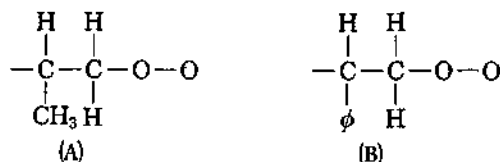


has a similar features in comparison with the EPR spectrum obtained by other method,<sup>11</sup> but not the same completely. As this reason, the following is considered. In the presence of a minute quantity of oxygen, some peroxide radicals are produced by the reaction of the oxygen with radicals. In our experiment, this possibility cannot be excluded. The possibility is strengthened from the fact that the spectrum obtained from our experiment is similar to the EPR spectrum for polypropylene.<sup>12</sup> In the latter case, the peroxy radical (A) may be produced whereas in our case, a similar peroxy radical (B) is formed:



We believe that this spectrum is a direct evidence for producing radicals by breaking bonds in the polymer by mechanical force.

**Acknowledgments.** Our grateful acknowledgment is due to the support of this work by the Korea Research Center for Theoretical Physics and Chemistry. We also express our sincere thanks to the Hannam Chemical Corporation (Seoul, Korea) who generously endowed the polystyrene samples.

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## Determination of Reactivity by MO Theory (XX). An MO Theoretical Study on Mechanism of Thiocarbonyl Addition.

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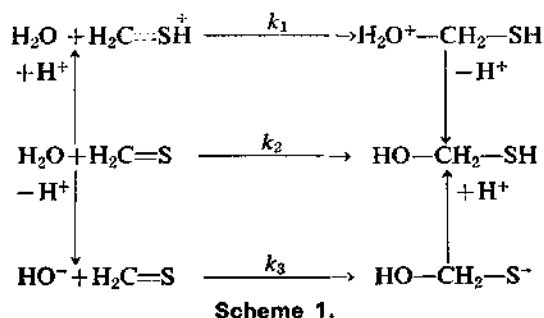
*Ab initio* molecular orbital calculations have been performed in an effort to determine which types of chemical interactions play essential roles for the system,  $\text{OH}^- + \text{CH}_2\text{S}$ ,  $\text{H}_2\text{O} + \text{CH}_2\text{SH}^+$ , and  $\text{H}_2\text{O} + \text{CH}_2\text{S}$ . The most important contribution to the interaction energy in controlling reaction path is the exchange repulsion energy, EX, which is largely responsible for the shape of the total interaction energy curve. In the ion-molecule reaction, prior protonation of thioformaldehyde or prior deprotonation of water leads to formation of the corresponding ionic adducts ( $\text{H}_2\text{O}^+\text{CH}_2\text{SH}$  and  $\text{HOCH}_2\text{S}^-$ ), with no barrier to reaction, simulating specific acid and base catalysis, respectively, as in the case of formaldehyde. Otherwise, approach of water to thioformaldehyde gives rise to a completely repulsive interaction.

## Introduction

Nucleophilic substitution mechanisms on a carbonyl carbon have been studied extensively<sup>1</sup>. It has been shown theoretically<sup>2</sup> as well as experimentally<sup>3</sup> that a nucleophile

attacks the carbonyl  $\pi$ -orbital from above and slightly rear of the carbonyl carbon and proceeds via a tetrahedral intermediate.

In this work characteristics of thiocarbonyl hydration mechanism have been studied using a simplest thiocarbonyl



Scheme 1.

compound, thioformaldehyde, and comparison was made with those for carbonyl addition.

As Schowen and coworkers have done in studies of carbonyl addition, we followed the three additions as shown in Scheme I; ion-molecule reactions of  $\text{H}_2\text{O}$  with  $\text{H}_2\text{CSH}^+$  ( $k_1$ ) and of  $\text{HO}^-$  with  $\text{H}_2\text{CS}$  ( $k_3$ ), and undatalyzed neutral-neutral addition of  $\text{H}_2\text{O}$  to  $\text{H}_2\text{CS}$  ( $k_2$ ).

The former two reactions correspond to specific acid-base catalysis, while the observed mode in solution is general acid-base catalysis<sup>4</sup>. There are two MO theoretical approaches to these types of mechanistic studies. One is distinguished coordinate method<sup>5</sup>, in which a distinguished coordinate is selected and is incremented with energy minimization at each point with respect to the remaining internal degrees of freedom, and then mechanism is discussed based on the structure of adduct and interaction energy.

The other is to calculate interaction energies for various reactants geometries at the initial and transition states, and examine energy components<sup>6</sup>. One popular method developed by Morokuma<sup>7</sup> involves *ab initio* Hartree-Fock SCF calculations on complete system (supermolecule or complex) and energy decomposition performed with a separate SCF cycle. In this work the Morokuma's method of energy decomposition was carried out on the reactants and transition states, and in addition deformation energies<sup>8</sup> of reacting molecules were considered.

