposed between the reactants, catalyst, and an intermediate compound. However, these authors also considered MBT-accelerated vulcanization as an exception to this scheme. The above theory involving a radical attack was recently supported by a number of Russian workers, including Bresler¹⁰ and Dogadkin and Tutorskii.¹¹ The latter workers expounded this theory to include secondary radical fragments and regeneration of the accelerator.



It would be evident from consideration of eq. (1) that the necessity of bringing Z into a favorable collision with S₈ represents a steric requirement which must lower the frequency factor considerably, compared to the purely thermal intramolecular splitting, a contention which is supported

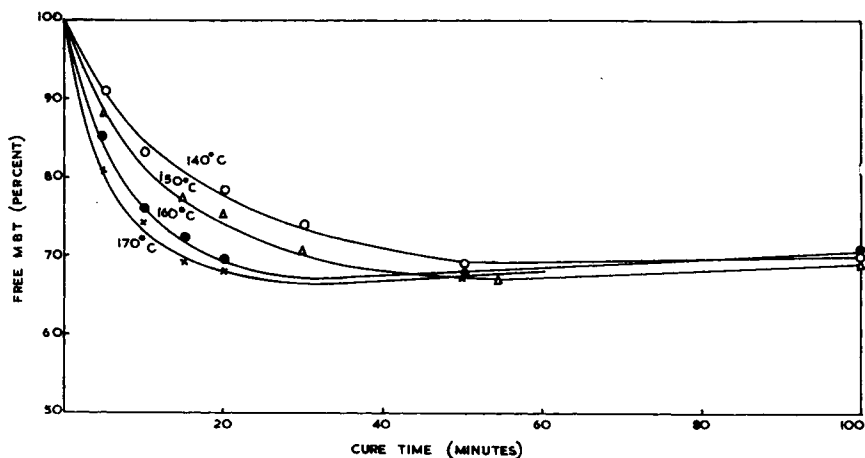


Fig. 3. Disappearance of MBT with time. Stock: rubber, 100 parts; sulfur, 4.654 parts; MBT, 0.8896 part.

TABLE III
Disappearance of MBT with Time at Different Temperatures^a

Cure temperature, °C.	Cure time, min.	Free MBT, %
140	5	91.27
	10	83.50
	20	78.96
	30	74.61
	50	68.97
	100	70.22
	150	69.47
150	5	88.85
	15	78.06
	20	76.00
	25	75.70
	30	71.20
	54	67.99
	100	69.08
160	207	69.64
	5	85.94
	10	76.19
	15	72.59
	20	70.19
	50	69.45
	100	71.59
170	5	80.93
	10	74.85
	15	69.18
	20	68.95
	50	67.95

^a Composition of the stock: rubber, 100 parts by weight, sulfur, 4.654 parts; MBT, 0.8896 parts.

by the data presented. This must be counterbalanced by sufficient decrease of activation energy in order that the reaction may be accelerated. It is seen that the activation energy is decreased by about 7 kcal., which must have contributed to the acceleration as found in these experiments. This means that the accelerator should be relatively more effective at lower temperatures, which also agrees with the practical observations.

Equation (1) may appear to be second-order, i.e., first-order in sulfur and first-order in accelerator, but it should be remembered that accelerator concentration is too small in comparison to sulfur. Also, secondary reactions, as shown in eq. (2), take place, and these may generate radicals by decomposition of the primary products and regeneration of the accelerator. Due to these reasons, consumption of the accelerator is very small compared to sulfur as will be seen in Tables II and III and Figures 1 and 3. The over all reaction would thus still be unity owing to the disappearance of sulfur only.

Figure 3 and Table III show disappearance of the MBT accelerator at different temperatures. It will be observed that almost a constant amount of accelerator is consumed, irrespective of the temperature of vulcanization.

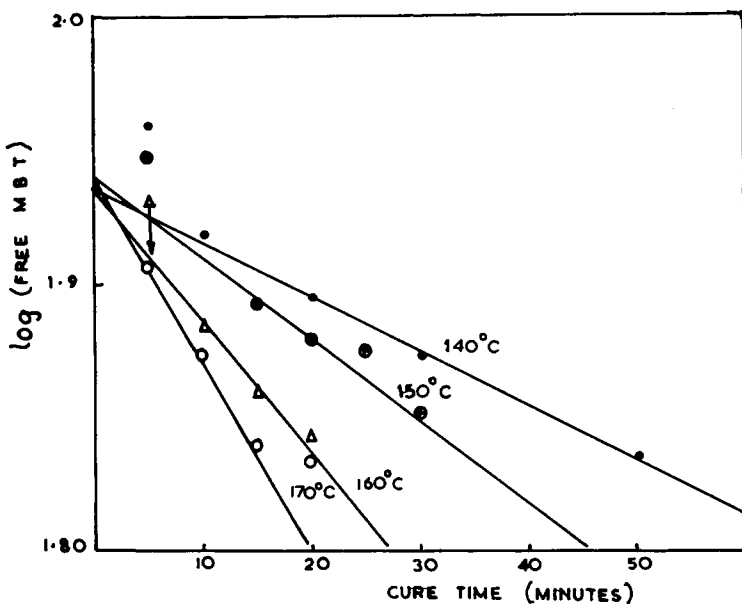


Fig. 4. First-order kinetic plot of disappearance of MBT with time. Stock: rubber, 100 parts; sulfur, 4.654 parts; MBT, 0.8896 part.

