

◀Original▶ Nucleophilic Substitution at a Carbonyl Carbon Atom

Part I. MO-theoretical studies on methyl chloro-and fluoro-formates

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Abstract

CNDO/2 and INDO calculations have been carried out on varying geometries of methyl chloro-and fluoro-formates. Results show that the configuration in which halogen atom is trans to methyl group is the most stable. Atomic charges and overlap population show that the trans form is stabilized by conjugation of carbonyl double bond with the unshared pairs of the ether oxygen and by electrostatic attraction of carbonyl oxygen to methyl group. Dipole moments of the trans forms agree reasonably well with the experimental values but showed that any generalizations made with dipole moments from bond moments should be accepted with considerable reservations.

요 약

메틸 클로로 및 플로로 휘메이트의 각종 구조에 대한 CNDO/2 및 INDO 계산을 실시하였다. 결과로 가장 안정한 구조는 할로겐 원자와 메틸기가 trans 인 형 임을 알았다. 원자의 전하와 결합전자밀도를 볼때 에텔 산소의 비공유 전자쌍의 공액과 카보닐 산소와 메틸기 간의 정전기적인 상호작용으로 분자가 안정화 되어 있음을 알수 있었다. 쌍극자 모멘트는 trans 의 값이 실험값에 가까우며 결합모멘트로 계산된 쌍극자 모멘트로 부터 일반적인 결론을 내리기 어려움을 밝혔다.

1. Introduction

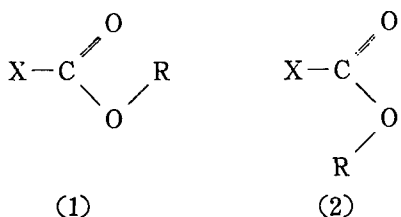
Nucleophilic substitution reaction at a carbonyl carbon atom has been a subject of extensive study with the view to clarifying the mechanism involved¹⁾. The mechanism of this reaction has been shown to be of considerable complexity and experimental evidence shows that not a single unified mechanism but a multiple mechanism is operating. The

mechanism proposed can be classified into three categories; (a) SN1, (b) SN2, and (c) addition-elimination¹⁾. In this series of work we intend to extend the studies in this field by investigating the reaction theoretically as well as experimentally and hope to shed some light on the mechanism.

Chloroformate esters undergo solvolysis much slowly than other acid chlorides²⁾. This has been attributed to their increased initial

state conjugation. Insights may be obtained into this conjugative stabilization of the initial state by looking into electronic structures of these compounds more closely.

There seems to be general agreement that the most favorable configuration of alkyl formates is that in which the alkyl group and carbonyl oxygen are cis to each other (1, X=H)³⁾.



It has been however reported by Bock *et al.*, through their dipole moment studies that the corresponding chloro- and fluoro-formate esters prefer the configuration that the halogen atoms are cis to the alkyl group (2, X=Cl or F)⁴⁾. This is a surprising conclusion as the authors had noted in their paper, since the two have the structures differing only in that the hydrogen atom of alkyl formate is replaced by the halogen atom. Furthermore there is direct experimental evidence by electron diffraction that the stable conformation of methyl chloroformate is not cis(2) but trans (1)⁵⁾.

In order to solve this inconsistency and to obtain some information on the conjugative stabilization of initial states of methyl chloro- and fluoro-formates, we have carried out the CNDO/2 (Complete Neglect of Differential Overlap) calculations on these compounds. This approximate self-consistent field (SCF) MO theory of Pople and Segal⁶⁾ is a reasonably good approximation to exact quantum mechanical calculations. It has been successfully applied to theoretical predictions of conformations⁷⁾ as well as reactivities⁸⁾ of sigma electron systems. In this paper we have computed the charge distributions and resu-

lting dipole moments, the energies for rotation about C₍₁₎-O₍₄₎ bond, (Fig. 1), thereby obtaining the energy barrier and energy difference between the cis and trans forms, and energies of ionization for the two compounds. In the case of methyl fluoroformate we have also conducted an INDO (Intermediate Neglect of Differential Overlap) calculation⁹⁾.

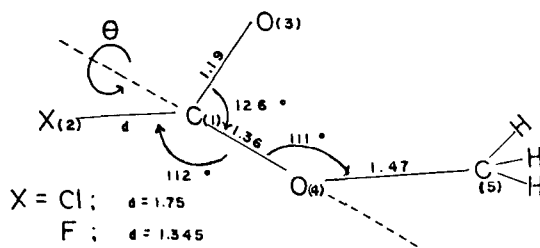


Fig. 1. Geometry of molecules showing axis of rotation and numbering scheme

2. Calculations

CNDO/2 and INDO methods are approximate solutions of a Hartree-Fock equation for many-electron problem, and are described in detail in the original publications^{6, 9)}. These SCF methods treat all valence electrons and employ zero differential overlap but include electron interactions explicitly. In the INDO method differential overlaps in one-center exchange integrals are retained, and therefore a better approximation than the CNDO/2 method, although improvements in the results of calculation may not always warrant the use of extra computer time. The two methods correspond to the two different ways of restoring rotational invariance.

