

MO Theoretical Studies on Organic Accelerators of Vulcanization

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(Received Oct. 1, 1971)

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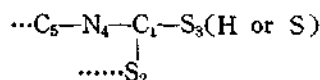
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Abstract The extended Hückel calculations on five organic accelerators of vulcanization have been carried out. Various MO quantities *e. g.*, electron populations and AO coefficients, are used to explain accelerator reactivity of the compounds. Results of these analyses lead us to support free radical mechanism of acceleration in vulcanization.

요약 : 5종의 유기 가황촉진제에 대하여 EHT법을 적용하였다. 전자밀도, 원자궤도함수의 계수 등을 이용하여 각 화합물의 촉진 반응을 검토하였으며 결과로 유기 가황촉진 반응은 라디칼 반응을 입증하였다.

Introduction

The principal organic accelerators of vulcanization today are dithiocarbamates and thiram sulfides, thiazoles and their derivatives, arylsubstituted guanidines, and aldehyde-amine condensation products. The most popular and common accelerators are the first two classes of compounds and structurally they are interrelated; they have interesting common structural features of the following type, (numbring is for DDC and MTZ)

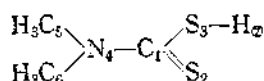


The effectiveness of these compounds as accelerators seem to depend particularly on N-C-S type of linkage, S being linked to either H or another S atoms of the next identical unit.² It is this aspect of basic common structure that has drawn our attention and prompted us to investigate theoretically as to electronic characteristics of accelerator activity, hopefully extending to the elucidation of acceleration mech-

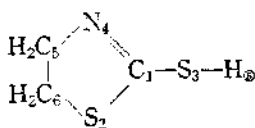
anism.

The compounds investigated in this work were basic types of dithiocarbamates and thiazoles, namely; (numbering schemes are shown for nonhydrogen atoms and for hydrogen numberings are differentiated by circling numbers)

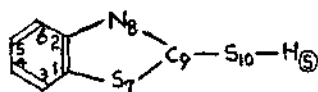
(I) Dimethyldithiocarbamic Acid (DDC)



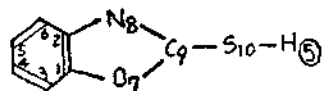
(II) 2-Mercaptothiazoline (MTZ)



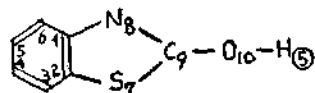
(III) 2-Mercaptobenzothiazole (MBT)



(IV) 2-Mercaptobenzoxazole (MBO)



(V) 2-Oxybenzothiazole (OBT)



DDC represents the class of compounds, dithiocarbamates and thiuram sulfides, and MTZ has been chosen to see the effect of ring formation of saturated carbon linkage. Finally compounds (III) to (V) were selected in order to investigate the effect of O atom in place of S atom.

In view of computational simplicity and successes in studies of various structural characteristics³ and reactivities⁴ of molecules with the extended Hückel theory (EHT)⁵, we have used this method throughout in this work. In the approximate sigma MO method dealing with large molecules, the computational simplicity

is one of the more important factors to be taken into consideration at the outset, especially when only semiquantitative results are required.

In the EHT method the molecular orbitals are expressed as a linear combination of the Slater type atomic orbitals (AO) ϕ_i ,

$$\psi = \sum_{i=1}^n C_i \phi_i \dots\dots\dots(1)$$

which is in turn given as,

$$\phi_i = N r^{n-1} \exp(-rZ) Y_{lm}(\theta, \phi) \dots\dots(2)$$

where Z is the orbital exponent for the AOs and other terms have their usual significances⁶.

Table I The Slater Exponents, Z, and Valence State Ionization Potential, -I

AO	Z ^(a)	-I ^(b)
H1s	1.00	13.60
C2s	1.59	21.01
2p	1.59	11.27
N2s	1.92	26.92
2p	1.92	14.42
O2s	2.24	36.07
2p	2.24	18.53
S3s	1.98	20.08
3p	1.98	13.32

(a) E. Clementi and D.L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963)

(b) J. Hinze and H.H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540(1962)

The summation in (1) is over all valence orbitals used in constructing the molecular orbital (MO), namely the 1s orbital for hydrogen, 2s, 2p_x, 2p_y, and 2p_z orbitals for the second row elements, and 3s, 3p_x, 3p_y, and 3p_z orbitals for the third row elements. In solving the usual secular equation (3) in this method the coulomb

