

## 카보닐 탄소원자의 친핵 치환반응. 제 2보. Methyl chloroformate의 티오 치환체들의 구조와 반응성에 관한 CNDO/2 계산

이 의 춘

서울대학교 공과대학 응용화학과

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### Nucleophilic Substitution at a Carbonyl Carbon Atom. Part II. CNDO/2 Studies on Conformation and Reactivity of the Thio-Analogues of Methyl Chloroformate

Ikchoon Lee

Department of Applied Chemistry, College of Engineering, Seoul National University

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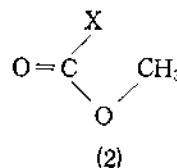
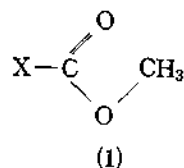
요 약 메틸 클로로 티올, 메틸클로로 티오노 및 메틸 클로로 디티오 황에이트에 대하여 CNDO/2 계산을 실시하였다. 결과로 이들 화합물은 trans 형이 안정한 것임을 밝혔다. 또 유황 원자는 산소원자에 비하여 그 고립쌍 전자들을  $\pi$ -결합 형성에 사용할려는 경향이 적고 티올 황에이트의 경우는 메틸기의 hyperconjugation에 의하여 안정화됨을 알았다. 가용매 반응성의 순서는 양이온의 안정도와 일치하며 이것은 알려진  $S_N1$  형 반응 메카니즘과 부합된다.

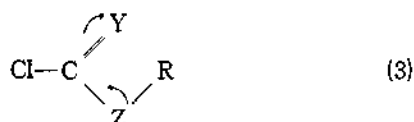
**Abstract** CNDO/2 calculations have been carried out on methyl chloro-thiol-, methyl chloro-thiono-, and methyl chloro-dithio-formates. Results show that the trans is the stable configuration for these compounds. It was found that sulfur atom has much less tendency to use its lone pair electrons for  $\pi$  bond formation compared with oxygen, and that thioformates are stabilized by hyperconjugation of methyl hydrogens. The order of solvolytic reactivity was found to follow the order of cation stability, which is consistent with the  $S_N1$  mechanism proposed for these compounds.

#### Introduction

Our previous CNDO/2 studies (hereafter, Paper I)<sup>1</sup> on methyl chloro- and methyl fluoroformates have established that, (a) the stable configuration of these compounds is the trans (1; X=Cl or F) rather than the cis (2; X=Cl or F), and (b) these compounds are stabilized by conjugative electron release from lone pair

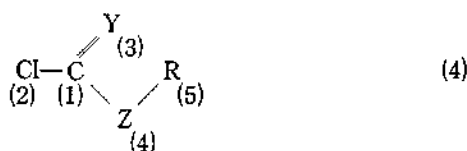
electrons of ether oxygen to carbonyl oxygen and by electrostatic interaction of the carbonyl oxygen with methyl group. The  $\pi$  electron conjugation (3; Y=Z=O and R=CH<sub>3</sub>) was re-



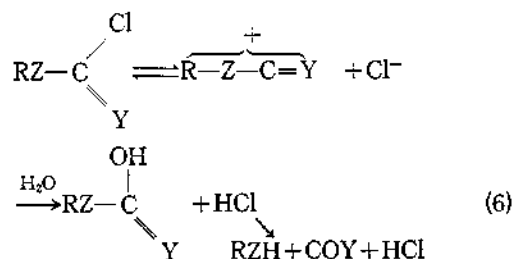
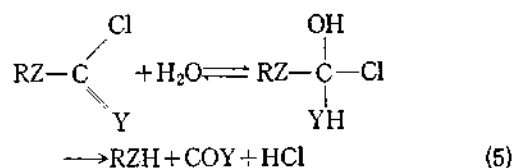


responsible for the partial double bond character of C-Z bond, which in turn was responsible for the barrier to internal rotation around this bond and gave a planar structure for these molecules.

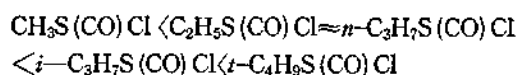
It has been reported that rates of solvolysis of chloroformate and thioformate esters (4; Y=Z=O or S.) are much slower than other acid chlorides and this was attributed to the initial state stabilization.<sup>2</sup> This effect was shown to be enhanced by structural changes that increase electron donation by the hydrocarbon group (R) and diminish in compounds where the heteroatom (Z) has only a limited tendency to share its lone pair electrons for  $\pi$ -bond formation.<sup>2</sup> It was also found that chloroformates are much less reactive than their thio analogues. It has therefore been concluded that when



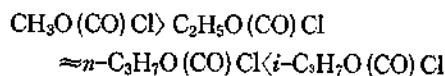
chloroformates solvolyze by addition-elimination mechanism (5), their thio analogues react unimolecularly (6).



