

## KINETICS AND MECHANISM OF THE REACTION OF 2-MERCAPTOBENZOTHAZOLE WITH N-(CYCLOHEXYLTHIO)PHTHALIMIDE AND RELATED COMPOUNDS

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### 要 約

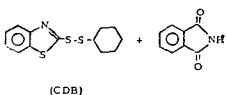
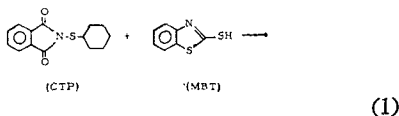
反應速度面에서의 動力學的 研究結果에 依하면 2-메르카토펜조티아졸(MBT)은 N-*t*-부틸-2-벤조티아졸설펜아미드(BBTS) 또는 2-(4-몰폴리노티오) 벤조티아졸(OBTS)과 같은 加黃促進劑들 보다는 N-(사이클로헥실티오)프탈이미드(CPT)가 훨씬 더 빨리 反應한다는 事實을 探知하였다.

또한 優秀한 加黃遲延劑는 MBT와 急速히 反應하여야 하지만은 窒素와 黃과의 化學結合이 너무 弱하여 耐熱安定성이 없으므로 아무리 MBT와 빠른 速度로 反應하여도 좋은 加黃지연제가 될수는 없다. 예를들면 N-(사이클로헥실티오)-*O*-벤조티아졸설펜아미드(CTBS))는 CTP보다 더 빨리 MBT와 反應하지만 熱安定성이 不足하여 加黃지연제로서는 CTB 보다 좋지 못하다.

### INTRODUCTION

N-(Cyclohexylthio)phthalimide (CTP) is a new commercial retarder which is very effective in a wide range of conventional sulfur cure systems.

The mechanism of scorch delay by CTP was recently published<sup>1</sup>. In their paper, Leib and coworkers concluded that retardation of rubber vulcanization by CTP is due to the removal of 2-mercaptobenzothiazole (MBT) by CTP forming 2-cyclohexyldithiobenzothiazole (CDB) as shown in Reaction (1).



This facile reaction was extended to synthesize unsymmetrical disulfides<sup>2,3</sup>. To our knowledge there are no published reports on the kinetics and mechanism of the above and related reactions.

In this paper we describe the results of our work on the studies of the kinetics and mechanisms of these reactions. We also correlated this data with the scorch delay shown by various sulfenamide type retarders.

*Abbreviations.* ~N-(Cyclohexylthio) phthalimide (CTP), 2-mercaptobenzothiazole (MBT), N-*t*-butyl-2-benzothiazole sulfenamide (BBTS), 2-(4-morpholiniothio) benzothiazole (OBTS), N-(trichloromethylthio) phthalimide (TCMP), N-(trichloromethylthio)-*o*-benzoic sulfimide (TCMS), N-(cyclohexylthio)-*o*-benzoic sulfimide (CTBS), N-(*p*-tolylthio)-*o*-benzoic sulfimide (PTTS).

### RESULTS AND DISCUSSION

Our kinetic studies were carried out in a UV

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**Table 1. Kinetic Data of Reactions between 2-Mercaptobenzothiazole and Various Sulfenamides At Equimolar Concentration of  $1.79 \times 10^{-5}$  mole.**

Experiment	Reactants		Temp., °C	Solvent	$k_1$ , $l\text{mole}^{-1}\text{sec}^{-1}$	$t_{30\%}^a$ , min	$\frac{k_1}{k_1(\text{run}2)}$	$\frac{t_{30\%}}{t_{30\%}\text{run}2}$
1	1 CTP	1 MBT	23	CH <sub>2</sub> Cl <sub>2</sub>	0.22	124	0.03	16.1
2	1 CTP	1 MBT	100	$\phi\text{CH}_3$	0.78 <sup>b</sup>	7.7	1.00	1.00
3	1 CTP	1 MBT	100	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	0.93 <sup>b,d</sup>	6.5	1.20	0.8
4 <sup>e</sup>	1 CTP	1 MBT	100	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	0.93 <sup>d</sup>	6.5	1.20	0.8
5	1 CTP	1 MBT	23	DMF	very fast	instantaneous		
6 <sup>c</sup>	1 BBTS	1 MBT	100	$\phi\text{CH}_3$	0.17	33.6		4.4
7 <sup>c</sup>	1 BBTS	1 MBT	100	$\phi\text{Cl}$	0.23	21.0		2.7
8 <sup>c</sup>	1 OBTS	1 MBT	100	$\phi\text{CH}_3$	0.17	82.7		10.7
9	1 TCMP	1 MBT	100	$\phi\text{CH}_3$	0.007 <sup>b</sup>	227.0	0.09	29.5
10	1 TCMS	1 MBT	100	$\phi\text{CH}_3$	4.30 <sup>b</sup>	<1.4	5.5	
11	1 PTTS	1 MBT	23	$\phi\text{CH}_3$	very fast <sup>f</sup>	instantaneous		
12	1 CTBS	1 MBT	23	CH <sub>2</sub> Cl <sub>2</sub>	very fast <sup>f</sup>	instantaneous		
13	1 CTP	1 BBTS	100	$\phi\text{CH}_3$	very slow	>90		
14	1 CTP	1 BBTS	100	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	very slow	>420		

<sup>a</sup> Time required to react 30% (weight per cent) of MBT.

<sup>b</sup> Data obtained by using computerized least square method.

<sup>c</sup> Data obtained by analogue computer.

<sup>d</sup> An average of two experimental values.