### Calculations

Intermolecular interaction energy (INT) is given as a difference between the total energy of a supermolecule (or complex)  $A \cdots B$  and sum of the energies ( $E_A + E_B$ ) for isolated molecules  $A$  and  $B$ .

Molecular orbitals ( $\phi_i$ ) of the complex are constructed with the MO's of the isolated molecule  $A$ ,  $\phi_k$ , and  $B$ ,  $\phi_\mu$  as shown below

$$\phi_i = \sum_k C_{ik} \phi_k^A + \sum_\mu C_{i\mu} \phi_\mu^B \quad (1)$$

and the Hartree-Fock (H-F) equation for the complex is written as,

$$(F - \epsilon S)C = 0 \quad (2)$$

with the usual significance of the notations. The quantity  $(F - \epsilon S)$  is then expanded in order to define the molecular interaction as follows:

$$(F - \epsilon S) = (F^0 - \epsilon I) + \Sigma \quad (3)$$

Here  $F$  is the H-F matrix at infinite separation,  $I$  is unit matrix, and  $\Sigma$  is the molecular interaction matrix.

One then considers the following H-F equations which contain only selected component interaction matrices with the rest of the matrix set to zero

$$0 = (F^X - \epsilon S^X)C^X \equiv (F^0 - \epsilon I + \Sigma^X)C^X \quad (4)$$

where  $X$  represents the electrostatic (ES), polarization (PL), exchange (EX), or charge transfer (CT) interactions. The interaction energy due to  $X$  is given by

$$\text{INT}(E_X) = \sum_i^{\text{occ}} C_i^X (F^X + H^X) C_i^X - (E_A + E_B) \quad (5)$$

Here the first term on the right is the total energy of the model system due to the interaction  $X$ .

The stabilization energies are obtained separately from the model H-F equations and the total INT is given as,

$$\text{INT} = \text{ES} + \text{EX} + \text{PL} + \text{CT} + \text{MIX} \quad (6)$$

The term MIX is the coupling interactions between components introduced by Morokuma.

The electron density change  $\Delta\rho$ , of atom  $r$  can also be calculated using the following equation,

$$\Delta\rho(r) = \rho_{\text{PL}}(r) + \rho_{\text{EX}}(r) + \rho_{\text{CT}}(r) + \rho_{\text{MIX}}(r) \quad (7)$$

Calculations were performed using the GAUSSIAN-70<sup>9</sup> *ab initio* package and the Morokuma's EDA (Energy Decomposition Analysis)<sup>10</sup> subroutine with the STO-3G basis set. Geometry was optimized according to the standard three-point parabolic fitting procedure of GAUSSIAN-70.

For the negatively charged nucleophile  $\text{OH}^-$ , we took account of the diffuseness of the orbitals in the negative ion by reducing the orbital exponent for the oxygen 2s and 2p shell from 2.25 to an optimized 2.10.

### Results and Discussions

Optimized geometries and energies for reactants and adducts considered in this work are presented in Table 1. Figure 1 shows the optimized structures of adducts formed in the ion-molecule reactions  $\text{OH}^- + \text{H}_2\text{CS}$  and  $\text{H}_2\text{O} + \text{H}_2\text{CSH}^+$ .

$\text{CH}_2\text{S} + \text{OH}^-$ . This reaction is an ion-molecule reaction which is preceded by deprotonation and then proceeds by base catalysis. Extensive works on nucleophilic attack of  $\text{OH}^-$  on the carbonyl group of  $\text{CH}_2\text{O}$  have shown that atoms of  $\text{HO} \cdots \text{CO}$  are approximately collinear at  $\text{O} \cdots \text{C}$  distance of about 4.0 Å and  $\text{O} \cdots \text{C} - \text{O}$  angle changes to tetrahedral value at closer range<sup>2c,d</sup>. It has also been reported that at  $\text{O} \cdots \text{C}$  3.0 Å there are two conformers which differ in energy by 0.2 kcal/mol and they are separated by a negligibly

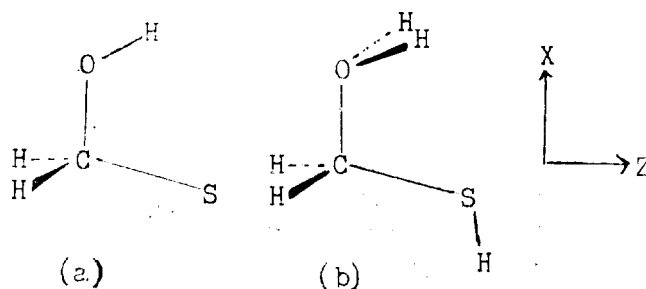
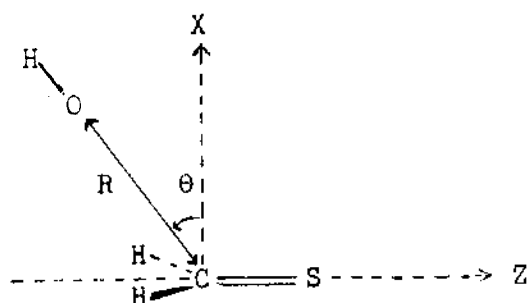


