Study on Vulcanization Promoters

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The present paper is devoted primarily to a study of vulcanization promoters indicated by a general formula R–X–C–ZH, where R is methyl or phenyl group and X, Y and Z are heteroatoms such as nitrogen, oxygen and sulfur.

The compounds indicated by the above formula were found to be excellent promoters for vulcanization accelerators, especially for those of the disulfide type. From the results of experiments it is concluded that the promoting action is attributed to the accelerating property of the substances which are produced from the promoters in the vulcanization process. It was found that these promoters were often effective even in the absence of sulfur, and that non-sulfur vulcanization proceeded when disulfide type accelerator-promoter combinations were used. We have assumed the formation of intermediate having six-membered structure, *i.e.*, the combination of the N=C–S 1, 3-dipolar system in accelerators with the Z–C=Y system in promoters. The stabilization of the intermediate ring systems was estimated by the perturbation technique based on the simple LCAO-MO theory. A roughly linear relationship between the stabilization energy in ring system and the promoting ability was found.

INTRODUCTION

Rubber industry has been developed with improvement of rubber chemicals such as vulcanization accelerator, antioxidant, antiscorch agent and peptizer. Tremendous chemicals have been proposed and patented for rubber chemicals, but little work has been done to elucidate the relation between their property and chemical structure. The authors have previously proposed a general principle which governs the chemistry of the above reagents.[1] This paper reports further study on vulcanization accelerators, emphasizing the important role of promoters or the so-called secondary accelerators in vulcanization.

It is found that most of conventional accelerators can be indicated simply by a general formula R–X–C–Z ‖ Y, where X, Y and Z are heteroatoms such as nitrogen, oxygen and sulfur. The compounds of this type contain more than one double bond attached to heteroatoms and form the so-called 1,3–dipolar π–electron system[2] by conjugation of double bond with lone electron pairs on the heteroatoms. A number of compounds can be summarized according to this formula as shown in Tables 1 (a) and 1 (b). The former table involves sulfur atom

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Table 1 (a). Type, $CH_3-X-\underset{\underset{Y}{\|}}{C}-SH$

=Y / -X-	=CH$_2$	=O	=S	=NH
-CH$_2$-	⟨benzene⟩-SH (1)	$CH_3-\underset{\underset{O}{\|}}{C}-SH$ (5)	$CH_3-\underset{\underset{S}{\|}}{C}-SH$ (9)	$CH_3-\underset{\underset{NH}{\|}}{C}-SH$ (13)
-O-		$CH_3-O-\underset{\underset{O}{\|}}{C}-SH$ (2)	$CH_3-O-\underset{\underset{S}{\|}}{C}-SH$ (6) ...	
-S-				
-NH-				

Table 1 (a). Type, $CH_3-X-\underset{\underset{Y}{\|}}{C}-SH$

=Y \ -X-	=CH$_2$	=O	=S	=NH
-CH$_2$-	⟨⟩-SH (1)	$CH_3-\underset{\underset{O}{\|}}{C}-SH$ (5)	$CH_3-\underset{\underset{S}{\|}}{C}-SH$ (9)	$CH_3-\underset{\underset{NH}{\|}}{C}-SH$ (13)
-O-		$CH_3-O-\underset{\underset{O}{\|}}{C}-SH$ (2)	$CH_3-O-\underset{\underset{S}{\|}}{C}-SH$ (6)	$CH_3-O-\underset{\underset{NH}{\|}}{C}-SH$ (10) ... (14)
-S-		$CH_3-S-\underset{\underset{O}{\|}}{C}-SH$ (3)	$CH_3-S-\underset{\underset{S}{\|}}{C}-SH$ (7)	$CH_3-S-\underset{\underset{NH}{\|}}{C}-SH$ (11) / (15)
-NH-		$CH_3-NH-\underset{\underset{O}{\|}}{C}-SH$ (4)	$CH_3-NH-\underset{\underset{S}{\|}}{C}-SH$ (8)	$CH_3-NH-\underset{\underset{NH}{\|}}{C}-SH$ (12) / (16)

