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The Effect of Solvent on the Dipole Moments for Organotin(IV) Complexes

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The effect of solvent on the dipole moments for (chloromethyl) stannanes has been investigated by applying EHT calculation for the isomers of trigonal bipyramidal $\text{Sn(IV)Cl}_4\text{X}$ and $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$, octahedral $\text{Sn(IV)Cl}_4\text{2X}$ and $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{6-n}$ 2X type complexes in dioxane and ethylacetate solutions (X: dioxane or ethylacetate). For Sn(IV)Cl_4 in dioxane solution, the calculated dipole moment for the trigonal bipyramidal $\text{Sn(IV)Cl}_4\text{X}$ type complex [Isomer (b)] is closer to the experimental dipole moment than octahedral $\text{Sn(IV)Cl}_4\text{2X}$ type complexes. This calculated dipole moment suggests that Sn(IV)Cl_4 may have the trigonal bipyramidal structure in dioxane solution. However, the calculated dipole moment for octahedral $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)2X}$ type complex [Isomer (d)], $\text{ClSn(IV)(CH}_2\text{Cl)}_3\text{2X}$ type complex [Isomer (k)] and $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2\text{2X}$ type complex [Isomer (h)] are closer to the experimental dipole moments than other isomers for octahedral complexes and trigonal bipyramidal complexes. Such theoretical results indicate that $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)}$, $\text{ClSn(IV)(CH}_2\text{Cl)}_3$ and $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ complexes may have octahedral structures, Isomer (d), (k) and (h) in ethylacetate solution, respectively.

1. Introduction

For a decade considerable interest has been concentrated on solvent effects on molecular electronic spectra. Solvent effects on molecular electronic spectra were first quantitatively investigated by applying perturbation theory for solvent-solute interaction.¹⁻³

The expression for the total dipole moment of a solute molecule could be derived using quantum mechanical perturbation treatment of the system consisting of a solute molecule in a solvent.⁴ The reaction field method, which is the actual field at the solute molecule obtained by the statistical-mechanical averaging over all possible liquid configurations, was developed to calculate the dipole moments for excited state and polarizabilities from solvent shift effects.⁵ The calculated results for nitrobenzene are large and differ depending on which calculation method is used. However, large differences in the experimental dipole moments in several solvents could not be interpreted in terms of theory of solvent-solute interactions.⁶

The effect of solvent on the dipole moments was reported to be attributed to definite formation of coordination complexes which are polar in their own right.⁷ For some transi-

tion metal complexes, it was found that variation of the physical properties of these complexes such as the dipole moments, paramagnetism can be attributed to change in the geometric structures when dissolved in non-coordinating or coordinating solvents.^{8,9}

The various kind of organotin compounds was synthesized¹⁰ and their physical properties and structures were investigated by NMR method.¹¹ However, measurement of the electric dipole moments has been used to determine the geometric structures for organotin(IV) complexes.¹²⁻¹⁸ The measured dipole moments for (chloromethyl) stannanes in benzene solutions were reported to differ greatly from those in ethylacetate solutions.¹⁹ These large differences in the measured dipole moments were interpreted qualitatively in terms of intramolecular coordination between chlorine and tin atoms that do not have acceptor properties.

The large differences in the measured dipole moments in non-coordinating solvent, benzene and coordinating solvent, ethylacetate, are attributed to formation of addition compounds of ethylacetate with (chloroethyl) stannanes.

The purpose of this work is to perform EHT calculation for the various geometric isomers which are expected to form in ethylacetate solutions and to elucidate the geometric structures

of (chloromethyl) stannanes in coordinating solvent comparing the calculated dipole moments with the experimental dipole moments. As far as we are aware, no previous attempt has been made to investigate the effect of solvent on the measured dipole moments for the case where coordinating solvents involve in intermolecular addition compounds. We adopt SCF basis set of functions for tin and ligand atoms which have integer values of n , l and m and then transform them into real form.²⁰ Orbital transformation schemes for tetrahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$, trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{2X}$ complexes are listed in Tables 1, 2 and 3,²¹⁻²³ respectively.

It is also necessary to mention that the bond length is chosen to be a sum of the covalent radii for Sn(IV) and ligand atoms²² to calculate the dipole moments for tetrahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$, trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{2X}$ type complexes.