The input data for the computer program (CNINDO, obtained from Quantum Chemistry Program Exchange, Indiana Univ., USA) are given in Fig. 1 (atomic coordinates, expressed in terms of bond lengths and bond angles), and Table 1 (the Slater orbitals and bonding parameters, β_0)⁹⁾. The bond lengths and bond angles were taken from the literature¹⁰⁾ and the Cartesian coordinates were calculated using another program¹¹⁾. Geometries of the mole-

Table 1. Parameters used in the calculation

atom	Slater exponent	Bonding parameter, β_0
H	1.300	-9.00
C	1.625	-21.00
O	2.275	-31.00
F	2.600	-39.00
Cl	2.050	-22.330

cules were varied by rotating around $C_{(1)}-O_{(4)}$ bond axis (see Fig. 1) by $\theta=0^\circ, 45^\circ, 90^\circ, 180^\circ$ and 270° anticlockwise. CNDO/2 calculations were also carried out on methyl formate which are formed when the carbonyl carbon-halogen bond fission occurs heterolytically.

The output from the program includes; (1) the calculated energy levels, total energy and binding energy of molecules, (2) the wave functions, (3) electron densities on each atom, (4) the bond order or overlap population¹²⁾, (5) excitation energies, and (6) dipole moments.

3. Results and Discussion

The results of calculations will be presented and discussed in three sections; (1) energetics, (2) dipole moments, and (3) charges, overlap population and reactivities.

(1) **Energetics:** Total energies calculated are shown in Fig. 2 and energy differences and barriers to internal rotation are given in Table 2. Barrier heights for the two methyl haloformates are approximately the same, but the energy difference between the two conformations is larger for the chloroformate. For both compounds the cis form has higher energy than the trans form. This is strong evidence that the stable configuration of methyl haloformates is the trans form not the cis, contrary to the conclusion reached by Bock *et al.*,⁴⁾ based on their dipole moment studies.

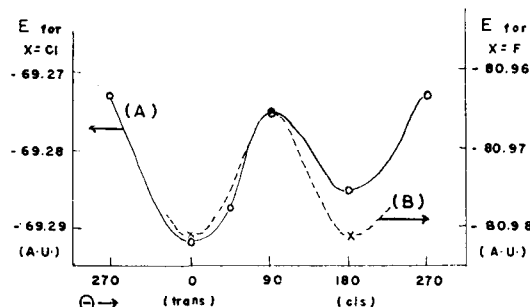


Fig. 2. CNDO/2 Energies for $CH_3O(CO)X$
(A): $X=Cl$ (B): $X=F$

Table 2. Barriers to internal rotation and energy differences, $\Delta E_{cis-trans}$, (in kcal/mole)

X	Barrier	ΔE
Cl	10.3	3.9
F	10.4	1.1

Ab initio LCAO-MO-SCF calculations¹³⁾ of the energy difference between the two conformers of methyl formate have been reported to yield a similar result, namely that the trans conformer is about 9 kcal/mole lower in energy than the cis conformer. As we have already pointed out there is other more direct evidence⁵⁾ that the trans is the stable form for methyl chloroformate. We therefore conclude that the stable configuration is the trans not the cis.

It is interesting to compare the energy differences of the cis and trans forms of the two compounds with those of N-methyl formamide (~ 2 kcal)¹⁴⁾ and N-methyl acetamide (3 kcal)¹⁵⁾. For these compounds the barrier heights to internal rotation calculated by CNDO/2 method were much higher (18 kcal) but nearly the same for the two¹⁶⁾.

The difference in binding energies between cation and molecule may be taken as energy of ionization of a molecule into an anion and a cation. The values thus calculated for me-

Table 3. Ionization energies (in kcal/mole)

	X	ΔE_{ioniz}	Bond energy #
CNDO/2	Cl	377.5	177.2
"	F	494.9	206.6
INDO	F	395.0	

#. R. T. Sanderson, "Chemical Bonds and Bond Energy", Academic Press, New York, 1971.

thyl haloformates are given in Table 3, together with bond energies of the C-X bonds. We naturally do not expect an agreement between the bond energy and ΔE_{ioniz} since the former is the average energy necessary to break C-X bond homolytically while the latter is the energy to break the bond heterolytically. However the Table shows that in both cases C-F bond requires more energy than C-Cl bond.