Table 1 (b). Type, $CH_3-X-\underset{\underset{Y}{\|}}{C}-NH_2$

=Y \ -X-	=CH$_2$	=O	=S	=NH
-CH$_2$-	⟨⟩-NH$_2$ (17)	$CH_3-\underset{\underset{O}{\|}}{C}-NH_2$ (21)	$CH_3-\underset{\underset{S}{\|}}{C}-NH_2$ (25)	$CH_3-\underset{\underset{NH}{\|}}{C}-NH_2$ (29)
-O-	(18)	$CH_3-O-\underset{\underset{O}{\|}}{C}-NH_2$ (22)	$CH_3-O-\underset{\underset{S}{\|}}{C}-NH_2$ (26)	$CH_3-O-\underset{\underset{NH}{\|}}{C}-NH_2$ (30)
-S-	(19)	$CH_3-S-\underset{\underset{O}{\|}}{C}-NH_2$ (23)	$CH_3-S-\underset{\underset{S}{\|}}{C}-NH_2$ (27)	$CH_3-S-\underset{\underset{NH}{\|}}{C}-NH_2$ (31)
-NH-	(20)	$CH_3-NH-\underset{\underset{O}{\|}}{C}-NH_2$ (24)	$CH_3-NH-\underset{\underset{S}{\|}}{C}-NH_3$ (28)	$CH_3-NH-\underset{\underset{NH}{\|}}{C}-NH_2$ (32)

while the latter, nitrogen atom as the terminal group Z. These tables involve not only conventional accelerators, *i.e.* xantate (6), thiazol (12), imidazol (16) guanidyl compound (32) *etc.*, but also a lot of new compounds, which have not yet been investigated as rubber chemicals. A systematic work which has been done in our laboratory promises a new field of rubber chemicals. This paper deals with the compounds indicated in Tables 1(a) and 1(b), some of which are found to be excellent promoters for vulcanization.

1. Promotion of Vulcanization by Benzmercaptimide (BMI)

BMI is a pale-yellow crystal (line substance) melting at 116°C and is prepared from benzonitrile and hydrogen sulfide. The compound has in itself no accelerating ability but is found to exhibit promoting action on vulcanization in the presence of accelerator. In other words, it acts as so-called promoter or secondary accelerator. Fig. 1 indicates the promoting action together with the scorching tendency in the Mooney test for gum stock, the compounding recipe
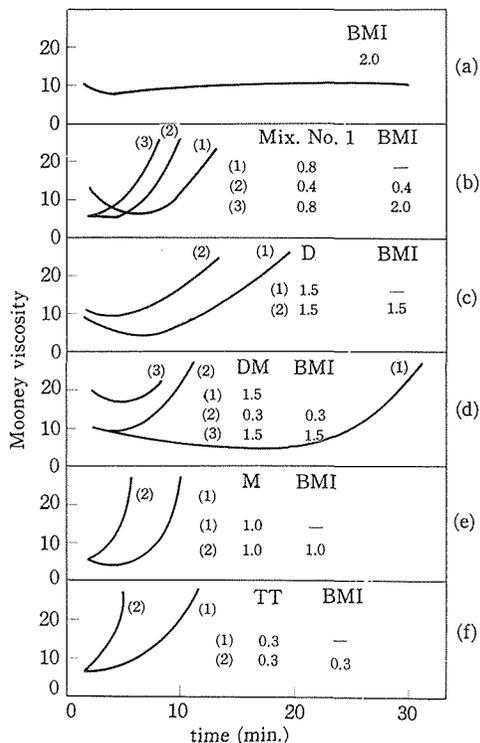
Fig. 1. Secondary vulcanization acceleration
effect of Benzmercaptimide (BMI) with
various accelerator.

of which is shown in Table 2. From Fig. 1 it is seen that BMI has no effect
in itself (a), but it has considerable promoting effect when it is used with an
accelerator such as mercaptobenzothiazol (M), (b) and (e), dibenzothiazyl disul-
fide (DM) (d), or tetramethylthiuram disulfide. Table 3 shows the tensile
properties of vulcanizate obtained by using the mercaptobenzole-hexamethylene-
tetramine curing system at 143°C. Here BMI seems to have no significant effect.
However, the considerable improvement in vulcanization is observed when BMI
is used together with DM (Table 4).