Table II. Cartesian Coordinates for 2-mercaptothiazoline

	X	Y	Z
C ₁	0.0	0.0	0.0
S ₂	-0.8750	-1.5155	0.0
S ₃	1.6000	0.0	0.0
N ₄	-0.6450	1.1172	0.0
C ₅	-1.8394	0.5675	0.4508
C ₆	-2.2132	-0.4924	-0.5752
H ₁	-2.5987	1.3471	0.5116
H ₂	-1.6890	0.1298	1.4377
H ₃	-2.1434	-0.0694	-1.5773
H ₄	-3.2336	-0.8302	-0.3942
H ₅	1.9215	1.2895	0.0

integrals H_{ii} are chosen as the negative of valence state ionization potential (VSIP) and

$$\sum_{i=1}^m (H_{ij} - ES_{ij}) C_{ij} = 0, \quad j=1, 2, \dots, m \quad (3)$$

for estimating the off-diagonal matrix elements H_{ij} the Wolfsberg-Helmholtz approximation⁷ (4) is used.

$$H_{ij} = \frac{1}{2} K (H_{ii} + H_{jj}) S_{ij} \quad (4)$$

The values of K has been chosen as 1.75 in accordance with the earlier works.^{3, 4, 5}

Calculations

The computer input data consisted of the orbital exponents Z , valence state ionization potential and accurate coordinate of atoms. The Z and VSIP values are summarized in Table I.

The geometry of molecule was determined by using interatomic distances and valence angles obtained from *Tables of Interatomic Distances and Configuration in Molecules and Ions*, edited

by L. E. Sutton, Special Publications No. 11 and 18, The Chemical Society London. Precise atomic coordinates of various atoms in molecules were calculated by another program.⁸ An example of the input coordinates is given in Table II for 2-mercaptothiazoline. The Mulliken population analysis⁹ has been carried out and the following MO quantities have been calculated.

The partial AO population of AO r ;

$$N(r) = 2 \sum_i^{i \in A} \sum_j^{j \in A} C_i C_j S_{ij} \quad (5)$$

The atom population of atom A ;

$$M_A = \sum_r N(r) \quad (6)$$

The valence-inactive atom population of atom A ;

$$P_A = \sum_r \sum_i^{i \in A} 2(C_i)^2 \quad (7)$$

The atom bond population between the atoms A and B ;

$$M_{AB} = 4 \sum_r \sum_i^{i \in A} \sum_j^{j \in B} C_i C_j S_{ij} \quad (8)$$

where C_i is the coefficient of AO r in the i -th MO and \sum signifies the summation over all the AO's of atom A . The calculation on free radical was not possible with EHT since this method can not account for open shell. We have therefore varied the distances between the mercapto S and H atoms until completely one electron is transferred to the H atom and $M_{SH} \cong 0$. This state closely approximates free radical and the S-H distance for this state for DDC was found to be 1.9040 Å.

Results and Discussion

Energetics The total electronic energies E and energies for the highest occupied (HO) and the lowest unoccupied (LU) levels of molecules, ϵ , are summarized in Table III.

In this table $\Delta\epsilon$ is the difference in energy between HO and LU orbitals and ΔE is the energy difference between radical (or anion) and the corresponding neutral molecule. The total electronic energies indicate that stabilities

are in the order molecule > radical > anion. There is a definite trend of decrease of energy gap between HO and LU for radicals while the gaps are relatively large for molecules and anions for MTZ and DDC. This is seen to be caused mainly by the energy lowering of LU levels in radicals. This is in good accord with the fact that radicals are the most reactive species.¹⁰ The ΔE values clearly indicate that free radical formations are favored over anion formations for both MTZ and DDC. Actually

Table III Energetics

	$E(ev)$	$\epsilon^{HO}(ev)$	$\epsilon^{LU}(ev)$	$\Delta\epsilon(ev)$	$\Delta E(kcal/mol)$
DDC	-605.926	-10.680	-5.900	4.780	
DDC-R ^(a)	-604.060	-8.559	-7.904	0.655	43.048
DDC-A ^(b)	603.566	-8.325	-6.382	1.943	54.434
MTZ	-593.916	-11.881	-7.394	4.487	
MTZ-R ^(a)	-591.557	-11.936	-9.504	2.433	54.425
MTZ-A ^(b)	-587.554	-11.934	-7.393	4.541	146.773
MBT	-862.126	-9.827	-8.098	1.729	
MBO	-924.490	-12.085	-8.109	3.976	
OBT	-920.593	-12.024	-8.021	4.002	

the energy of free radical formation is less than the bond energy of the $S-H$ bond, which is ~ 85 kcal.¹¹ For compounds with benzene ring $\Delta\epsilon$ increases in the order $MBT < MBO < OBT$, which is interestingly the reverse order of accelerating ability.²