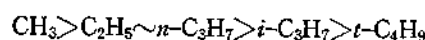
The increased reactivity of thiochloroformates compared with the oxygen analogues are consistent with the fact that sulfur is less electronegative than oxygen and also has less tendency to use its unshared electrons for  $\pi$ -bond formation. The rate sequence found for thiochloroformates was;<sup>2</sup>



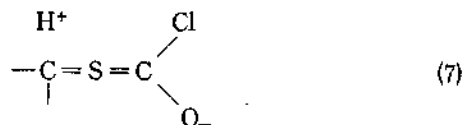
in contrast with the rate sequence for chloroformates;



On the other hand, the dipole moment data indicated that inductive electron release by the RS-groups in the thiochloroformates is modified by a secondary effect which decreases as R changes in the order



It has therefore been suggested that hyperconjugative electron release by alkyl group of the type in (7) to the d orbitals of sulfur occurs in these compounds.<sup>4</sup>



In order to investigate theoretically these various aspects of sulfur replacement for oxygen in methyl chloroformate, we have now carried out CNDO/2 calculations<sup>5</sup> on methyl chloro-thiol-, methyl chloro-thiono- and methyl chloro-dithio-formates.

### Calculations

The method of calculation was the same as reported in Paper I. Bond angles and bond lengths used in these calculations, that are different from Paper I, are listed in Table I.

Table I. Bond Parameters Used in Atomic Coordinate Calculation.

$d(C_{(1)}-S_{(4)})=1.58\text{\AA}$	$\angle Y_{(3)}C_{(1)}Z_{(4)}=126^\circ$
$d(C_{(1)}-S_{(4)})=1.76\text{\AA}$	$\angle Z_{(4)}C_{(1)}Cl_{(2)}=112^\circ$
$d(C_{(1)}-S_{(4)})=1.86\text{\AA}$	$\angle C_{(1)}S_{(4)}C_{(5)}=104^\circ$

[Numberings are those in Scheme (4)]

For all the three compounds calculations were carried out on both the trans and cis configurations and also for cations.

### Results and Discussion

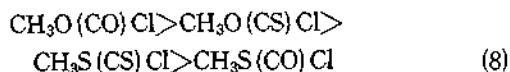
**Energetics.** The energy differences calculated from total electron energies for the trans and cis configurations are given in Table II.

Although for dithio-compounds the energy difference is rather small, for all three compounds the trans form is more stable than the cis form which is in accord with our previous conclusion but again contrary to the conclusion reached by Queen et al, based on their dipole moment calculations.<sup>4</sup> The energy difference between the cis and trans forms is the greatest for chlorothionoformate (4; R=CH<sub>3</sub>, Z=O and Y=S) and the least for chlorodithioformate (4; CH<sub>3</sub>=R, Y=Z=S). The energy of ionization,  $\Delta E_{\text{ioniz}}$ , calculated by the difference in binding energies between cation and the stable molecule is also maximum for thionoformate, (Table II) It may therefore be expected that thiono-

Table II. Energy Differences,  $\Delta E_{\text{cis-trans}}$ , and Energy of Ionization,  $\Delta E_{\text{ioniz}}$  (Kcal/mole)

	CH <sub>3</sub> O(CO)Cl <sup>4</sup>	CH <sub>3</sub> O(CS)Cl	CH <sub>3</sub> S(CO)Cl	CH <sub>3</sub> S(CS)Cl
$\Delta E_{\text{cis-trans}}$	3.9	2.4	2.1	0.1
$\Delta E_{\text{ioniz}}$	377.5	368.7	340.4	350.3

formate will have the least reactivity if these compounds solvolyzed unimolecularly (S<sub>N</sub>1 mechanism, 6) with solvent. The experimental results of Queen confirm this prediction.<sup>2,3</sup> The order of decreasing  $\Delta E_{\text{ioniz}}$  (and hence the order of increasing S<sub>N</sub>1 reactivity) is,



**Dipole Moments.** The CNDO/2 dipole moments,  $\mu$ , are summarized in Table III. For chlorothiolfomate experimental value determi-

ned in benzene solution is available.<sup>4</sup> Table III shows that  $\mu$  value for the trans form is larger and that for the cis is smaller than the experimental value. Since normally one would expect the dipole moment derived from solution measurement in benzene to be lower than the true vapor phase value, the result of this work supports the contention that the trans form is the more stable. Queen et al., calculated  $\mu$  values based on bond moments and have concluded that the cis form was more stable than the trans since  $\mu$  value for the cis was larger than the trans according to their calculation.