Results of calculated excitation energies from the highest occupied (HO) orbital to the lowest singlet or triplet state show that the trans form has the largest excitation energies. This is an indication that the trans has the lowest HO level, which again is in accord with the fact that it has the greatest stability.

(2) Dipole Moments; CNDO/2 method has been reported to give quite reliable dipole moment^{7, 8, 9}, μ . The CNDO/2 μ value (Table 4) for the trans form is smaller for $X=F$ while it is larger for $X=Cl$ as compared to the μ values for the two respective cis conformers. Bock *et al.*,⁴ has concluded based on their dipole moment studies from bond moments that the trans forms have smaller values than the cis forms for methyl chloro- and fluoro-formates, and that the cis form is the more stable since their μ values for the both configurations were smaller than the experimental value and hence the μ value for the cis form was nearer to the experimental

value.

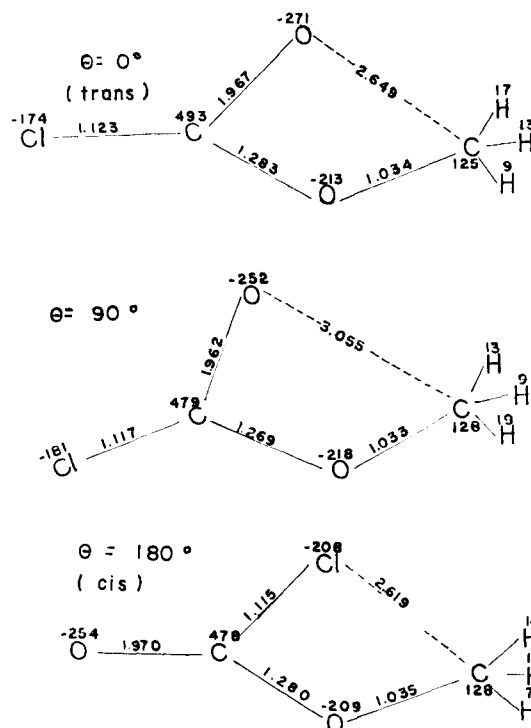
Since the CNDO/2 method of dipole moment calculation is believed to be a much superior method compared with the calculation by bond moments, their generalization and conclusion are considered misleading. One further comment is that the INDO method does give improvement in the calculated μ value.

Table 4. Dipole moments

	X	$\theta=0^\circ$	$\theta=90^\circ$	$\theta=180^\circ$	exptl. *
CNDO/2	Cl	2.91	2.15	2.61	2.38
CNDO/2	F	2.18	2.40	3.07	2.61
INDO	F	2.27			2.61

* Values determined in benzene solution, ref. (4).

(3) Charge Overlap Population and Reactivity; The computed total charges ($\sigma+\pi$) for methyl chloroformate, methyl fluoroformate

**Fig. 3.** Atomic charge and overlap population for $\text{CH}_3\text{O}(\text{CO})\text{Cl}$.

Charges are 10^3 times of electronic charge units. (..... indicates distance in Å.)

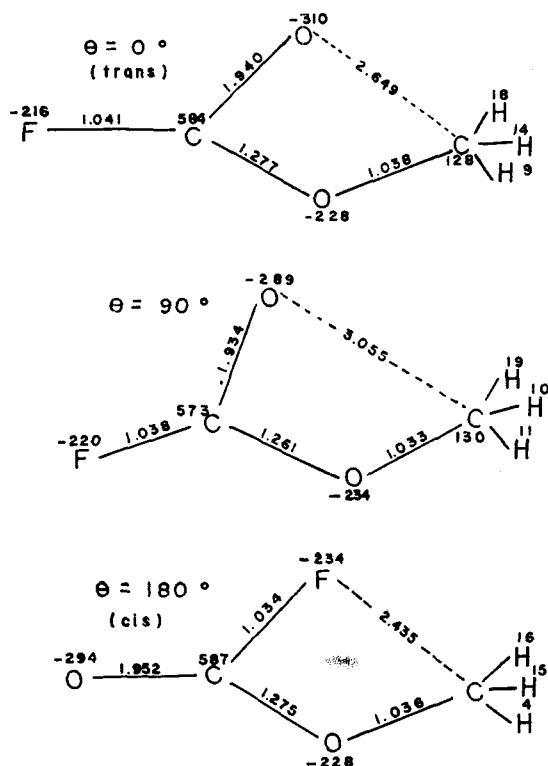


Fig. 4. Atomic charge and overlap population for $\text{CH}_3\text{O}(\text{CO})\text{F}$
Charges are 10^3 times of electronic charge units. (.....indicates distance in Å).