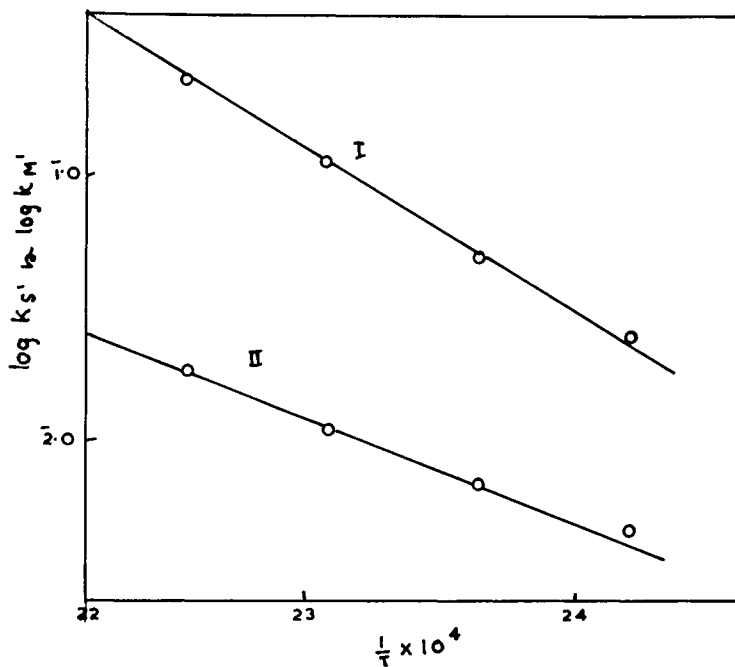


Fig. 5. Arrhenius plot for the reaction of sulfur and MBT: (I) sulfur consumption; (II) MBT consumption. Stock: rubber, 100 parts; sulfur, 4.654 parts; MBT, 0.8896 part.

TABLE IV
 Arrhenius Parameters for Reaction of MBT^a

Cure temperature, °C.	Rate constants $K_M \times 10^2, \text{min.}^{-1}$	Energy of activation, kcal./mole	Frequency factor
140	0.4609	18.8	3.2×10^7
150	0.6909		
160	1.1050		
170	1.6120		

^a Composition of the stock.

Also, accelerator consumption takes place only as long as sulfur is consumed, indicating that accelerator is tied up with the consumption of sulfur by a particular reaction or reactions. A first-order kinetic plot of MBT