For thiono- and dithio-formates, CNDO/2  $\mu$  values for the cis form are very much larger than those for the trans form. The  $\mu$  values for the cis form seem rather unrealistic and therefore the cis forms for these compounds

Table III. Dipole Moments,  $\mu$ , (CNDO/2) (in debye unit)

	trans	cis	exptl.
CH <sub>3</sub> O(CS)Cl	3.38	4.56	—
CH <sub>3</sub> S(CO)Cl	3.09	2.43	2.69
CH <sub>3</sub> S(CS)Cl	2.73	4.26	—

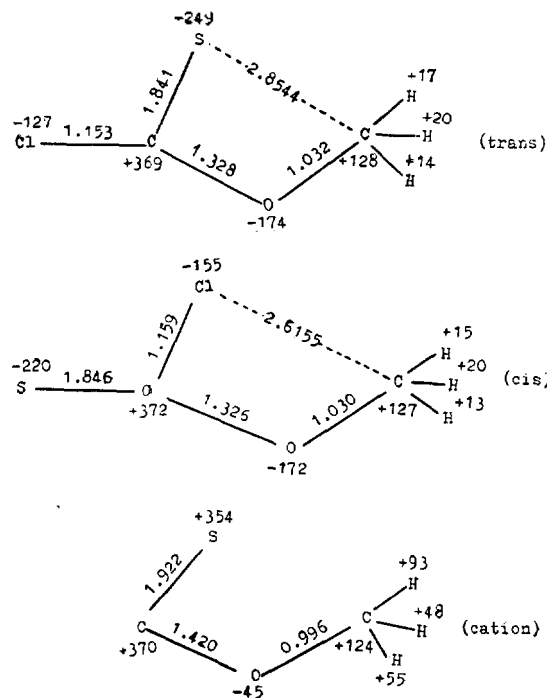
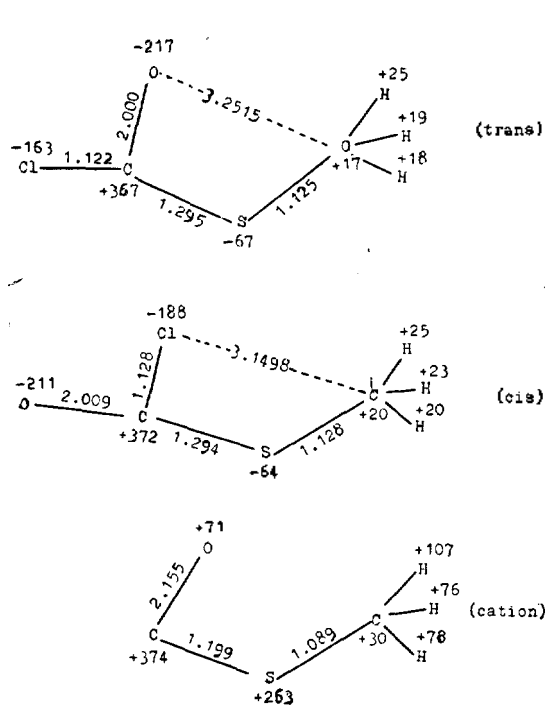


Fig. 1. Atomic charge and overlap population for methyl chlorothiolformate. Charges are  $10^3$  times of electronic charge units. (.....indicates distance in Å)

Fig. 2. Atomic charge and overlap population for methyl chlorothionoformate. Charges are  $10^3$  times of electronic charge units. (.....indicates distance in Å)

are unlikely to be the more stable. Unfortunately no experimental values for these compounds are available for comparison.

**Charge Density, Overlap Population and Reactivity.** Computed total (sigma+pi) charge densities and overlap populations are shown in Fig. 1~3. For all the three compounds, the trans form has larger electron density on carbonyl oxygen (or sulfur) and higher overlap population between carbonyl carbon and ether oxygen (or sulfur) compared with the cis form, as it was found the case for methyl chloroformate in Paper I. Here again we can therefore conclude that the same type of electron conjugation from ether oxygen (or sulfur) to carbonyl oxygen (or sulfur), and electrostatic interaction between carbonyl oxygen (or sulfur) and methyl group stabilize the trans form.