Table 2.

Basic recipe	
Natural rubber	100
Stearic acid	1
Zinc oxide	5
Sulfur	3
Accelerator and benzmercaptimide	Necessary weight

Table 3.

Accelerator (phr.)	Cure time (min.)	400% modulus (kg/cm²)	Tensile strength (kg/cm²)	Elongation (%)	Hardness
M+H* (0.4)	5	5,5	234	867	31
	7	5,7	256	828	33
	10	8,8	272	806	36
	15	16,1	281	748	40
M+H* BMI** (0.4)	5	2,5	154	926	26
	7	3,8	215	879	30
	10	4,9	229	879	31
	15	5,6	239	847	33

* The mixture included equivalent weight of mercaptobenzothiazole and hexamethylene-tetramine.
** Benzmercaptimide.

Table 4.

Accelerator (phr.)	Cure time (min.)	400% modulus (kg/cm²)	Tensile strength (kg/cm²)	Elongation (%)	Hardness
DM* (1.5)	5	1,7	140	930	26
	10	5,5	180	850	32
	15	8,2	223	837	35
	20	8,8	203	800	38
DM (0.3) and Benzmercapti-mide (0.3)	5	5,2	169	880	30
	10	8,7	223	840	34
	15	10,8	232	830	36
	20	13,0	215	770	40
	25	14,2	183	750	40

* Dibenzothiazyl disulfide.
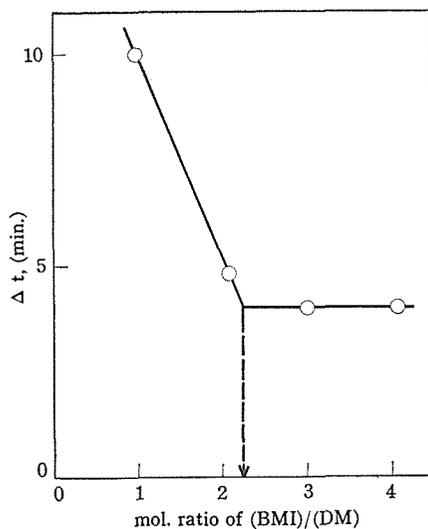
Fig. 2. Time required for Mooney-10 point rising (Δt) vs. mol. ratio of (BMI/(DM).

Experiments with various amounts of BMI showed that the effect of BMI reaches a saturated point of 2.2 mole ratio against DM, when 0.8 phr. of DM is used (Fig. 2).

BMI was found to react on DM to produce mercaptobenzothiazol and therefore the promoting action may possibly be attributed to the accelerating property of the latter substance which is produced from BMI in vulcanization condition. In fact, the vulcanizate cured with DM and BMI is found to be almost identical in tensile property with that cured with the same amount of M (0.8 phr.) (Table 5), but the Mooney scorch test shows different results for the two vulcanizates. DM-BMI combination seems to be more active than M (Fig. 3).

Table 5.

Accelerator (phr.)	Cure time (min.)	400% modulus (kg/cm²)	Tensile strength (kg/cm²)	Elongation (%)	Hardness
M (0.8)	5	9,5	248	875	31
	7	10,5	262	817	33
	10	15,5	259	765	36
	15	17,1	236	763	36
DM (0.8) and Benzmercaptimide (0.78)	5	9,4	250	838	32
	7	11,4	249	812	33
	10	15,8	248	772	36
	15	17,6	216	742	37

DM–BMI combination seems to be more active then M (Fig. 3).
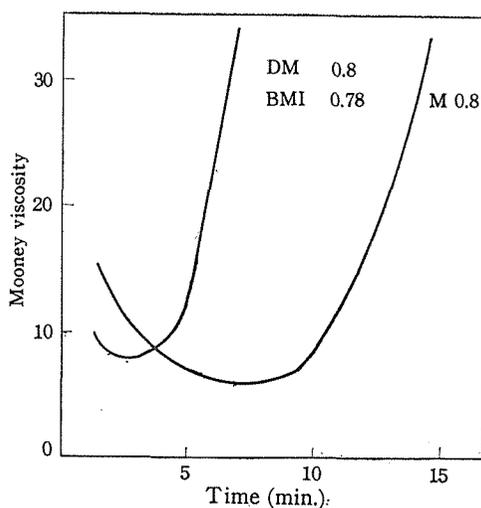

Fig. 3. Comparision of scorch between M
compound and DM+BMI compound.