Figure 1. Drawings of STO-3G optimized structures: (a)  $\text{HOCH}_2\text{S}^-$  spp, Cs conformer; (b)  $\text{H}_2\text{O} + \text{H}_2\text{CSH}^+$ , Cs conformer.

**TABLE 1: STO-3G Optimized Geometries and Energies for Stable Structure. (a) The Methylene Hydrogen Atoms *cis* and *trans* to the Sulfur-bound Proton H in CH<sub>2</sub>SH<sup>+</sup>**

Species	$E_{tot}(\text{au})$	Bond length $\text{\AA}$	Bond angle deg.	Dihedral angle deg.
OH <sup>-</sup>	-74.1225	O-H 1.068		
H <sub>2</sub> O	-74.9625	O-H 0.956	H-O-H 105.2	
CH <sub>2</sub> S	-431.6711	C-S 1.579 C-H 1.078	H-C-S 123.9	
CH <sub>2</sub> SH <sup>+</sup> (a)	-432.0552	C-S 1.623 C-H 1.080 S-H 1.357	H-C-S 119.0 H-c-S 124.9 C-S-H 95.6	H-C-S-H 0.0
OHCH <sub>2</sub> S <sup>-</sup>	-505.9519	C-S 1.784 C-O 1.478 C-H 1.120 O-H 0.990	H-O-C 102.0 O-C-H 102.1 O-C-H 121.3	H-C-S-O 113.1 S-C-O-H 0.0
H <sub>2</sub> OCH <sub>2</sub> SH	-507.0966	C-S 1.799 C-H 1.080 C-O 1.500 O-H 0.956	C-S-H 95.6 O-C-S 107.7 O-C-H 103.0 H-C-H 112.0	S-C-O-H 61.3 H-C-S-O 113.0

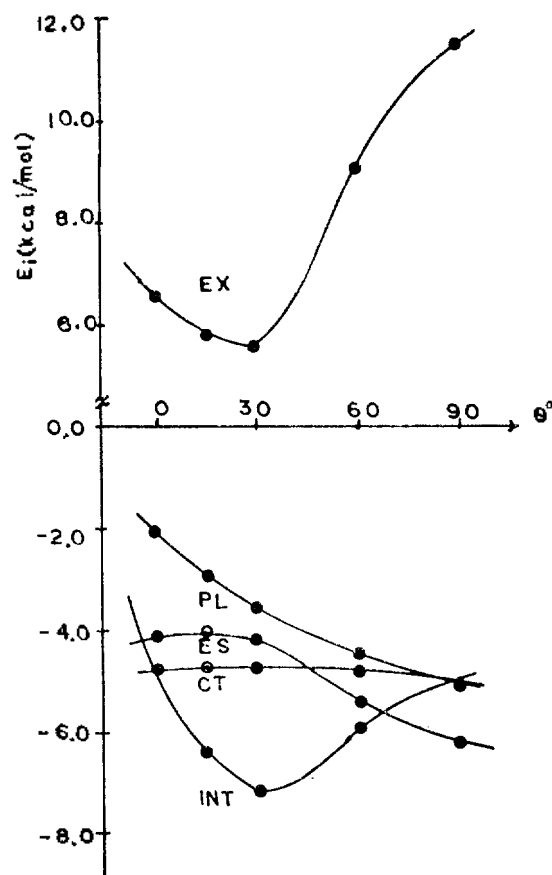
**Figure 2.** Symmetrical attack of hydroxide ion on thioformaldehyde. The atoms H—O...C are assumed to be collinear.  $R=2.5 \text{ \AA}$ **TABLE 2: Energy Components for Various Directions of Attack of Hydroxide ion on Thioformaldehyde, in kcal/mol. O...C Distance = 2.5  $\text{\AA}$** 

$E_i$	$\theta^\circ$				
	0	15	30	60	90
ES	-4.16	-4.21	-4.14	-5.40	-6.31
EX	6.48	5.72	5.67	9.08	11.50
PL	-2.11	-3.10	-3.57	-4.64	-5.08
CT	-4.76	-4.71	-4.70	-4.79	-5.10
MIX	-0.16	-0.23	-0.48	-0.15	-0.03
INT	-4.71	-6.53	-7.22	-5.90	-5.02

small potential energy barrier to internal rotation about the O...C axis. Based on these information, coordinates for the attack of OH<sup>-</sup> on CH<sub>2</sub>S were chosen as shown in Figure 2. The molecular plane is on the YZ-plane and  $\theta=0^\circ$  at X-axis perpendicular to this plane.