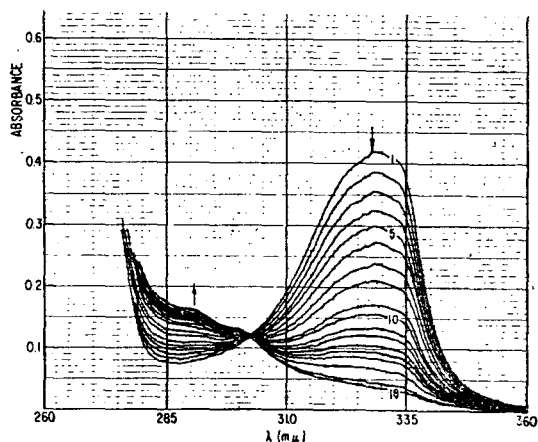
<sup>e</sup> The reaction was run in the presence of di-*t*-butyl-*p*-cresol ( $8.95 \times 10^{-5}$  or  $4.48 \times 10^{-5}$  mole).

<sup>f</sup> Various concentrations(1 to 0.1 molar ratios to MBT) were used. All reacted instantaneously.

cell maintained at constant temperature. The progress of the reaction was followed by taking a UV spectrum of the reaction mixture at desired intervals. 2-Mercaptobenzothiazole (MBT) has a maximum at 328nm( $\epsilon=25,090$  in *s*-tetrachloroethane). Since there is no interference by the compounds we are interested in at this wavelength, the rate of disappearance of MBT in the presence of various sulfenamides can be obtained conveniently. In order to simplify the kinetic studies further, equimolar amounts of reactants were used in most cases. A summary of the kinetic data is shown in Table 1.

The reaction between MBT and N-(cyclohexylthio) phthalimide (CTP) was studied under various conditions (Experiments 1 through 5). The reaction is very slow at room temperature and only 8 per cent of MBT reacts after about 38 min in dichloromethane. However, at 100°C the reaction is quite fast. In either toluene (see Figure 1) or 1,1,2, 2-tetrachloroethane (see Figure 2) the rate constant increases more than 30 times at 100°C. In DMF the reaction was so fast

that we could not measure the reaction rate. 2,6-Di-*t*-butyl-*p*-cresol (CAO-1) has no effect on



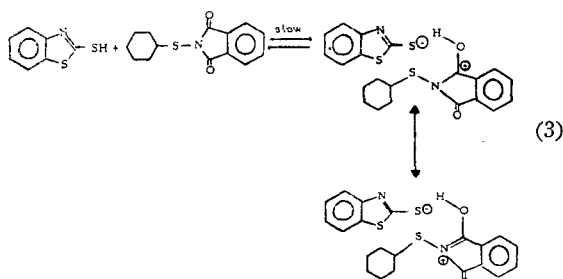
**Fig. 1. Ultraviolet absorption spectra which show the progress of the reaction between N-(cyclohexylthio) phthalimide (CTP) and MBT (equimolar) in toluene at 100°C. The maximum of MBT at 328 nanometers (nm =  $m\mu$ ) decreases progressively: line 5(after 7.00 min), line 10 (after 21.50 min), line 38 (after 90.25 min).**

the reaction rate (see Experiment 4). Thus, we ruled out a free radical chain mechanism and concluded that the reaction between MBT and CTP [Reaction(1)] is an ionic reaction.

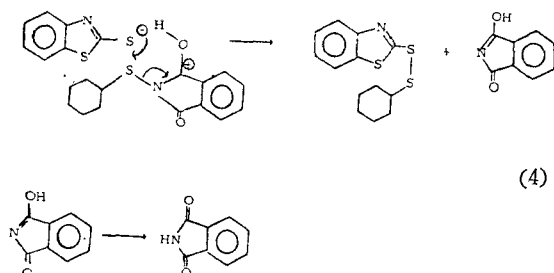
Moreover, the rate of disappearance of MBT in Reaction (1) is first order in MBT concentration and first order in CTP concentration as shown in Figures 3, 4, and 5. The rate expression for Reaction (1) is simply

$$-d[\text{MBT}]/dt = k_1[\text{MBT}][\text{CTP}] \quad (2)$$

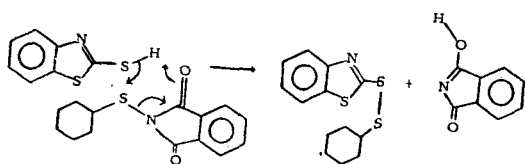
From these observations we believe that the rate controlling step is the formation of ion pair as shown in resonance structure a of Reaction (3).



This is followed by the formation of a —S—S— bond and the breakage of a —S—N< bond as shown below in Reaction (4).



An alternative mechanism is the six-center concerted reaction shown in Reaction (5).



In view of the large rate enhancement in polar solvents we favor the mechanism which involves the ion-pair a, shown in Reaction (3). The

reaction is quite fast in toluene at 100°C, and more than 90 per cent of the MBT reacts with CTP within 90 min. The reaction is practically irreversible.

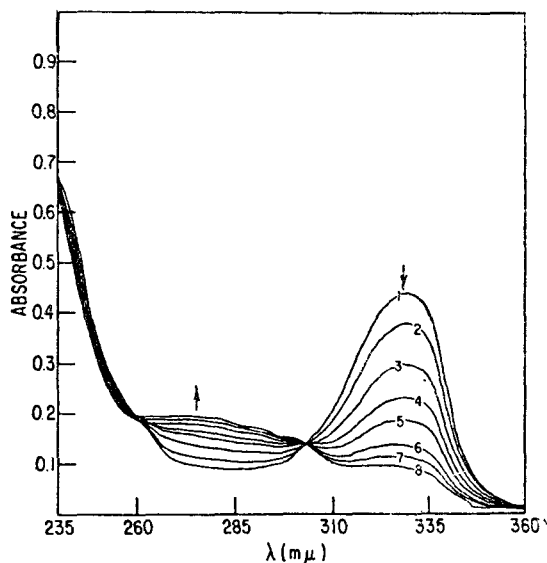
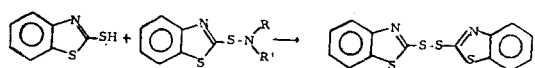


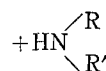
Fig. 2. Ultraviolet absorption spectra which show the progress of the reaction between N-(cyclohexylthio) phthalimide (CTP) and MBT (equimolar) in 1, 1, 2, 2-tetrachloroethane at 100°C. The maximum of MBT at 328 nanometers ( $\text{nm} = \text{m}\mu$ ) decreases progressively: line 3 (7.25 min), line 5 (15.00 min), line 8 (38.50 min).