Population Analysis The atom and atom-bond populations for DDC are given in Fig. 1. The notable features are high electron population of the mercapto hydrogen, and C_1 , S_2 , S_3 , and N_4 atoms. The latter four atoms constitute basic skeleton of accelerators studied in this work. Excess electrons on these atoms are located on their π orbitals. These excess electrons are donated by the two methyl groups and are nearly evenly distributed on atoms in the basic skeleton. The extra electron in anion evenly distri-

buted over this skeleton.

Figure 2 shows the result of population analysis for MBT, MBO and OBT. Oxygen atoms in the latter two compounds have high electron population compared with S atoms replaced. This causes the increase of ionic bond character of O atom with neighboring atoms. One outstanding feature of OBT, however, is the much lower atom population of H_5 compared with H atoms of corresponding position of other compounds. This is of course due to large electronegativity of O atom which attracts excess electrons and thereby weakening covalent bond character to its neighbors. The formal charge on H of OH group in OBT is +0.6475 which is comparable to that of formic acid. According to EHT calculation¹² H atom of OH group in

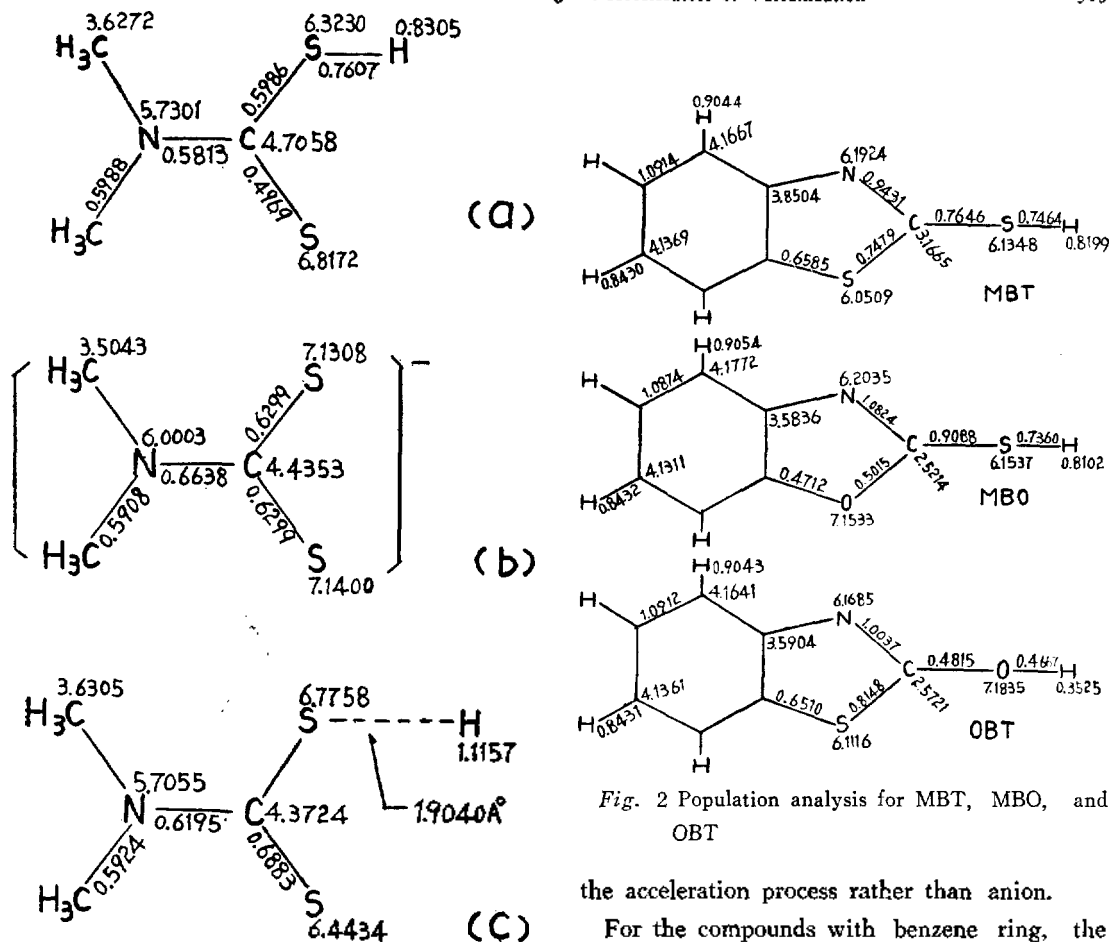


Fig. 1 Population analysis for DDC, (a) Molecule, (b) Anion, (c) Radical.

formic acid has a formal charge of +0.621. Thus OH hydrogen is highly acidic compared with SH hydrogen of MBT and MBO which were found to have formal charges of +0.1800, magnitude comparable to that of methyl hydrogens. It would be much easier then for OBT to form anion than to form free radical since it would require extensive redistribution of electrons for the homolytic scission of OH bond. This relative uneasiness of free radical formation due to the strong ionic character of OH bond may well be the reason for inactiveness of OBT as an accelerator² and provide supporting evidence that free radical is involved in