BMI has no effect on other accelerator like M and D in contrast to DM.

2. Other Promoters

Other chemicals are tested as promoters by Mooney test, the results of which are summarized in Table 6. Here Δt_5 means the time required for attaining five-Mooney-point rising from the minimum Mooney value corresponds to the reciprocal rate of vulcanization. These compounds exhibit more or less promoting

Table 6. Five-point rising from the minimum Mooney values.

| Reagents	No.[a]	t_5 (min.)
Thiophenol	(1)	12,5
Thioacetic acid	(5)	6
Dithioacetic acid	(9)	19,5
Thioacetamide	(13)	4
Methylxanthogenimide	(14)	9
Methyl trithiocarbonate	(11)	26
Methylthiourea	(16)	4,5
Aniline	(17)	20
Acetamide	(21)	17
Acetamidine hydrochloride	(30)	12
Urethane	(22)	26
S–Methyl monothiocarbamate	(23)	14,5
Pseudo-methylthiourea hydroiodide	(31)	9
Methylurea	(24)	13
Methyl dithiocarbamate	(15)	6,8
None	(0)	45,0

a) The numbers below indicate those in Tables 1 (a) and (b).
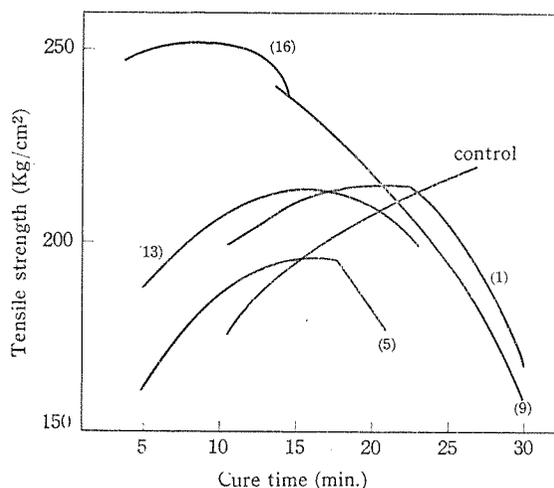
1 : Thiophenol.   5 : Thioacetic acid.
9 : Dithioacetic acid. 13 : Thioacetamide.
16 : Methylthiourea.

Fig. 4.
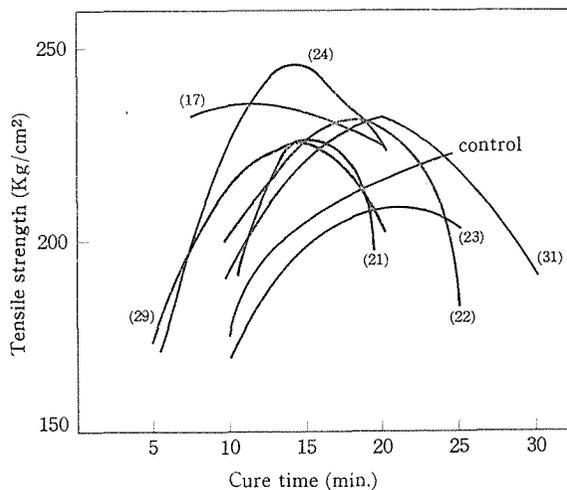
17 : Aniline.   21 : Acetamide.
22 : Urethane.   22 : S-methyl monothiocarbamate.
24 : Methylurea.   29 : Acetamidine hydrochloride:
31 ; Pseudo methylthiourea hydroiodide.