On the other hand, the reaction of MBT with either N-*t*-butyl-2-benzothiazole sulfenamide (BBTS) or 2-(4-morpholiniothio) benzothiazol (OBTs) is not a simple second order reaction. Here, the products are *bis*(benzothiazolyl) disulfide (MBTS) and *t*-butylamine or morpholine as shown in Reaction (6).



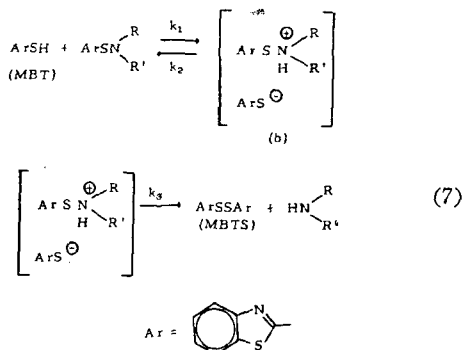
(MBT) BBTS:  $\text{R} = \text{H}$ ,  $\text{R}' = \text{C}(\text{CH}_3)_3$ , (MBTS) (6)

OBTs:  $\text{R}$  and  $\text{R}' = \begin{matrix} \diagup \\ \text{O} \\ \diagdown \end{matrix}$



The reactions were followed as in Reaction (1) by UV spectrophotometry. (See Figures 6 and 7). The kinetics of these reactions were analyzed by an analog computer. The excellent

agreements between the theoretical curves and the experimental points are shown in Figures 8 and 9. The rate expression for this theoretical curve involves an intermediate  $\underline{b}$  which does not establish a rapid equilibrium and  $d[b]/dt \neq 0$ . See Reaction (7).



The rate equation for the rate of [MBT] disappearance is shown in Equation(8).

$$-d[\text{MBT}]/dt = k_1[\text{MBT}] \left[ \text{ArSN} \begin{array}{l} \text{R} \\ \text{R}' \end{array} \right] - k_2[\underline{b}] \quad (8)$$

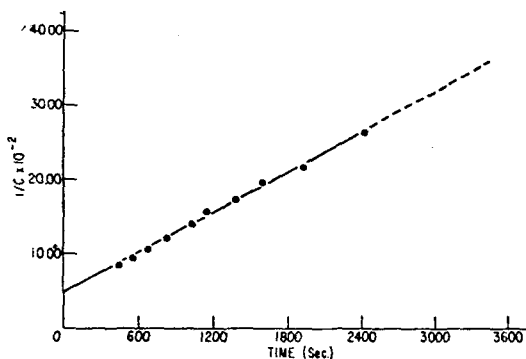


Fig. 3. A second order plot for the reaction of N-(cyclohexylthio) phthalimide (CTP) with 2-mercaptobenzothiazole (equimolar) in the presence of 2, 6-di-t-butyl-p-cresol(CAO-1) (the molar ratio of CTP to CAO-1 is 1:0.025 in 1, 1, 2, 2-tetrachloroethane at 100°C).

and that for the formation of MBTS is shown in Equation (9),

$$d[\text{MBTS}] = k_3[\underline{b}] \quad (9)$$

Surprisingly, the  $k_1$  value for the BBTs-MBT reaction is the same as that for the OBTS-MBT reaction. But, we see a big difference in  $k_3$  values. The  $k_3$  value for the OBTS-MBT reaction is about  $\frac{1}{5}$  of that for the BBTs-MBT reaction. It is noteworthy that these reactions also fit,

within experimental error, to the following kinetic expression, Equation (10).

$$-d[\text{MBT}]dt = k_1[\text{MBT}][\text{OBTS or BBTs}] - k_2[\text{MBTS}] \quad (10)$$

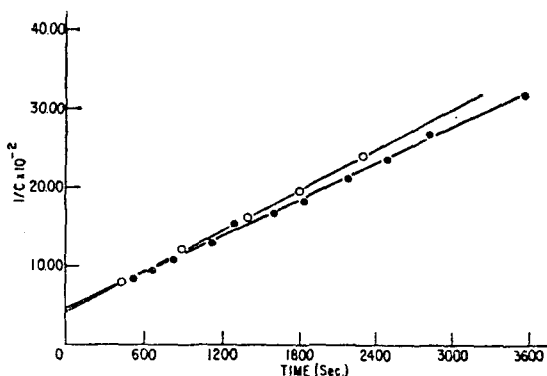
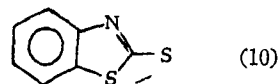


Fig. 4. Second order plots for the reaction of N-(cyclohexylthio) phthalimide (CTP) with 2-mercaptobenzothiazole (equimolar) in different solvents at 100°C: •, in toluene, ○, in 1, 1, 2, 2-tetrachloroethane.

This rate equation is readily derived if one assumes the formation of MBT from the reaction of the MBT radical, with solvent and if one makes a steady-state approximation of the concentration of the MBT radical which arises from MBTS. If the rate expression, Equation (10), operates rather than Equations (8) and (9), then we expect great differences in values of rate constants by changing the solvent from toluene to chlorobenzene because chlorobenzene cannot donate a hydrogen atom to MBT radical as toluene can. As shown in Table 1 (Experiments 6 and 7), there was no great difference. Thus, we can exclude the rate expression, Equation (10), for the reaction between MBT and sulfenamide type accelerators.