Interaction energies were calculated varying  $\theta$  until  $\theta=90^\circ$  when atoms of HO...C=S are collinear. Here the C...O distance  $R$  was 2.5  $\text{\AA}$  at which molecular deformation can be assumed not important. Interaction energies, INT, calculated are given in Table 2 and presented graphically in Figure 3.

In general the shape of the curve for INT is similar to that

**Figure 3.** Interaction energy and its contribution for various directions of attack of hydroxide ion on thioformaldehyde O...C distance = 2.5  $\text{\AA}$ .

obtained for CH<sub>2</sub>O using intermolecular SCF perturbation theory by Stone and Erskine<sup>11</sup> but the minimum is now at about  $\theta=30^\circ$ , which is somewhat greater than  $\theta=17^\circ$  for the attack on CH<sub>2</sub>O.

The shape of the INT curve is seen to parallel that of EX. This indicates, as was in the case of CH<sub>2</sub>O, that the reaction path is mainly controlled by steric effect and the minimum is reached at the most favorable interatomic repulsion. The larger angle obtained for CH<sub>2</sub>S compared to that for CH<sub>2</sub>O

may be explained using size effect; since the atom S is larger than the atom O the angle of approach should also be greater for S to minimize the exchange repulsion.

The rest of the energy components contribute about the same degree to the stabilization energy. The polarization term, PL, becomes more stabilizing as the angle  $\theta$  approaches to  $90^\circ$ , which is in contrast with the essentially independent nature of PL term on  $\theta$  in the attack on  $\text{CH}_2\text{O}$ ; the approach of  $\text{OH}^-$  to the carbon along axis rather than toward  $\pi$ -orbital of  $\text{C}=\text{S}$  from above seem to polarize S more efficiently. The ES term appears to be favored as  $\text{OH}^-$  approaches from the molecular plane of  $\text{CH}_2\text{S}$  due to attractive interaction with positively charged methylene hydrogen. The CT term does not show any notable dependence on  $\theta$ .

Gross atomic and bond populations at the most favored angle of approach of  $\theta=30^\circ$  are shown in Table 3. Weak bond formation between C and O, and the charge increase due to the polarization of S are evident in the Table.

The stable adduct shown in Figure 1(a) has  $C_s$  symmetry as it was in the case of  $\text{CH}_2\text{O}^{24}$ , and this adduct can be considered as an intermediate in base-catalysis reaction.

In assessing the interaction energy for this type of adduct however the molecular deformation energy (DEF) should also be considered together with the stabilizing adduct formation energy. The DEF for  $\text{OH}^-$  and  $\text{CH}_2\text{S}$  calculated were 38.96 and 44.15 kcal/mol respectively, giving the total DEF of 83.02 kcal/mol. Energy components obtained were  $\text{ES}=-91.41$ ,  $\text{PL}=-16.29$ ,  $\text{CT}=-126.83$ ,  $\text{EX}+\text{MIX}=52.20$  giving  $\text{INT}=-183.33$  kcal/mol and  $\Delta E=\text{INT}+\text{DEF}=-99.32$  kcal/mol. The change in atomic and bond populations at the transition state are given in Table 4.

It can be seen that the main contribution to the changes comes from the CT. The contribution of ES is excluded since

TABLE 3: Gross Atomic and Bond Populations of Isolated Molecules and Their Changes for the Complex of  $\text{CH}_2\text{S}+\text{OH}^-$ ,  $R=2.5 \text{ \AA}$ .

	Atom or bond	Reactant	Complex	$\Delta\delta$
Gross atomic population	O	8.871	8.861	-0.010
	C	6.240	6.163	-0.080
	S	15.881	16.030	0.150
Bond population	O-H	0.169	0.176	0.006
	C-O	0.0	0.005	0.005
	C-S	0.416	0.408	-0.008

TABLE 4: Gross Atomic and Bond Populations of Isolated Molecules and Their Component Changes for the Transition State of  $\text{OH}^-+\text{CH}_2\text{S}$ . A or B is Referred to Isolated Molecule

	Old bond C-S	New bond C-O	C	S	O
A or B <sup>a</sup>	0.417	0.0	6.241	15.881	8.871
T.S	0.237	0.235	6.108	16.576	8.354
Tot. change	-0.180	0.235	-0.133	0.695	-0.517
DEF	-0.085	0.0	-0.052	0.027	0.075
PL	-0.082	0.0	-0.380	0.417	-0.029
CT	-0.106	0.228	0.323	0.197	-0.592
EX+MIX	0.093	0.007	-0.024	0.054	0.029

the ES is a simple electrostatic energy with no orbital mixing. The bond population for C-S approaches to that for a single bond as bond length in Table 1 indicates. Negative charge development on the S atom is substantial at the transition state, the main contribution being from the PL term.