Overlap populations due to  $\pi$  electron alone are listed in Table IV. for the two bonds of interest *i.e.*, for C-Y and C-Z. It is clear from this table that the electron conjugation of the type (3) is entirely due to  $\pi$  electrons. Reluctance of sulfur atom to share its lone pairs for  $\pi$  bond formation is easily seen from this table; when S is at Z, *i.e.*, for the thiols, the  $\pi$ -bonding between C<sub>(1)</sub> and Y(S) is reduced. As a result, thiono-compound has the strongest  $\pi$ -conjugation, since in this compound ether oxygen releases its lone pairs for  $\pi$ -bond formation appreciably while carbonyl sulfur atom has much less tendency to share its lone pairs thus reducing  $\pi$ -bonding between C<sub>(1)</sub> and S<sub>(2)</sub>. An exactly opposite situation prevails in thiol-compounds, where C<sub>(1)</sub>-S<sub>(2)</sub> has diminished  $\pi$ -bonding while C<sub>(1)</sub>-O<sub>(3)</sub> has enhanced  $\pi$ -bonding.

Table IV.  $\pi$ -Overlap Populations for

	$C_{(1)}-Y_{(3)}$	$C_{(1)}-Z_{(4)}$
methyl chlorothioformate		
( $Y_{(3)}=O, Z_{(4)}=S$ )		
trans	0.9211	0.2456
cis	0.9193	0.2441
cation	0.8427	0.3467
methyl chlorothionoformate		
( $Y_{(3)}=S, Z_{(4)}=O$ )		
trans	0.7932	0.4383
cis	0.7981	0.4324
cation	0.6823	0.5679
methyl chlorodithioformate		
( $Y_{(3)}=Z_{(4)}=S$ )		
trans	0.8600	0.3253
cis	0.8560	0.3253
cation	0.7194	0.4718
methyl chloroformate *		
( $Y_{(3)}=Z_{(4)}=O$ )		
trans	0.8893	0.3362
cis	0.8877	0.3357
cation	0.7956	0.4543

\* Ref. (1)

Dithio- and dioxygen-analogues are in between of these two extremes. Other features are the same as we have already discussed in Paper I. Other interesting features that are different from methyl chloroformate are that (1) thiol- and dithio-formates which have thio-ether sulfur atom have greatly increased overlap population between the ether sulfur atom and methyl carbon atom, and (2) they have decreased positive charge on methyl carbon atom but increased positive charge on methyl hydrogen atoms. This type of charge distribution is indeed an indication that the hyperconjugation stabilization of the structure (7) is actually operative in these compounds. This hyperconjugative initial state stabilization will make these molecules

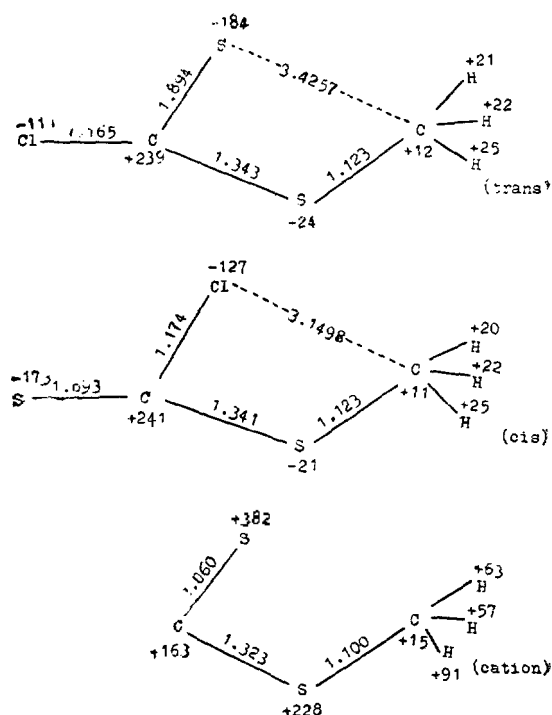
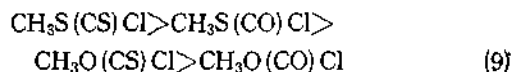


Fig. 3. Atomic charge and overlap population for methyl chlorodithioformate. Charges are  $10^3$  times of electronic charge units. (.....indicates distance in Å)

less reactive. This tendency is much reduced in thionoformate where no thio-ether sulfur is present, and is decreasing in the order.