These reactions can be compared with the CTP-MBT reaction in terms of  $t_{30\%}$  which is the time required to react 30 weight per cent of MBT. Clearly the CTP-MBT reaction is much faster than either the BBTs-MBT reaction (about 4.4 times the  $t_{30\%}$  of CTP-MBT reaction) or the OBTS-MBT reaction.

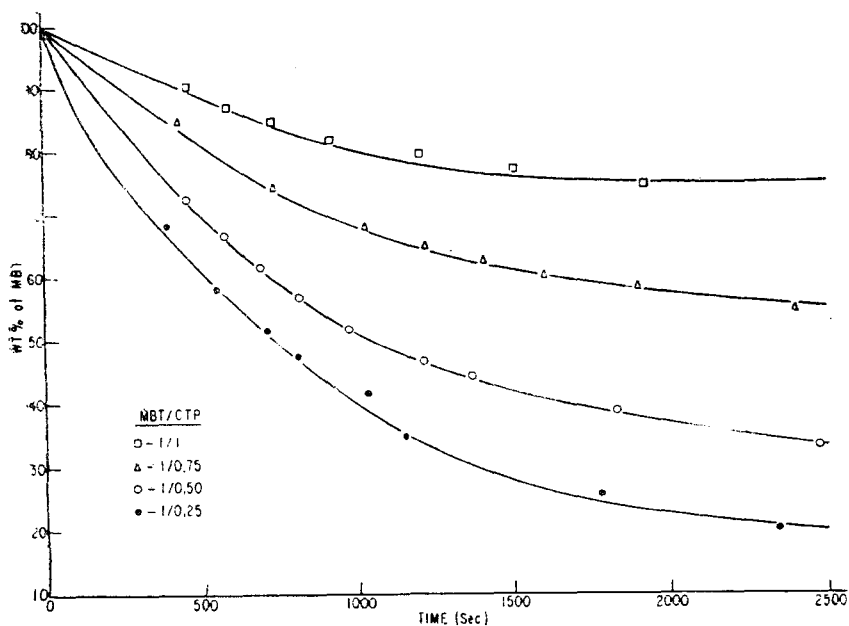


Fig. 5. Plots of weight per cent of MBT as a function of time for the reaction of N-(cyclohexylthio) phthalimide (CTP) with 2-mercaptobenzothiazole (MBT) in 1, 1, 2, 2-tetrachloroethane at 100°C.

(about 10.7 times the  $t_{30\%}$  of CTP-MBT reaction).

These results indicate that a good retarder should be able to react with MBT before MBT has a chance to attack a non-scorchy acselerator

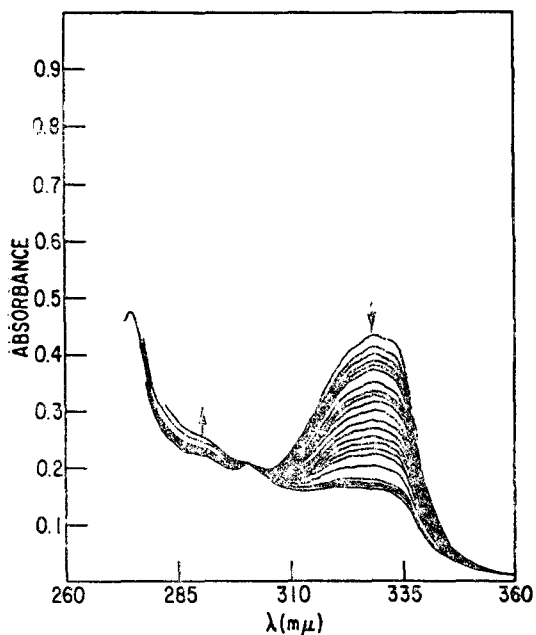
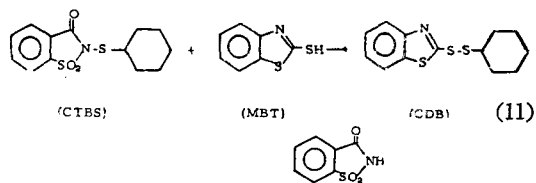


Fig. 6. Ultraviolet absorption spectra which show the progress of the reaction between N-t-butyl-2-benzothiazole sulfenamide(BBTS) and MBT (equimolar) in toluene at 100°C.

such as BBTS or OBTS. But this is not a sole requirement for a good retarder as shown in the following example.

N-(cyclohexylthio)-*o*-benzoic sulfimide (CTBS) reacts fast with MBT in the manner shown in Reaction (11).



Even at room temperature this reaction is 100 per cent complete instantaneously. This is true regardless of the ratio between MBT and CTBS (see Figure 10) We also note that curve 5 in Figure 10 is superimposable on either line a or b in Figure 11. This figure shows UV spectra of an authentic sample of 2-cyclohexyldithiobenzothiazole(CDB). (See Experimental.) CDB has two maxima, at 271nm ( $\epsilon=10,400$  in  $\text{CH}_2\text{Cl}_2$ ) and 224nm ( $\epsilon=19,700$  in  $\text{CH}_2\text{Cl}_2$ ).

Surprisingly, CTBS is not as good a retarder as CTP. In view of its extremely fast reaction with MBT, we expected CTBS to be a more

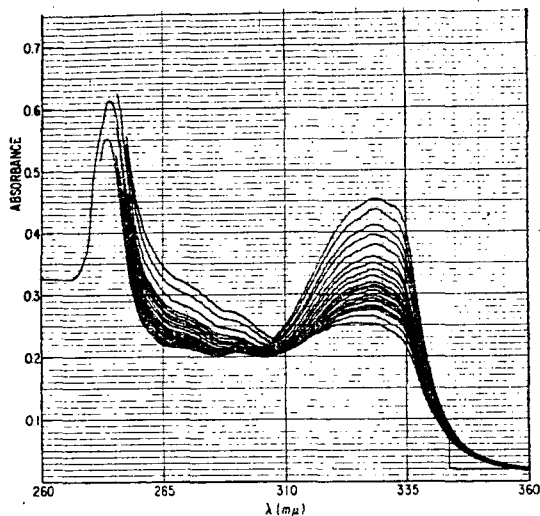


Fig. 7. Ultraviolet absorption spectra which show the progress of the reaction between 2-(4-morpholiniothio) benzothiazole (OBTS) and MBT (equimolar) in toluene at 100°C.