$\text{H}_2\text{O}+\text{CH}_2\text{SH}^+$ . This reaction corresponds to a specific acid-catalysis which is preceded by protonation on  $\text{CH}_2\text{S}$ . The STO-3G optimized bond parameters are given in Table 1(b). The coordinate system for the approach of nucleophilic water molecule was taken to be the same as in the case of  $\text{CH}_2\text{S}$ . Various orientation of water molecule may be possible but we have selected the one in which  $C_{2v}$  axis of  $\text{H}_2\text{O}$  is on the XZ plane passing through the carbon (Figure 4). The geometry in which water plane bisects the HCH angle did not differ energetically with that in Figure 4. The calculated values of INT varying the  $\theta$  from  $0^\circ$  to  $90^\circ$  at  $R=2.5 \text{ \AA}$  are given in Table 5 and Figure 5.

The predominant contribution to the INT is from the EX term as it was in the base-catalysis, but the minimum now appears at  $\theta=15^\circ$ .

The shift of the minimum point is due to the increased repulsive interaction between the two O-H of water and the two C-H of  $\text{CH}_2\text{SH}^+$ , which are oriented approximately face-to-face.

The PL term is practically independent of  $\theta$ ; polarization of charge on the S atom is decreased since the oxygen atom produces much weaker field compared with  $\text{OH}^-$  and in addition considerable charge transfer toward proton occurs. The main contribution to the stabilization energy is now the ES term. This is largely due to the increased positive charge on methylene hydrogens and nearly neutral carbonyl carbon

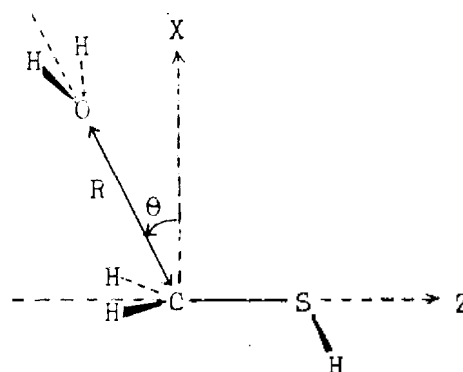
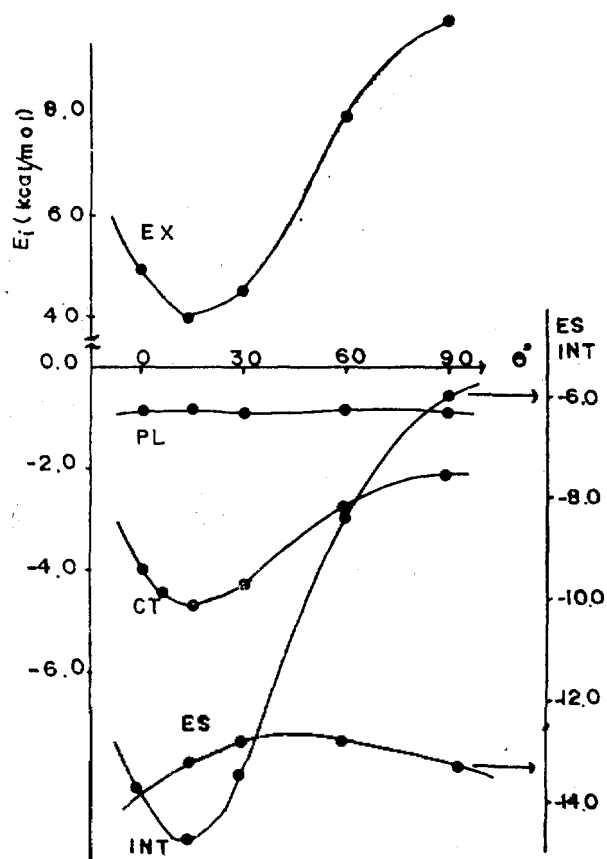


Figure 4. Symmetrical attack of water molecule on protonated thioformaldehyde. Attacking axis is  $C_{2v}$  axis of  $\text{H}_2\text{O}$ .