Fig. 5.

action and much effect on some sulfur-containing chemicals such as thioacetic acid (5), thioacetamide (13), methylthiourea (16) and methyl dithiocarbamate (15). Figs. 4 and 5 illustrate cure rate curves. It was also found that these promoters are often effective even in absence of sulfur, and therefore so-called non-sulfur vulcanization will be possible by using accelerator-promotor combination. Tables 7 (a) and 7 (b) indicate small Δt_5 values of DM–methylthiourea and DM–thioacetamide combinations in various mole ratios. Non-sulfur vulcanization is investigated according to the recipe shown in Table 8 at curing temperatures 120°C to 200°C. The degree of vulcanication is estimated from swelling data of vulcanizates (Table 9), where degree of cross-links is represented by ν-value. The data show the effective curing in comparison with conventional TT (tetra-methylthiurum disulfide) recipe. In the latter case effective curing temperature is 160°C, whereas in the former case it undergoes vulcanization easily even at 120°C. Table 10 indicates the qualitative curing properties of other promoters combined with DM.

Table 7 (a).		Table 7 (b).	
Moles ratio of methylthiourea to DM	Δt_5 (min.)	Moles ratio of thioacetamide to DM	Δt_5
0.5	6.5	0.5	44
1	4.5	1	4
1.5	3.5	1.5	1.8
2	4	2	2
3	3	3	2.7

Table 8.

Sample No.	1	2	3
Natural rubber	100	100	100
Stearic acid	1	1	1
Zinc oxide	5	5	5
Accelerator TT	—	—	3
Accelerator DM	5	5	—
Thioacetamide	3	—	—

Table 9.

Cure temp. (°C)	Sample No.	Cure time (min.)	$\nu \times 10^{-5}$
120	1	4	3.09
		8	4.54
		16	4.76
		32	5.22
	2		Dissolved
	3	32	2.10
160	1	1	3.97
		2	3.77
		4	5.01
		8	3.23
		16	3.01
	2		Dissolved
	3	1	0.91
		2	5.13
		4	11.2
		8	13.1
		16	11.9
200	1	0.25	16.5
		0.5	3.12
		1	2.81
		2	1.96
		4	0.97
		8	1.58
	2		Dissolved
	3	0.25	3.32
		0.5	8.60
		1	9.63
		2	12.4
		4	8.03
		8	8.34

Table 10.

Promoters	Successful or not
Thioacetamide	Good
Methylthiourea	Good
Methylxanthogenimide	Good
Methyl dithiocarbamate	Good
Thioacetic acid	Good
Methyl trithiocarbonate	No
Mercaptobenzothiazole	No
S–Methyl monothiocarbamate	No
Pseudo-methylthiourea hydroiodide	No
Tetramethylthiourea	No
Thiourea	Good
Unsymmetrical dimethylthiourea	Good
Symmetrical dimethylthiourea	Good
Trimethylthiourea	Good

3. Reaction Mechanism of Promoter

Promoter has no effect in itself, but it becomes active when it is used together with DM but not with M or D. Accordingly, the action of promoter seems to be correlated with interaction between promoter and disulfide such as DM. Disulfide-type accelrator is known to be promoted by the presence of amines. Dogadken[3] proposed the following mechanism:

$$RSSR + R'R''NH \rightarrow RSH + RR''N\cdot + RS\cdot$$
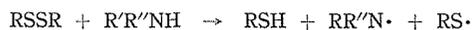
which means that amine reacts with disulfide to give rise to decomposition. Sulfide radical thus produced may be the active species for vulcanization, because it decomposes sulfur molecule of cyclic structure or abstracts hydrogen from rubber molecule to give sulfur atom and rubber radical respectively, and atomic sulfur or rubber radical thus formed may bring about cross-linking. Watson[4] explained the effect of thiourea on disulfide in terms of the following mechanism:

$$\begin{matrix} H_2\overset{+}{N} \\ \\ H_2N \end{matrix}\!\!\!\!\diagdown\!\!\!\!\diagup\! C-S^- + RSSR \rightarrow \begin{matrix} H_2^+N \\ \\ H_2\,N \end{matrix}\!\!\!\!\diagdown\!\!\!\!\diagup\! C-S-SR + RS^-$$
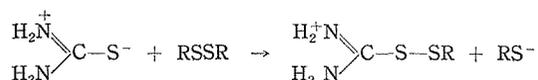
Here it is assumed that sulfide anion is formed by attack of thiuronium ion through ionic mechanism but not through radical one. Watson's mechanism does not essentially differ from Dogadkin's, because both mechanisms are similar in the point that disulfide linkage is decomposed by attack of the compounds possessing lone-pair electrons on nitrogen or sulfur atom. In these mechanisms a complex compound may be assumed as a transition state of reaction between disulfide and promoter. In our promoter-DM systems the cyclic intermediates can easily be assumed, since the promoters have the so-called 1,3–dipolar structure,