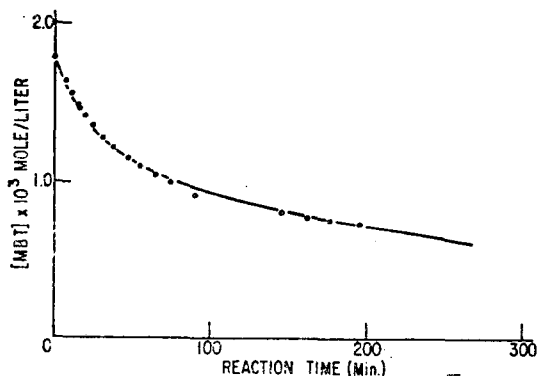


Fig. 8. On Analog computer analysis: the superposition of experimental points (circles) and of the best fit theoretical curve (curve) for the reaction of N-t-butyl-2-benzothiazole sulfenamide (BBTS) with an equimolar amount of 2-mercaptobenzothiazole (MBT) in toluene at 100°C.

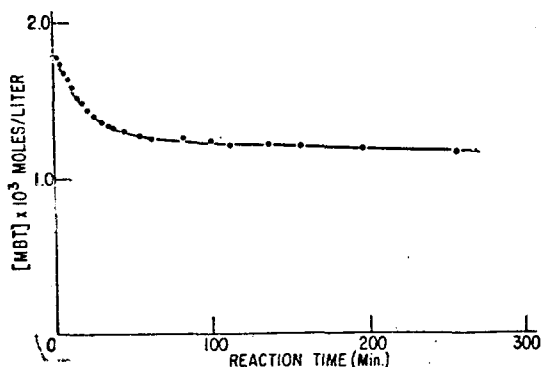


Fig. 9. Analog computer analysis: the superposition of experimental points (circles) and of the best fit theoretical curve (curve) for the reaction of 2-(4-morpholiniothio) benzothiazole (OBTS) with an equimolar amount of 2-mercaptobenzothiazole (MBT) in toluene at 100°C.

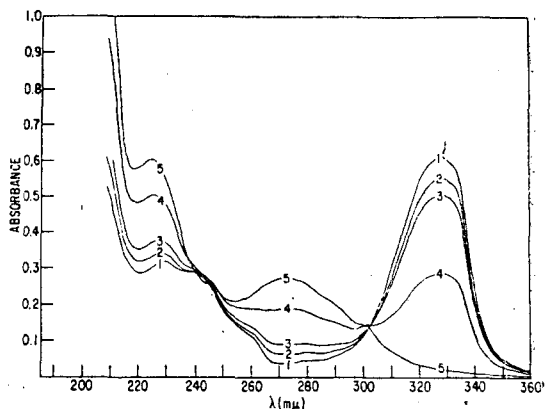


Fig. 10. Ultraviolet absorption spectra of 2-mercaptobenzothiazole (MBT, curve 1) and of the reaction product from MBT and N-(cyclohexylthio)-*o*-benzoic sulfimide (CTBS) in  $\text{CH}_2\text{Cl}_2$  at room temperature. The ratio between MBT and CTBS varies: 2, MBT:CTBS=10.0:1.0; 3, MBT:CTBS=10.0:2.0; 4, MBT:CTBS=10.0:6.0; 5, MBT:CTBS=10.0:10.0.

effective retarder than CTP (see Tables II and III). Further, we found that *o*-benzoic sulfimide, which is a reaction product of Reaction (11), has no effect on scorch time. However, we found that

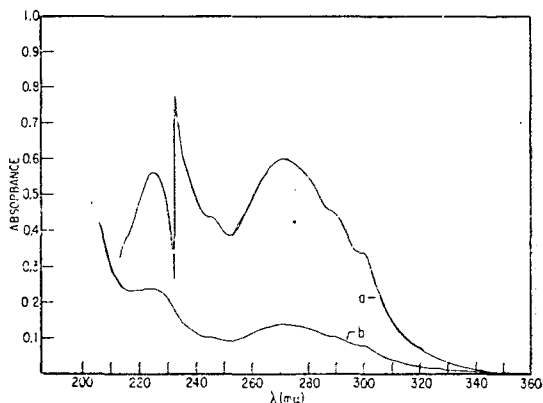
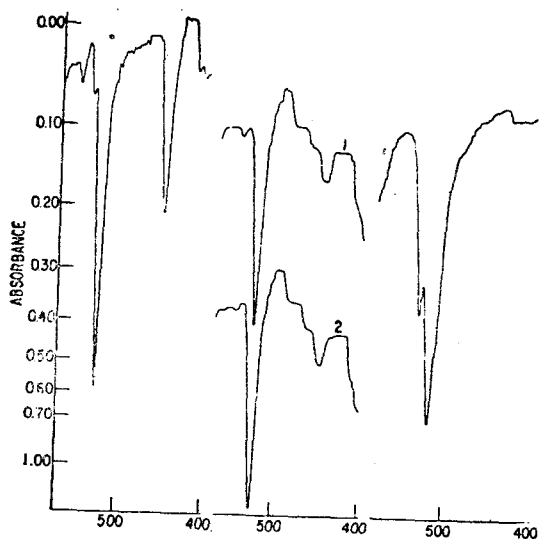


Fig. 11. Ultraviolet absorption spectra of 2-cyclohexyldithiobenzothiazole (CDB) in  $\text{CH}_2\text{Cl}_2$  at room temperature: a, cell path length = 0.0505cm, conc. = 0.300g/l; b, cell path length = 0.0103cm, conc. = 0.300g/l.