TABLE 5: Energy Components for Various Directions of Attack of  $\text{H}_2\text{O}$  on  $\text{CH}_2\text{SH}^+$ , in kcal/mol. O...C Distance= $2.5 \text{ \AA}$

$E_i$	$0^\circ$				
	0	15	30	60	90
ES	-14.00	-13.26	-12.92	-12.97	-13.27
EX	5.05	3.99	4.62	7.77	9.85
PL	-0.86	-0.84	-0.81	-0.76	-0.74
CT	-3.97	-4.68	-4.35	-2.72	-2.12
MIX	-0.09	-0.09	-0.04	0.10	0.16
INT	-13.87	-14.88	-13.50	-8.58	-6.12



**Figure 5.** Interaction energy and its contribution for various directions of attack of water on protonated thioformaldehyde. O...C distance = 2.5 Å.

**TABLE 6:** Gross Atomic and Bond Populations of Isolated Molecules and Their Component Changes for the Transition state of  $H_2O + CH_2SH^+$ . a A or B is referred to isolated molecule.

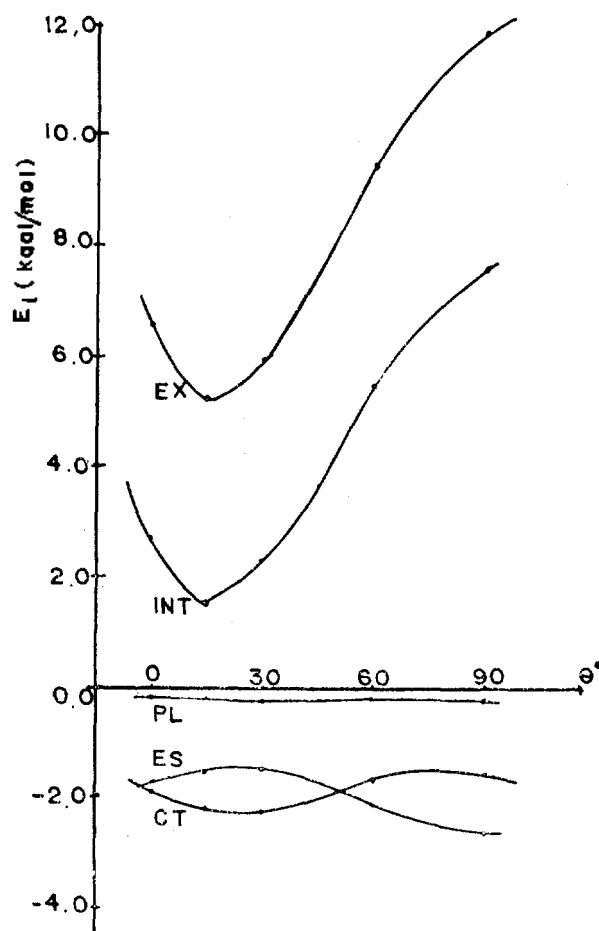
	Old bond C-S	New bond C-O	C	S	O
A or B	0.387	0.0	6.075	15.440	8.369
T.S	0.239	0.218	6.048	15.786	8.257
Tot. change	-0.148	0.218	-0.027	0.346	0.112
DEF	-0.164	0.0	-0.193	0.217	0.010
PL	-0.147	0.0	-0.277	0.254	0.173
CT	-0.170	0.239	0.163	0.218	-0.303
EX+MIX	0.333	-0.021	0.280	-0.343	0.008

in  $CH_2SH^+$  whereas the carbonyl carbon in  $CH_2S$  has partial negative charge. Thus in the acid-catalysis contribution of the ES term to the stabilization energy increases to 70.0 % from that in the base-catalysis of 32.1 %. The geometry of the transition state with  $C_s$  symmetry<sup>2d</sup> was optimized and is given in Table 1 and Figure 1(b).

The deformation energies (DEF) at the transition state were 2.21 and 64.01 kcal/mol for  $H_2O$  and  $CH_2SH^+$  respectively. The energy components of INT were ES = -86.38, EX = 113.41, PL = -7.84, CT = -82.38 and MIX = -52.53 kcal/mol giving the total INT of -115.72 kcal/mol. Thus the stabilization energy,  $\Delta E = DEF + INT$ , for the transition state becomes -49.05 kcal/mol. Stabilizing contributions of the ES and CT terms at the transition state are found to be approximately the same. Table 6 summarizes

**TABLE 7:** Energy Components for Various Directions of Attack of  $H_2O$  on  $CH_2S$ , in kcal/mol. O...C Distance = 2.5 Å

$E_i$	0°				
	0	15	30	60	90
ES	-1.75	-1.40	-1.49	-2.07	-2.59
EX	6.56	5.21	5.89	9.38	11.85
PL	-0.16	-0.19	-0.21	-0.21	-0.20
CT	-1.89	-2.29	-2.22	-1.64	-1.58
MIX	0.10	0.20	0.28	0.13	0.10
INT	2.86	1.53	2.25	5.59	7.59



**Figure 6.** Interaction energy and its contribution for various directions of attack of water on thioformaldehyde. O...C distance = 2.5 Å

the atomic and bond populations and their changes. The degree of C...O bond formation is somewhat less than in  $HOCH_2S^-$ , which is reasonable considering the similar trend in bond length of C...O in the respective adducts given in Table 1. The electronic reorganization is seen to be influenced to about the same degree by the various component energies.