which implies the allylic system containing heteroatoms possessing lone-pair electrons. Such a lone-pair π-bond system may react easily with the 1,3-dipolar system in mercaptobenzothiozyl compound as follows:
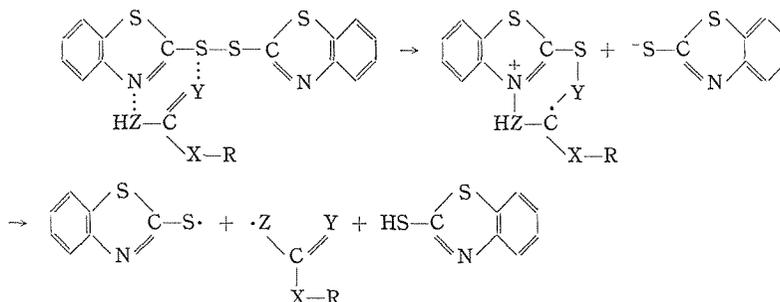
The combination of $N=C-S$ 1,3-dipolar system in accelerator with $Z-C=Y$ system in promoter results in the formation of intermediate six-membered structure, which becomes more stable by the resonance stabilization. The resonance is affected by the structure of promoter. Simply speaking, stabilization of the cyclic intermediate is much enhanced when the resonance stability of the promoter is poor. Acetamide is more stable than thioacetoamide. Thus the former amide is expected to have larger stabilization energy in ring formation and consequently stronger promoting ability than the latter. Indeed, ordinary acetamide has no significant effect in contrast to the excellent promoting ability of thioacetamide. Moreover, in the reaction of these compounds with DM, thioacetamide affords a quantitative amount of mercaptobenzothiazol (M), while ordinary acetamide does not (Table 11).

Table 11. Reaction products.

	Before reaction (g.)	After reaction (g.)
In reaction A		
DM	15.0	1.0
M	0	14.2
Thioacetamide	6.0	2.9 a)
In reaction B		
DM	15	14.5
M	0	Trace
Acetamide	4.0	2.7 a)

a) Amine-like product included.

4. Estimation of Resonance Stabilization in Intermeciate Cyclic Structurs
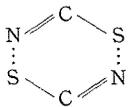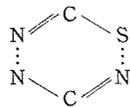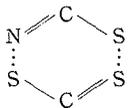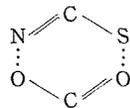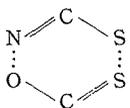
The π-electron systems in accelerator DM and promotor concerned are simply demonstrated as follows,

$$\underline{N}=C-\underline{S} + \underline{Z}-C=\underline{Y} \rightarrow \begin{array}{c} N=C-S \\ \vdots \quad \vdots \\ Z-C=Y \end{array}$$
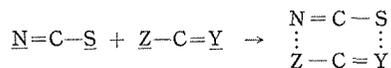
Both systems consist of one π-bond and two lone electron pairs and accordingly afford cyclic systems of six orbital with eight π-electron when both compounds react with each other. The stabilization in intermediate ring system can be estimated quantum chemically from perturbation between both systems according to the conventional method.[5][6] Table 12 summarizes the stabilization energy

Table 12.

Formation	ΔE	Formation	ΔE
N=C-S / S-C=N	0.5032	N=C-S / N-C=N	0.3858
N=C-S / S-C=S	0.4922	N=C-S / O-C=O	0.3630
N=C-S / O-C=S	0.4643	N=C-S / N-C=S	0.4453
N=C-S / O-C=N	0.4357	N=C-S / N-C=O	0.2958

Fig. 6.