CTBS is thermally unstable in EPDM at 140°C. It forms *o*-benzoic sulfimide after only 15 min heating. This change was monitored by IR spectroscopy. The spectral changes are shown in Figures 12 and 13. The bond at  $518\text{cm}^{-1}$ , which is characteristic only of *o*-benzoic sulfimide:

**Table II Recipe for the Control Stock**

	wt., g.
Natural rubber	100
Zinc oxide	5.00
Stearic acid	3.00
HAF black	50
OBTS	1.00
Sulfur	2.50



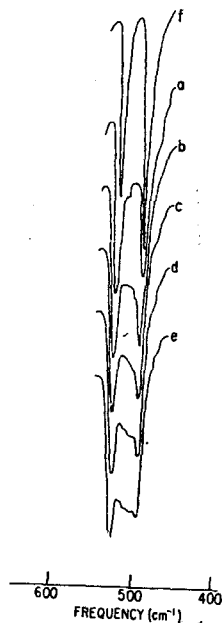
**Fig.12.** A (left). Infrared spectrum ( $500\text{cm}^{-1}$  region) of N-(cyclohexylthio) phthalimide (CTP) at room temperature (KBr pellets). B(center). Infrared spectra of N-(cyclohexylthio) phthalimide (CTP) in EPDM at  $140^\circ\text{C}$ : 1, 15 min heating; 2, 120 min heating. C (right). Infrared spectra (KBr pellets) of *o*-benzoic sulfimide at room temperature.

**Table III Delay of Vulcanization by Various Retarders<sup>a</sup> at  $284^\circ\text{F}$  in Natural Rubber**

	Scorch time (min.) <sup>a</sup>	Increase%
Control	8.9	—
Control+1 phr CTP	26.2	194
Control+1 phr TCMP	10.9	23
Control+1.14 phr <sup>b</sup> TCMP	11.0	23
Control+1 phr TCMS	10.8	21
Control+1.28 phr <sup>b</sup>	14.2	60
Control+1 phr CTBS	11.7	31
Control+1.18 phr PTTS	11.5	29

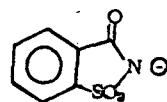
<sup>a</sup> Time required to rise 1 chart unit above the minimum torque. (Programmed BLG Cone Curometer was used to obtain scorch time.)  
<sup>b</sup> Equimolar to 1 phr CTP.

<sup>c</sup> Abbreviations: See Introduction.

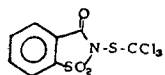


**Fig.13.** Infrared spectra ( $500\text{cm}^{-1}$  region) of N-(cyclohexylthio)-*o*-benzoic sulfimide(CTBS) in EPDM at  $140^\circ\text{C}$ : a, 15 min heating; b, 30 min heating; c, 45 min heating; d, 60 min heating; e, 120 min heating; f, an infrared spectrum (KBr pellet) of CTBS at room temperature.

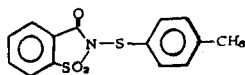
(among the compounds with which we are concerned), grows as CTBS is subjected to  $140^\circ\text{C}$  heating in EPDM. EPDM has no absorbance greater than 0.09 in the  $700\text{-}400\text{cm}^{-1}$  region. We observed no such thermal instability with CTP. As shown in Figures 12 A and 12 B, aging at  $140^\circ\text{C}$  has no effect on the infrared spectrum of CTP even after two hours. We ascribe the thermal instability of CTBS to the facile formation of a stable anion, c.



The thermal instability of the sulfenamides of *o*-benzoic sulfimide is such a predominant factor that introducing electron withdrawing or donating groups on the sulfur atom does not improve its efficiency as a retarder. For example, the reaction between MBT and N-(trichloromethylthio)-*o*-benzoic sulfimide (TCMS) in toluene at  $100^\circ\text{C}$  has a  $k_1$  value of  $4.30\text{ l mole}^{-1}$



(TCMS)



(PTTS)

$\text{sec}^{-1}$  (see Figure 14). This is about 5.6 times faster than the reaction between CTP and MBT. Yet TCMS is only one-third as effective as CTP. Similarly, *N*-(*p*-tolylthio)-*o*-benzoic sulfimide (PTTS) reacts very fast with MBT, but it is about one-seventh as effective as CTP.

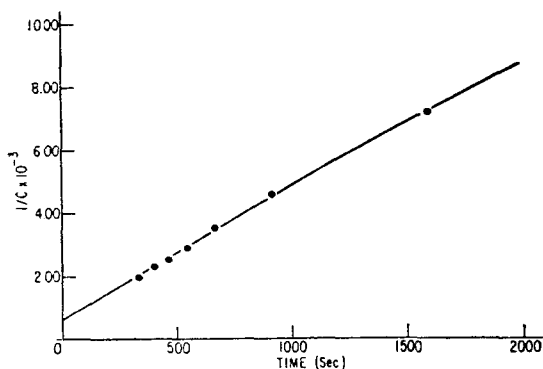
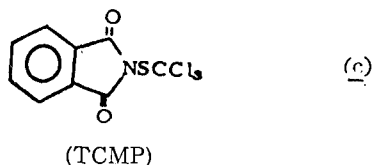


Fig.14. A second order plot for the reaction of *N*-(trichloromethylthio)-*o*-benzoic sulfimide with 2-mercaptobenzothiazole (equimolar) in toluene at 100°C.