$H_2O + CH_2S$ . It has been shown that in the addition of water to carbonyl no zwitterionic intermediate of the type  $H_2^+OCH_2O^-$  is possible owing to the strong repulsive force at short range and methanediol must be formed in a concerted proton transfer (PT) with heavy-atom reorganization (HAR) process<sup>2d</sup>.

In this study we first search a favorable route for approach

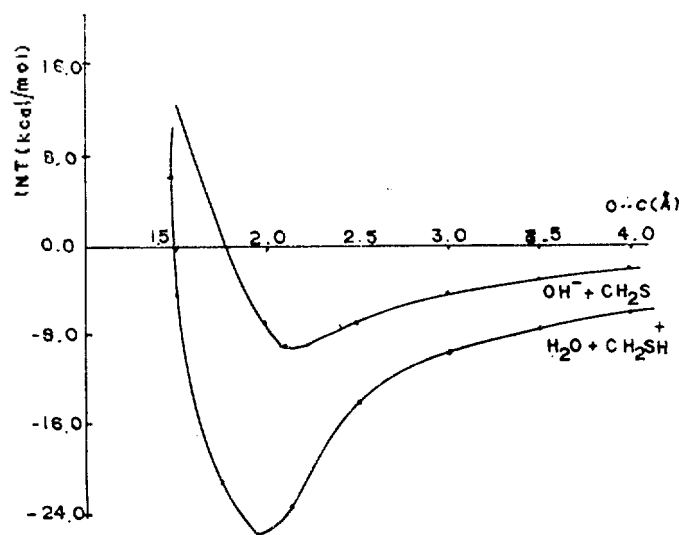


Figure 7. STO-3G interaction energies for  $\text{OH}^- + \text{CH}_2\text{S}$  and  $\text{H}_2\text{O} + \text{CH}_2\text{SH}^+$  additions as a function of intermolecular  $\text{O}\cdots\text{C}$  distance without deformation.

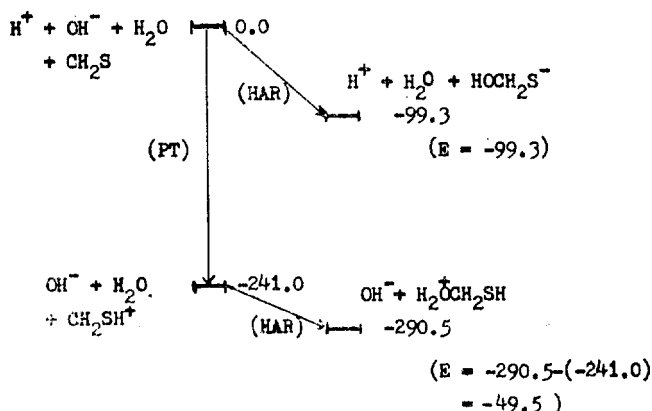


Figure 8. Energy diagram illustrating acid-base catalysis of thioformaldehyde, in kcal/mol; HAR=heavy atom reorganization, PT=proton transfer.

of  $\text{H}_2\text{O}$  and then examine factors contributing to the preferred geometry.

The coordinate system adopted was the same as that for the reaction  $\text{CH}_2\text{SH}^+ + \text{H}_2\text{O}$ . The angular dependence of INT is shown in Table 7 and Figure 6. It is apparent from these that the repulsive interaction, EX, is dominant in determining the reaction path as it was the case for the two preceding processes. The energy minimum is again at  $\theta = 15^\circ$  implying that the repulsive interaction between water hydrogens and methylene hydrogens are substantial as pointed out above for the reaction  $\text{H}_2\text{O} + \text{CH}_2\text{SH}^+$ . Magnitudes of stabilizing contributions from PL, CT and ES are in general smaller than those for preceding two processes.

The large stabilizing contribution of the ES term found in the reaction with  $\text{CH}_2\text{SH}^+$  is greatly reduced in this process, to about one tenth, due to the unfavorable charge distribution.

The overall repulsive interaction (INT) is a result of decreased stabilizing contributions of the ES, PL and CT terms while the destabilizing effect of EX being at the similar

level compared with those of the ion-molecule reactions. The intermolecular distance,  $\text{C}\cdots\text{O}$ , dependence of INT which does not include the DEF is shown in Figure 7 for the ion-molecule reactions  $\text{OH}^- + \text{CH}_2\text{S}$  and  $\text{H}_2\text{O} + \text{CH}_2\text{SH}^+$ . The results in Figure 7 indicate that the acid-catalysis is more favorable energetically than the base-catalysis in the initial stage of the reaction. However Figure 8 shows that when the DEF is taken into consideration the trend reverses;  $\Delta E (= \text{INT} + \text{DEF})$  values are  $-99.31$  and  $-49.50$  kcal/mol for the base- and acid-catalyses processes respectively and hence the base-catalysis is favored by 50 kcal/mol over the acid-catalysis.