Junji FURUKAWA, Shinzo YAMASHITA and Ryuzo YAMAMOTO
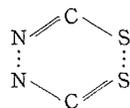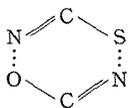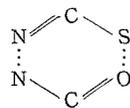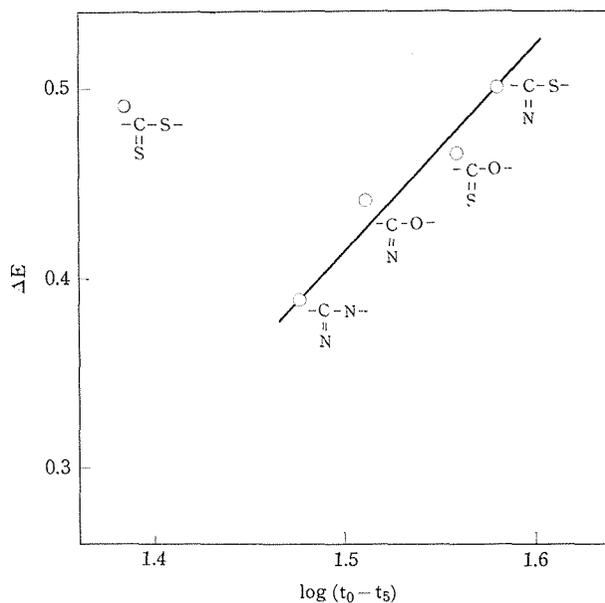
ΔE in ring systems of various compounds, which predicts that thioamides are the compounds capable of affording the largest stabilization energy and therefore, are the most powerful compounds against mercaptimide. There seems to be an almost linear correlationship between stabilization energy in ring system and promoting ability except for xanthate (Fig. 6). In Fig. 6 the promoting ability is demostrated by $\log (t_0 - t_5)$, where t_0 and t_5 respectively signify the times (in minutes) required for the Mooney value of the compounds to reach the reading five points above the minimum value in the absence and presence of promoters.

EXPERIMENTAL

Materials

(1) **Benzmercaptimide.**[7] Twenty grams of benzonitrile and 30 ml. of 28% aqueous ammonia solution were dissolved in 90 ml. of ethanol. The solution was saturated with hydrogen sulfide in a pressure bottle, and was kept at 100°C for about one hour.

The reaction mixture turned red in color. After reaction had been completed, ethanol was distilled off, leaving a pasty solid. The obtained solid was purified by recrystallization from boiling water. Pure benzmercaptimide is a pale-yellow crystal, melting at 116°C.

(2) **Dithioacetic acid.**[8] 8,6 g. of metallic magnesium and 50 g. of methyl iodide were added into 150 ml. of water-free ethyl ether. Then 31,7 g. of carbon disulfide was added and the mixture was kept in an ice bath for 24 hr. This reactant was decomposed with water and hydrochloric acid. The ethyl ether layer was separated, to which an aqueous solution of sodium hydroxide was added and thereby dithioacetic acid was extracted. The alkali solution was neutralized with hydrochloric acid. Crude dithioacetic acid was extracted with ethyl ether, dried over sodium nitrite, purified by vacuum distillation. The boiling point of pure dithioacetic acid is 37°C at 15 mmHg.

(3) **Methyl trithiocarbamate.**[9] 200 ml. of 28% aqueous ammonia solution was allowed to react with 40 ml. of carbon disulfide for 2 hr. The solution turned red in color. On addition of 20 g. of methyl iodide the solution become colorless. Methyl trithiocarbamate was extracted with ethyl ether and dried over calcium chloride and phosphorus pentoxide. The fraction boiling at 110°C/ 18 mmHg. was collected.

(4) **Methyl xanthogenimide.**[10] 60 ml. of carbon disulfide was dropped into a mixture of 56 g. of potassium hydroxide and 270 ml. of methanol. As soon as the color of the mixture turned green, 150 g. of methyl iodide was added into this mixture. The whole mixture was stirred for 15 min. On addition of a large amount of water, the reaction mixture was separated into two layers. The organic layer was dried and distilled. The run of 164°C was collected. This run was dissolved in 300 ml. of ethanol saturated with ammonia and was kept to stand overnight. When ethanol was distilled out, a solid mass was obtained. This solid was recrystallized from water is white needles melting at 42°C.