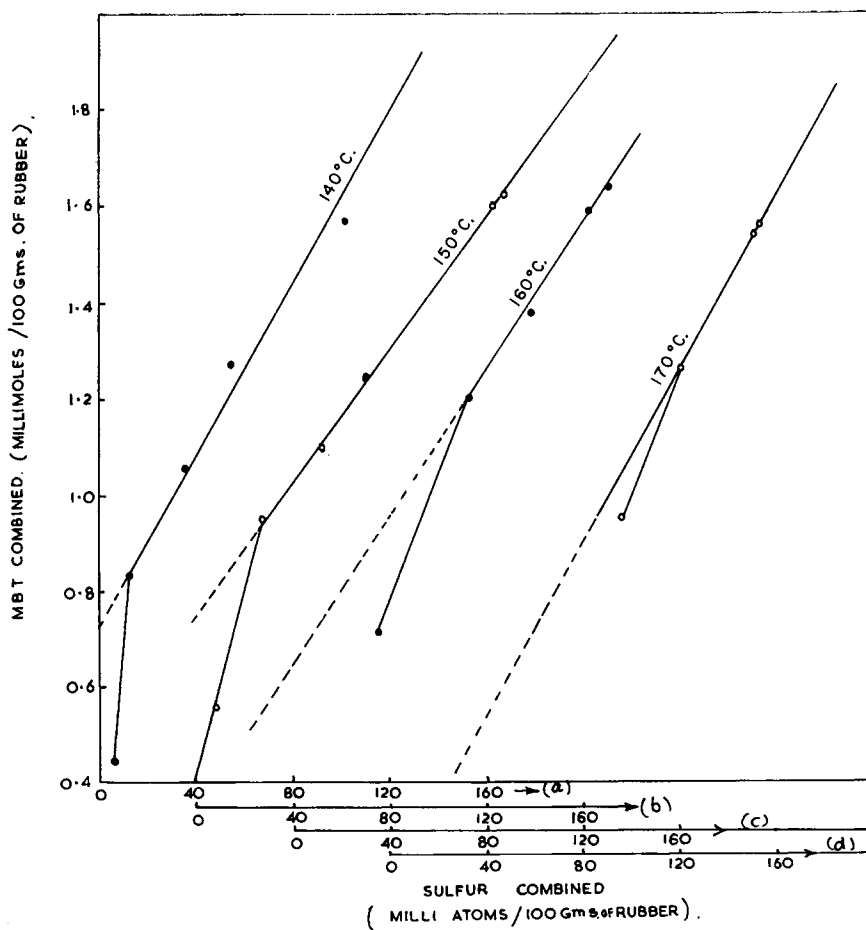


Fig. 6. Relation between combined sulfur and combined MBT during vulcanization. Stock: rubber, 100 parts; sulfur 4.654 parts; MBT, 0.8896 part.

consumption gives fairly good straight lines (Fig. 4) except at the beginning of the reaction, during which time rate of consumption is much faster. As stated above, the accelerator is also regenerated as vulcanization progresses, which may explain slower consumption of the accelerator compared to that at the beginning. Table IV gives the value of the rate constants, energy of activation, and frequency factor calculated from Figure 5. As the energy of activation (18.8 kcal./mole) is much lower than that obtained for the disappearance of sulfur, it may be inferred that accelerator radicals would be produced earlier than sulfur biradicals, which is in agreement with the mechanism supported in this investigation.

Figure 6 represents the plot of MBT consumption against sulfur consumption during vulcanization which follows a linear relation. The quicker disappearance of MBT at the beginning is shown clearly in this figure. It is also seen that the slope of the straight lines which are measures of the number of sulfur atoms consumed per molecule of MBT is almost constant at all temperatures and shows a combination of about 133 sulfur atoms for every molecule of MBT. This clearly shows that the reaction is not as simple as shown in the eq. (1). The regeneration of MBT as mentioned above may in some measure account for the low consumption of MBT compared to sulfur. It may mainly be ascribed to the formation of polysulfide bridges containing a good number of sulfur atoms. Apart from this, sulfur combination is also activated by secondary radicals which would also greatly increase the difference. However, sufficient information is not yet available about the role of the side reactions which take place.

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Résumé

On présente les résultats cinétiques de la vulcanisation du caoutchouc au moyen de soufre, accélérée par MBT. On détermine la diminution de concentration du soufre et du MBT durant la vulcanisation sous diverses conditions de températures par une méthode ampérométrique précise développée par les auteurs. On trouve l'unité pour l'ordre de la réaction de disparition du soufre. L'énergie d'activation et le facteur de fréquence sont de 28,8 Kcal par mole et de $4,0 \times 10^{13}$ respectivement. La vitesse de disparition du MBT est aussi du premier ordre et la vitesse de réaction, l'énergie d'activation aussi bien que le facteur de fréquence sont beaucoup plus bas que ceux pour la disparition du soufre. Le soufre se consomme aussi longtemps qu'il y a du soufre libre présent dans l'échantillon indiquant que la consommation de MBT est intimement liée à la disparition du soufre. On trouve qu'environ 133 atomes de soufre sont consommés par la disparition d'une molécule de MBT. Le mécanisme d'ouverture du cycle impliquant une attaque par le radical accélérateur proposé par Gordon est confirmé par l'étude présente.

Zusammenfassung

Es werden kinetische Daten für die mit MBT beschleunigte Vulkanisation von Kautschuk mit Schwefel angegeben. Der Verbrauch von Schwefel und MBT während der Vulkanisation bei verschiedenen Temperaturen wurde mittels der von den Autoren entwickelten genauen amperometrischen Methode bestimmt. Die Schwefelkonzentration nimmt nach erster Ordnung ab; Aktivierungsenergie und Häufigkeitsfaktor sind 28,8 kcal/Mol bzw. $4,0 \times 10^{13}$. Der Verbrauch von MBT verläuft ebenfalls nach erster Ordnung, Aktivierungsenergie und Häufigkeitsfaktor sind jedoch viel kleiner als beim Verbrauch von Schwefel. Es wird so lange Schwefel verbraucht, wie freier Schwefel in der Probe enthalten ist. Dies weist darauf hin, dass der Umsatz von MBT in enger Beziehung zum Schwefelverbrauch steht. Einem Umsatz von einem Molekül MBT entspricht ein Verbrauch von 133 Atomen Schwefel. Durch die vorliegende Untersuchung wird der von Gordon vorgeschlagene Mechanismus der Ringöffnung durch einen Angriff des Beschleunigeradikals gestützt.

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