This demonstrates the importance of deformation energy in the interpretation of interaction energies in studies of reaction mechanism.

### Conclusions

(1) The hydration of thiocarbonyl group involves a symmetrical attack of nucleophile from above and  $15\sim 30^\circ$  rear on the  $\pi$ -orbital of carbonyl carbon prior to the formation of tetrahedral transition state.

Dominant factor determining this orientation of nucleophile was the EX term, as it was in the carbonyl addition.

(2) The PL term emerges as a prominent factor contributing to the stabilization energy for base catalyzed process owing to the strong polarization of S atom caused by the negative charge field of  $\text{OH}^-$  ion.

(3) Inclusion of molecular deformation energy (DEF) in the total interaction energy reverses the preference of catalyzed reactions from the acid-catalysis (without DEF) to the base-catalysis (with DEF)

**Acknowledgement.** We thank the Ministry of Education and the Korea Research Center for Theoretical Physics and Chemistry for support of this work.

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## Kinetics of the Bromine-Exchange Reaction of Gallium Bromide with *i*-Butyl Bromide in 1,2,4-Trichlorobenzene and in Nitrobenzene

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The rate of the bromine-exchange reaction between gallium bromide and *i*-butyl bromide in 1,2,4-trichlorobenzene or nitrobenzene was measured at 19, 25 and 40 °C., using *i*-butyl bromide labelled with Br-82. The results indicated that the exchange reaction was second order with respect to gallium bromide and first order with respect to *i*-butyl bromide. The third-order rate constant determined at 19°C was  $3.28 \times 10^{-2} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$  in 1,2,4-trichlorobenzene and  $9.25 \times 10^{-3} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$  in nitrobenzene. The activation energy, the enthalpy of activation and the entropy of activation for the exchange reaction were also determined.

### Introduction

Previously we published the results of the kinetic studies, on the bromine exchange reactions of gallium bromide with methyl, ethyl, *n*-propyl, *i*-propyl and *n*-butyl in 1,2,4-trichlorobenzene or nitrobenzene<sup>1-5</sup>. The results indicated that the exchange reactions were second order with respect to gallium bromide and first order with respect to the alkyl bromides examined.

$$\text{Rate} = k_3 [\text{GaBr}_3]^2 [\text{RBr}]$$

We presented a reaction mechanism for the exchange reactions, which assumed the breaking of the carbon-bromine bond in the alkyl bromide molecules to play an important role for determining the rate of the exchange reactions<sup>2</sup>.

The third-order rate constants obtained at 19°C for the systems of gallium bromide with *n*-propyl and *i*-propyl bromides in nitrobenzene were  $4.5 \times 10^{-3}$  and  $3.2 \times 10^{-2} \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ , respectively<sup>3,5</sup>. Thus, fairly large difference was observed between the two isomeric propyl bromides regarding the rates of bromine-exchange with gallium bromide. It seemed of interest to compare *n*-butyl bromide with *i*-butyl bromide as to the rates of bromine-exchange with gallium bromide. Since the system of *n*-butyl bromide with gallium bromide in 1,2,4-trichlorobenzene or

nitrobenzene was already examined<sup>4</sup>, it was decided to extend the studies to the corresponding system of *i*-butyl bromide.

### Experimental Part

*Apparatus and Materials.* The apparatus used in the present study was essentially the same as that used previously<sup>1,2</sup>. The methods of preparation and/or purification of gallium bromide and solvents were described in previous papers of this series<sup>1-5</sup>.

*Preparation of *i*-Butyl Bromide (<sup>82</sup>Br).* A small quantity of solid potassium bromide (Reagent grade, Merck, Germany) was irradiated with neutrons to induce the (*n*,  $\gamma$ ) reaction of bromine. The irradiated potassium bromide was mixed with an appropriate amount of inactive potassium bromide, and used to synthesize *i*-butyl bromide (<sup>82</sup>Br) by the method described in the previous paper<sup>6,7</sup>.

*Procedures for Kinetic Study of the Exchange Reactions.* The procedures for the kinetic study and the method of calculation of the exchange rates were described previously<sup>1,2</sup>.

A solution of gallium bromide in 1,2,4-trichlorobenzene or nitrobenzene of known concentration was prepared inside the vacuum line. A known quantity of labelled *i*-butyl bromide vapor was introduced to the reaction vessel by expanding the vapor from the storage system. This was taken