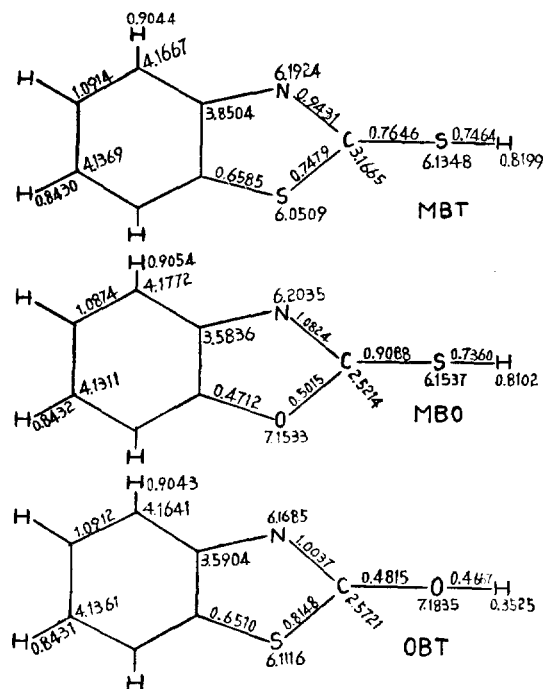


Fig. 2 Population analysis for MBT, MBO, and OBT

the acceleration process rather than anion.

For the compounds with benzene ring, the electron population is highest on C₆ atom among the ring carbons. An electron donating substituent on this carbon will therefore have maximum effect of electron donation and will result in maximum release of electrons to the reaction center of side chains. The reaction center is on the side chain, and high electron density on this group will facilitate homolytic scission and hence facilitate free radical formation. It has been found that an electron donating group on C₆ enhances accelerating ability while the same substituent on other positions has little or no enhancing effect.¹³ This is another piece of evidence in support of free radical mechanism of acceleration since high electron density on mercapto hydrogen will retard ionization and decrease accelerating ability if the reaction

proceeded by ionic mechanism.

Reactivities Reactivities based on energetics and population analysis have already been discussed above. The conclusion drawn from these was that the reactive form of accelerators is the free radical rather than the anion. If this conclusion is a valid one the easiness of free radical formation is an important factor determining accelerator reactivity.

Some insights into reactivities may be obtained by considering AO coefficients of HO and LU levels¹⁴. These are summarized in Table IV for the relevant AO's. In all cases SH or OH bond has antibonding character in the LU orbital. The antibonding nature of this orbital is the strongest for DDC and MBT, and the weakest for OBT. These correspond to their reactivities.² If the initiation involve attack of