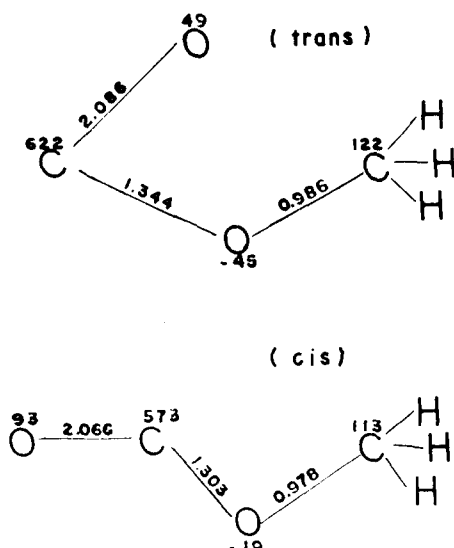


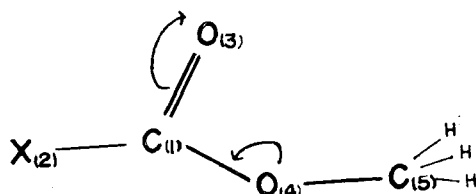
Fig. 5. Atomic charge and overlap population for formate cations
Charges are 10^3 times of electronic charge units

and cations are shown in Fig. 3~5. The figures show that there are charge alternations within molecules. Notable differences between the three configurations shown are that, (1) the trans form has more pronounced charge alternation, (2) the trans form has more negative charge on the carbonyl oxygen atom and more overlap population between carbonyl carbon and ether oxygen atoms. These features are results of electron conjugation of the carbonyl double bond with unshared pairs of the ether oxygen (3) as Marsden and Sutton predicted¹⁷. As a result of this conjugation the $\text{C}_{(1)}-\text{O}_{(4)}$ bond has extra ~30% of overlap population giving the bond a partial double bond character. This in fact is the cause of energy barrier to internal rotation around the $\text{C}_{(1)}-\text{O}_{(4)}$ bond axis, and gives the molecule a planar structure. This type of conjugative stabilization is the strongest in the trans form, which is in agreement with our conclusion from the energetics. Table 5 gives

Table 5. π -Overlap population

	$\text{C}_{(1)}-\text{O}_{(3)}$	$\text{C}_{(1)}-\text{O}_{(4)}$
Methyl fluoroformate		
CNDO/2, trans	0.8724	0.3305
CNDO/2, 90° -rot.	-0.3580	0.1929
CNDO/2, cis	0.8739	0.3292
INDO, trans	0.8552	0.3551
Methyl chloroformate		
CNDO/2, trans	0.8883	0.3362
CNDO/2, 90° -rot.	-0.3422	0.2115
CNDO/2, cis	0.8877	0.3357
CNDO/2, cation	0.7956	0.4543

overlap populations due to π electrons between the carbonyl carbon and the two oxygen atoms. In each compound, electron conjugation of the type in (3) is clearly shown to have



resulted from π -electrons. The extra ~30% of covalent bond in $C_{(1)}-O_{(4)}$ bond is entirely due to the π -bonding and somewhat less amount of π electrons are transferred from $C_{(1)}-O_{(3)}$ bond to the carbonyl oxygen atom. In both molecules, the trend is the strongest for the trans form. In the most unstable configuration where the trans has been rotated 90° anticlockwise around $C_{(1)}-O_{(4)}$ axis, the trend has much reduced and $C_{(1)}-O_{(3)}$ has now an antibonding π -electrons. Again in the cation this trend has enhanced and hence the cation gets stabilized accordingly. The INDO results on methyl fluoroformate shows this conjugative effect of π -electrons is more enhanced than that from CNDO/2 results.

It would also seem reasonable to assume from Fig. 3~5 that the electrostatic attraction between $O_{(3)}$ atom and methyl group is the greatest in the trans form since the charge on the oxygen is the largest and distance between them is the nearest for this conformation. This type of electrostatic attraction has been reported to exist in methyl formate according to component analysis of ab initio LCAO-MO-SCF calculation on the molecule¹³⁾. This is thought to be another factor contributing to the stability of the trans form^{3, 13)}.

In the cis form the halogen atom is nearer to the methyl group but the charge on it is much smaller than that of the carbonyl oxygen. In the case of methyl fluoroformate, fluorine atom is at relatively nearer position in the cis form. This may account for the somewhat enhanced stability of the cis form

of this compound, giving smaller energy difference, $\Delta E_{cis-trans}$, than that of chloroformate. We conclude therefore that the trans configuration is stabilized more from larger conjugative effect as well as from larger electrostatic interaction.

Solvolytic rates are much faster in acid chlorides where no conjugative stabilizations are expected. It is therefore correct to say that much slower rates of haloformates are due to this conjugative initial state stabilization, as Queen *et al.*, has argued²⁾.

In the cations we notice that the positive charge is delocalized over entire system. Since the charge delocalization would result stabilization of the cation, there is a possibility of SNI type reaction for these compounds.

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