(5) **Methyl dithiocarbamate.**[11] 50 g. of gaseous ammonia was dissolved in 300 ml. of ethanol, and 76 g. of carbon disulfide was added under ice cooling. When this mixture was kept to stand for a few hours, a solid mass was separated out. After filtration, the solid was transferred into a beaker and covered with ethanol. When 142 g. of methyl iodide was dropped, the solid mass was dissolved and ammonium iodide, was separated out. The iodide was filtrated. By dropping the filtrate into cool water, methyl dithiocarbamate was obtained as a yellow solid melting at 42°C.

(6) **Monomethyl thiourea.**[12] 274 g. of carbon disulfide, 144 g. of sodium hydroxide and 320 ml. of water were mixed in a beaker. In this mixture 360 ml. of 35% aqueous solution of methyl amine was dropped over 30 min. at 15°C. After this reactant had been heated over a water bath for one hour, 392 g. of ethyl chlorocarbonate was added to it over one hour at 40°C. Methyl thioisocyanate thus formed was separated, dried over sodium sulfate, and distillated. 95 g. of methyl isocyanate was added into 140 ml. of 28% aqueous ammonia within one hour, and the reaction mixture was heated over a steam bath for about half an hour with Norit. After filtration, the mixture was kept cool until crystals were separated out. The crystals were purified by recrystallization from water. The melting point is 120°C.

(7) **Methyl carbonate.**[13] An excess of gaseous ammonia was bubbled into the mixture of 25 g. of methyl chlorocarbonate and 45 g. of benzene. Ammonium chloride produced was filtrated off. Benzene was expelled out of the filtrate by distillation, leaving methyl carbonate as a solid melting at 51°C.

(8) **S-Methyl monothiocarbonate.**[14] 15 g. of methyl iodide was added into 10 g. of methylxanthogenimide. A solid was obtained. Recrystallization of the solid from water, gave pure S–methyl monothiocarbonate, m. p. 107°C.
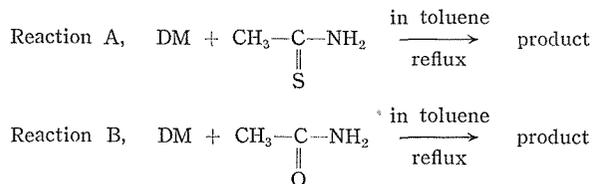
(9) **Pseudo-methylthiourea hydroiodide salt.**[15] 60 g. of methyliodide was added into the mixture of 20 g. of thiourea and 100 ml. of ethanol. The reaction mixture was heated at about 60°C for 6 hours until the completion of the salt formation.

Reaction of BMI with DM

1 mol. of DM and 1 mol. of benzmercaptimide were heated for 1 hour at 150°C. The reaction mixture which was homogeneous was poured into boiling water, filtrated and washed several times with small portions of hot water. When the filtrate was cooled, crystals were separated out. The crystals were identified to be mercaptobenzothiazole. The product will be referred to as M. Thus benzmercaptimide reduced DM to give M.

Reaction of Thioacetamide or Acetamide with DM

Since the vulcanization usually is carried out in the presence of zinc oxide as well as stearic acid, the analysis of the reaction products in rubber is very complex. Thus the following reactions were undertaken as model reactions,

Junji FURUKAWA, Shinzo YAMASHITA and Ryuzo YAMAMOTO

$$\text{Reaction A,}\quad \text{DM} + \underset{\displaystyle \underset{\text{S}}{\|}}{\text{CH}_3\text{—C—NH}_2}\quad \xrightarrow[\text{reflux}]{\text{in toluene}}\quad \text{product}$$

$$\text{Reaction B,}\quad \text{DM} + \underset{\displaystyle \underset{\text{O}}{\|}}{\text{CH}_3\text{—C—NH}_2}\quad \xrightarrow[\text{reflux}]{\text{in toluene}}\quad \text{product}$$

The reaction mixture of A can effect the non-sulfur vulcanization whereas that of B can not.

In reaction A, 15 g. of DM and 6 g. thioacetamide were allowed to react by refluxing in toluene for 2 hours.

In reaction B, 15 g. of DM and 4 g. of acetamide were subjected to reaction in the same manner as in reaction A.

The analysis data of the reaction products are shown in Table 11.

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