Conspicuously, the reaction between MBT and *N*-(trichloromethylthio)-phthalimide (TCMP) in toluene at 100°C, follows the kinetics of a second order reaction for about 2.5h. It then deviates



(TCMP)

from the second order reaction (see Figure 15). Since the "normal" reaction is very slow ( $k_1 = 0.007 \text{ l mole}^{-1} \text{ sec}^{-1}$ ), we believe the displacement of chloride ion by MBT by from a carbon atom<sup>4</sup> parallels the "normal" reaction. TCMP is about oneeighth as efficient as CTP as a retarder.

Extending the argument for the reactivity of the sulfenamides of *o*-benzoic sulfimide, we postulate that the sulfenamides of *o*-benzenedisulfonimide are poor retarders due to their thermal instability, but they should be excellent substitutes<sup>5</sup> for the synthesis of unsymmetrical disul-

fides with various mercaptans.

## EXPERIMENTAL

UV spectra were obtained from Beckman spectrophotometer DK2A. All the solvents were spectral grade and were used as received. Absorptivity of 2-mercaptobenzothiazole (MBT) changes with temperature and solvent. These changes are shown in Figures 16 and 17, and the corrected absorptivities were used in the calculations of the MBT concentrations.

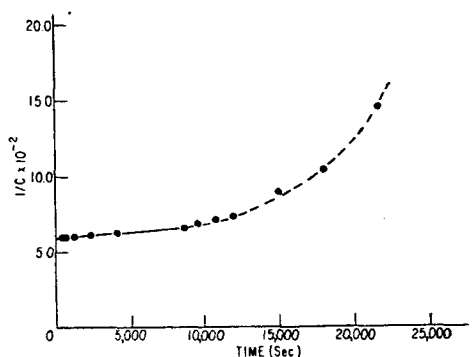


Fig.15. A second order plot for the reaction of *N*-(trichloromethylthio)-phthalimide with 2-mercaptobenzothiazole (equimolar) in toluene at 100°C.

All the chemicals were recrystallized from a suitable solvent before use. Elemental analyses were obtained only for new compounds. The structures of the new compounds were further substantiated by IR, NMR, and mass spectral data.

The commercially available 2-mercaptobenzothiazole (MBT) was recrystallized from ethanol to obtain a solid which melts at 183-186°C. *N*-*t*-butyl-2-benzothiazole sulfenamide (BBS) was prepared via a conventional method using commercial bleach as the oxidizing agent. The solid which recrystallized from hexane-acetone melted at 108-110°C. Commercial 2-(4-morpholiniothio)benzothiazole (OBTS) was recrystallized from benzene to give water white crystals which melt at 80-81°C. *N*-(Trichloromethylthio)-phthalimide (TCMP) was prepared by the method described by Hendrickson and coworkers<sup>5</sup>. The recrystallized products (from benzene) melted at 175-178°C



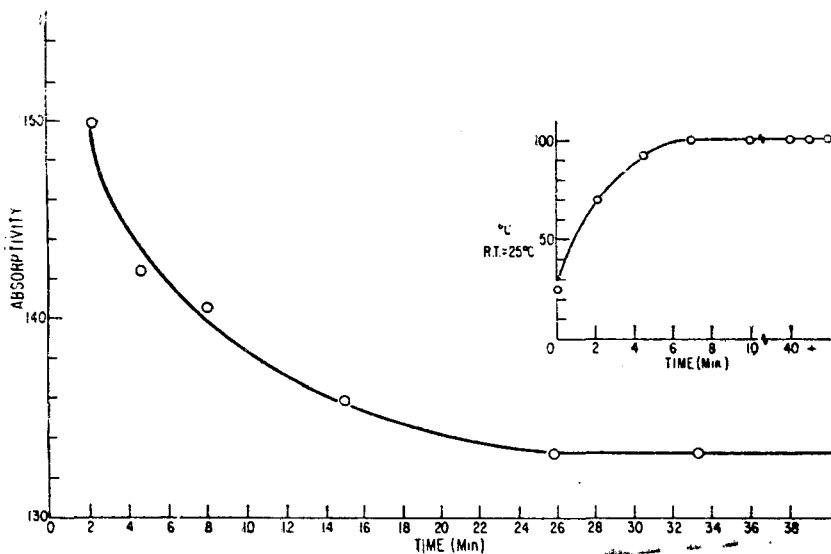


Fig. 16. Absorptivity of MBT as a function of time in *s*-tetrachloroethane in a temperature controlled cell holder at 100°C.

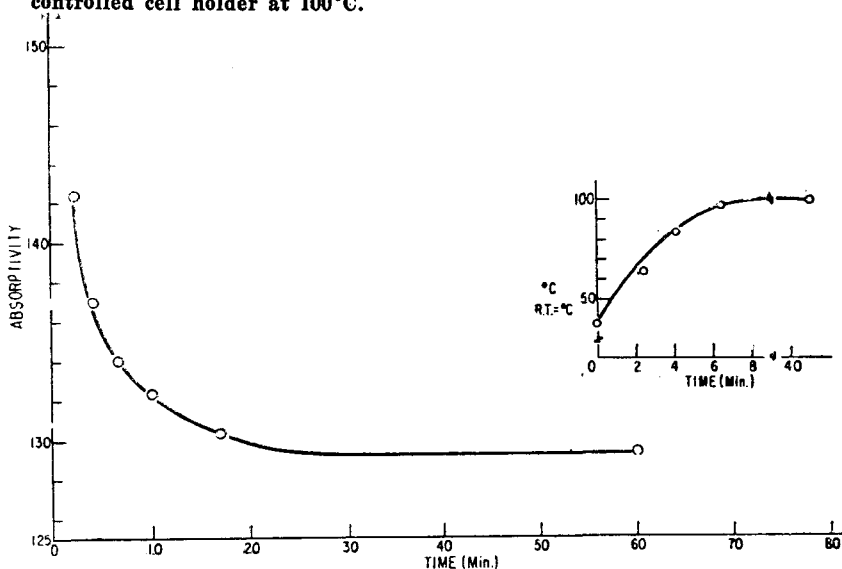


Fig. 17. Absorptivity of MBT as a function of time in toluene from room temperature to 100°C.