Table IV AO Coefficients

	AO	HO	LU
DDC	H ₇ s	-0.0807	0.0204
	S ₃ s	0.1210	-0.0257
	P _x	-0.1002	0.0742
	P _y	0.6248	0.0856
	P _z	0.1775	-0.6220
MBT	H ₅ s	0.0083	0.0284
	S ₁₀ s	0.0046	-0.0376
	P _x	0.0675	-0.1451
	P _y	0.0190	-0.1353
	P _z	-0.1307	-0.1461
MBO	H ₅ s	0.0101	0.0153
	S ₁₀ s	0.0232	-0.0904
	P _x	0.3116	-0.2414
	P _y	0.1830	-0.2029
	P _z	0.3013	0.1783
OBT	H ₅ s	0.0034	0.0147
	O ₁₈ s	-0.0074	0.0314
	P _x	-0.0110	-0.0812
	P _y	-0.0038	-0.0638
	P _z	0.0539	-0.0577
MTZ	H ₅ s	0.1206	0.1445
	S ₃ s	-0.1602	-0.2571
	P _x	-0.0505	-0.2344
	P _y	0.2365	0.5422
	P _z	0.4164	0.0323

accelerator by an electron rich reagent such as nucleophile or radical, the antibonding nature of the LU orbital can be a measure of easiness

of bond breaking. On the other hand the homolytic scission of SH bond will be facilitated by large valence inactive atom population of atoms

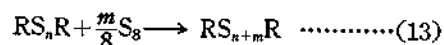
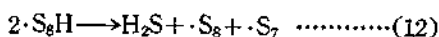
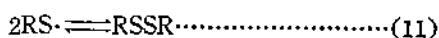
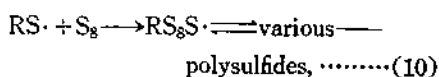
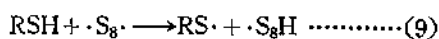
S and H. The $1/2p_H$ values for the compounds studied are given in Table V. The notable differences of this value for OBT from others

Table V Valence-Inactive Atom Population

Molecule	$\frac{1}{2}p_H$
DDC	0.4764
MTZ	0.4779
MBT	0.4774
MBO	0.4620
OBT	0.1673
DDC-R	0.9919

are readily seen. The least value of $1/2p_H$ is consistent with the fact that it is the least reactive compound. The near unity value for DDC radical is not unexpected because H atom here has one electron without bonding to any atom. Other values of $1/2p_H$ are nearly the same except for MBO which has slightly smaller value. Here again agreement with the experimental findings are very good.

The limited evidence available from these studies tends to favor free radical mechanism of acceleration of vulcanization. Specifically the initiation of acceleration involves free radical formation by a homolytic scission of mercapto group. In this step the open chain biradical form of sulfur, $\cdot S_8$, may act as an attacking group which abstract hydrogen from the mercapto group.



According to the results of the present work, reaction (9) is the rate determining in the initiation. Various polysulfides formed in (10) reversibly form polysulfide radical since polysulfide linkage is easily broken homolytically. These polysulfide radicals attack polymer chains of rubber and add various polysulfide cross links.

Acknowledgments

The author wishes to thank to Dong-A Natural Science Research Fund Committee of Dong-A Il Bo, for a research grant for this work, and to the National Research Council of Canada for an allowance of computer time. The actual computation has been carried out by IBM 360/50 of the University of Calgary Computing Center, Canada.

He is also indebted to Mr. Kyung Hoon Jung for assistance in computation.

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DAEHAN HWAHAK HOWOJEE
(Journal of the Korean Chemical Society)
Vol. 15, No. 6, 1971
Printed in Republic of Korea

양이온 교환 크로마토그래피에 의한 Babbitt

금속의 분리 및 정량

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고려대학교 화학과

(1970, 6. 22 접수)

The Separation and Analysis of Babbitt Metal by the Cation Exchange Chromatographic Method

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(Received June 22, 1970)

Abstract The cation exchange chromatographic method for the analysis of Babbitt metal has been studied. The quantitative separation of the mixture of Sb, Cu, Pb, and Sn ions has been obtained by elution, through 5cm column of resin, Rexyn 101 (Na form, 100~200 mesh), using 0.1 M NaCl solution for Sb, pH 4.5 and pH 7 solution of 0.01 M Na-Citrate+0.1 M NaNO₃ for Cu and Pb, and 2NHCl solution for Sn as eluent.

서 론

Babbitt 금속에는 일반적으로 두 가지가 있다.

*한국과학 기술 연구소

즉, Sn을 주성분으로 하고 Sb, Cu, Pb가 들어 있는 것과, Pb를 주성분으로 하고 Sb, Cu, Sn이 들어 있는 것이 있다. 이 두 종류의 Babbitt 금속을 분석함에 있어서 주성분을 정량하는 데는