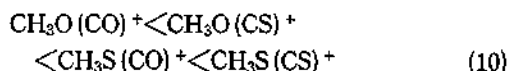
On the other hand, the delocalization of positive charge in cation is greatly enhanced in these compounds with thio-ether sulfur atom. This will stabilize the cation appreciably and will therefore increase the  $S_N1$  reactivity of these compounds. For thiol- and dithio-formate cations, the positive charge is delocalized over entire system, while thiono-formate cation has some negative charge left over on ether oxygen atom. This cation stabilization by charge delocalization is increasing in the order,

Table V. Frontier Electron Densities of Carbonyl Carbon

	CH <sub>3</sub> O (CO) Cl <sup>1</sup>	CH <sub>3</sub> O (CS) Cl	CH <sub>3</sub> S (CO) Cl	CH <sub>3</sub> S (CS) Cl
$f^{(LU)}$	0.946	1.288	0.704	0.956

Table VI. Comparison of Reactivity Sequences

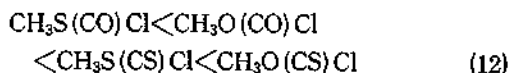
source	order of increasing reactivity →	mechanism expected
electron conjugat. $f^{(LU)}$	CH <sub>3</sub> O (CS) Cl, CH <sub>3</sub> O (CO) Cl ≈ CH <sub>3</sub> S (CS) Cl, CH <sub>3</sub> S (CO) Cl, CH <sub>3</sub> S (CO) Cl, CH <sub>3</sub> O (CO) Cl ≈ CH <sub>3</sub> S (CS) Cl, CH <sub>3</sub> O (CS) Cl,	S <sub>N</sub> 2 or Add-Elim
ΔE of Ion.	CH <sub>3</sub> O (CO) Cl, CH <sub>3</sub> O (CS) Cl, CH <sub>3</sub> S (CS) Cl, CH <sub>3</sub> S (CO) Cl,	S <sub>N</sub> 1
hypercon. stabiliz.	CH <sub>3</sub> S (CS) Cl, CH <sub>3</sub> S (CO) Cl, CH <sub>3</sub> O (CS) Cl, CH <sub>3</sub> O (CO) Cl,	
cation stabiliz.	CH <sub>3</sub> O (CO) Cl, CH <sub>3</sub> O (CS) Cl, CH <sub>3</sub> S (CO) Cl, CH <sub>3</sub> S (CS) Cl,	S <sub>N</sub> 1
expetl. <sup>2,3</sup>	CH <sub>3</sub> O (CO) Cl, CH <sub>3</sub> O (CS) Cl, CH <sub>3</sub> S (CO) Cl, CH <sub>3</sub> S (CS) Cl,	?



Lastly we have calculated the frontier electron densities for<sup>6</sup> nucleophilic reaction at carbonyl carbon as a measure of reactivity of direct substitution, *i.e.*, S<sub>N</sub>2 mechanism and/or addition-elimination mechanism (5). This reactivity index,  $f^{(N)}$ , is believed to be an excellent parameter for such reactions<sup>6</sup>, and is defined as;

$$f^{(N)} = 2 \sum_i (C^{LU}_i)^2 \quad (11)$$

where  $C^{LU}_i$  is the coefficient of atomic orbital (AO)  $i$  in the lowest unoccupied (LU) MO and the summation is over all AO's on atom C. The calculated values are given in Table V, which shows that the order of increasing  $f^{(N)}$  value is,



This represents the order of increasing S<sub>N</sub>2 reactivity, since the larger the value of  $f^{(N)}$ , the greater the reactivity.

In order to facilitate the comparison of reactivities and decide the probable mechanism involved in solvolysis of thio-analogues of methyl

chloroformates, various sequences are tabulated in Table VI together with the sequence found experimentally. Some interesting features emerge from the comparison of sequences; (1) Reactivity sequence judged by  $\pi$  electron conjugation is opposite of that due to frontier electron densities. It appears therefore that the frontier electron density is controlled by  $\pi$ -electrons, since the most strongly stabilized by  $\pi$ -electron conjugation has the largest frontier electron density. At present the author has no ready explanation for this. (2) The reactivity sequence due to hyperconjugative stabilization is opposite to that due to cation stabilization. Since the experimental reactivity sequence follows that due to cation stabilization, it can be concluded that the initial state stabilization is a minor factor determining reactivity compared with cation stabilization. This is reasonable if we think of the transition state for solvolysis of thio-compounds to be something similar to the actual cation. In other words, the transition state is more important in determining the reactivity sequence than the initial state. It is clear that these thio-analogues of chloroformate react unimolecularly in the solvolytic reaction as Queen suggested.<sup>3</sup>

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