(lit.<sup>5</sup>, 165–170°C). *N*-(Trichloromethylthio)-*o*-benzoic sulfimide (TCMS) was recrystallized from benzene and melted at 143–150°C (lit.<sup>6</sup>, 144–144.5°C). *N*-(Cyclohexylthio) phthalimide was prepared by following Cohen's procedure<sup>7</sup>. The solid recrystallized from heptane had a m.p. of 93–95°C (lit.<sup>7</sup>, 93–94°C).

Preparation of *N*-(Cyclohexylthio)-*o*-benzoic Sulfimide (CTBS).—To a stirred solution of cyclohexyl mercaptan (29.0g, 0.25 mole) in 250 ml 250ml of heptane introduced 17.7g (0.25 mole) of chlorine. The temperature was maintained at

–13° to 5°C. Chlorination took one h and 25 min. For about two h a stream of nitrogen was bubbled into the above cyclohexanesulfonyl chloride solution to remove hydrogen chloride. The resulting cyclohexane sulfonyl chloride solution was added dropwise to the slurry of *o*-benzoic sulfimide (45.8g, 0.25 mole) in 500ml CCl<sub>4</sub> and 37.5g of triethylamine. The addition took 30 min. The resulting white slurry was filtered to remove a solid. The filter cake was washed with water to remove triethylammonium hydrochloride. The water insoluble solid weighed

25.9g. This crude product was recrystallized from heptane to give a white solid; m.p., 129-131°C.

Anal. Calc. for  $C_{13}H_{15}NO_3S_2$ : %C, 52.50; %H, 5.08; %N, 4.71; %S, 21.56.

Found: %C, 52.16; %H, 5.21; %N, 4.79; %S, 21.23.

Preparations of 2-Cyclohexyldithiobenzothiazole (CDB).—In all three-necked flask were placed 16.7g (0.1 mole) of 2-mercaptobenzothiazole (MBT) and 26.1g (0.1 mole) of N-(cyclohexylthio)phthalimide in 400 ml of benzene. The above mixture was refluxed for 24h, cooled, and filtered. The mother liquor was concentrated on a rotary evaporator, leaving a mixture of liquid and solid. The solid was separated by addition of hexane followed by filtration. The combined solid weighed 14.7g (quantitative); m.p., 230-233°C. The IR spectrum of this solid is identical with that of phthalimide.

The solvent was removed from the hexane solution leaving a brown syrup. A part of this syrup was further purified by elution chromatography using silica gel as the adsorbant. The eluents were heptane, benzene, ether, acetone, and ethanol in that order. After evaporation of the solvents from a total of 29 cuts, IR spectra were taken. The cuts 10 through 17 yielded a light brown syrup whose IR spectra showed no contamination by phthalimide. They were combined and gave one spot on thin layer chromatography (TLC). TLC showed no impurities such as MBT, MBTS, or phthalimide. The mass spectra showed a molecular ion, m/e, of 281.

Preparation of N-(p-Tolylthio)-o-benzoic Sulfinamide (PTTS).—Following a procedure similar to the synthesis of CTBS, a run was carried out in carbon tetrachloride on a 0.2 mole scale. Filtration of the resulting solid left a white solid, which was washed with water leaving 33.0g of solid. This crude product melts at 139-198°C. An analytically pure sample was obtained as follows: The crude product is partially soluble in cold benzene. The benzene insoluble solid was recrystallized from benzene to give a solid which melts at 190-197°C. Further recrystallization from alcohol failed to raise the melting

point (186.5-195.0°C). The mass spectrum shows a molecular ion at m/e=305.

Anal. Calc. for  $C_{11}H_{11}NO_3S_2$ : %C, 55.06; %H, 3.63; %N, 4.59

Found: %C, 54.73; %H, 3.77; %N, 4.60.

Measurement of Scorch Time.—Scorch time is the time required to rise one chart unit from the minimum torque. These data were obtained from the pressure programmed-B.F.G. Cone Curvometer at 284°F. The pressure (2 or 3 in-lb/min) was applied after a rise of three chart units from the minimum torque. This applied pressure prevents slippage resulting from the shrinkage of the sample during cure.

## CONCLUSIONS AND SUMMARY

Kinetic studies show that 2-mercaptobenzothiazole (MBT) reacts faster with N-(cyclohexylthio)phthalimide (CPT) than with such accelerators as N-*t*-butyl-2-benzothiazole sulfenamide (BBTS) or 2-(4-morpholiniothio)benzothiazole (OBTS). Furthermore, the reaction between N-(cyclohexylthio)-*o*-benzoic sulfimide (CTBS) and MBT is so fast that it reacts almost instantaneously even at room temperature. However, CTBS is not a good retarder due to its thermal instability.

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## REFERENCES

1. R.I. Leib, A.B. Sullivan, and C.D. Trivette, Jr., *Rubber Chem. Technol.*, **43**, 1188 (1970).
2. K. Boustany and A.B. Sullivan, *Tetrahedron Letters*, 3547 (1970).
3. David N. Harpp and coworkers, *Tetrahedron Letters*, 3551 (1970).
4. J. Horák, *Clolec. Czech. Chem. Commun*, **31**, 3189 (1966).
5. J.B. Hendrickson and coworkers, *J. Org. Chem.* **34**, 3434 (1969).
6. A.R. Kittleson, Cranford, U.S. Patent 2,553,770, May 22, 1951.
7. C.A. Cohen, U.S. Patent 2,553,773, May 22, 1951.
3. M. Behforouz and J.E. Kerwood, *J. Org. Chem.* **34**, 51 (1969).