TABLE 1: Orbital Transformation Schemes for Tetrahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$ Type Complexes

(A) $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)}$ Complex

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{2}(\sigma_1 + C\sigma_2 + \sigma_3 + \sigma_4)$
$t(x)$	5p _x	$\frac{1}{2}(\sigma_1 - C\sigma_2 + \sigma_3 - \sigma_4)$
$t(y)$	5p _y	$\frac{1}{2}(\sigma_1 + C\sigma_2 - \sigma_3 - \sigma_4)$
$t(z)$	5p _z	$\frac{1}{2}(\sigma_1 - C\sigma_2 - \sigma_3 + \sigma_4)$

(B) $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ Complex

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{2}(\sigma_1 + \sigma_2 + C\sigma_3 + C\sigma_4)$
$t(x)$	5p _x	$\frac{1}{2}(\sigma_1 - \sigma_2 + C\sigma_3 - C\sigma_4)$
$t(y)$	5p _y	$\frac{1}{2}(\sigma_1 + \sigma_2 - C\sigma_3 - C\sigma_4)$
$t(z)$	5p _z	$\frac{1}{2}(\sigma_1 - \sigma_2 - C\sigma_3 + C\sigma_4)$

(C) $\text{ClSn(IV)(CH}_2\text{Cl)}_3$ Complex

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{2}(\sigma_1 + C\sigma_2 + C\sigma_3 + C\sigma_4)$
$t(x)$	5p _x	$\frac{1}{2}(\sigma_1 - C\sigma_2 + C\sigma_3 - C\sigma_4)$
$t(y)$	5p _y	$\frac{1}{2}(\sigma_1 + C\sigma_2 - C\sigma_3 - C\sigma_4)$
$t(z)$	5p _z	$\frac{1}{2}(\sigma_1 - C\sigma_2 - C\sigma_3 + C\sigma_4)$

Where $C = \frac{\text{Electronegativity of C atom}}{\text{Electronegativity of Cl atom}} = 0.8834$

TABLE 2: Orbital Transformation Schemes for Trigonal Bipyramidal $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{X}$ Type Complexes

(A) Sn(IV) Cl_4X Type Complex (X: Dioxane)

(a) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}}C(\sigma_1 + \sigma_2 + \sigma_3)$
	5d _{z²}	$\frac{1}{\sqrt{2}}(\sigma_4 + C\sigma_5)$
e'	5d _{xy} , 5d _{x²-y²}	$\frac{1}{\sqrt{2}}C(\sigma_2 - \sigma_3), \frac{1}{\sqrt{6}}C(2\sigma_1 - \sigma_2 - \sigma_3)$
a_2''	5p _z	$\frac{1}{\sqrt{2}}(\sigma_4 - C\sigma_5)$

(b) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}}(\sigma_1 + C\sigma_2 + C\sigma_3)$
	5d _{z²}	$\frac{1}{\sqrt{2}}C(\sigma_4 + \sigma_5)$
e'	5d _{xy} , 5d _{x²-y²}	$\frac{1}{\sqrt{2}}(C\sigma_2 - C\sigma_3), \frac{1}{\sqrt{6}}(2\sigma_1 - C\sigma_2 - C\sigma_3)$
a_2''	5p _z	$\frac{1}{\sqrt{2}}(C\sigma_4 - \sigma_5)$

(B) $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)X}$ Type Complex (X: Ethylacetate)

(c) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}}C(\sigma_1 + \sigma_2 + \sigma_3)$
	5d _{z²}	$\frac{1}{\sqrt{2}}(C'\sigma_4 + \sigma_5)$
e'	5d _{xy} , 5d _{x²-y²}	$\frac{1}{\sqrt{2}}C(\sigma_2 - \sigma_3), \frac{1}{\sqrt{6}}C(2\sigma_1 - \sigma_2 - \sigma_3)$
a_2''	5p _z	$\frac{1}{\sqrt{2}}(C'\sigma_4 - \sigma_5)$

(d) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}}(C'\sigma_1 + C\sigma_2 + C\sigma_3)$
	5d _{z²}	$\frac{1}{\sqrt{2}}(C\sigma_4 + \sigma_5)$
e'	5d _{xy} , 5d _{x²-y²}	$\frac{1}{\sqrt{2}}(C\sigma_2 - C\sigma_3), \frac{1}{\sqrt{6}}(2C'\sigma_1 - C\sigma_2 - C\sigma_3)$
a_2''	5p _z	$\frac{1}{\sqrt{2}}(C\sigma_4 - \sigma_5)$

(e) Isomer (3)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}}(\sigma_1 + C\sigma_2 + C\sigma_3)$
	5d _{z²}	$\frac{1}{\sqrt{2}}(C'\sigma_4 + C\sigma_5)$
e'	5d _{xy} , 5d _{x²-y²}	$\frac{1}{\sqrt{2}}(C\sigma_2 - C\sigma_3), \frac{1}{\sqrt{6}}(2\sigma_1 - C\sigma_2 - C\sigma_3)$
a_2''	5p _z	$\frac{1}{\sqrt{2}}(C'\sigma_4 - C\sigma_5)$

(C) $\text{Cl}_2\text{Sn (IV)} (\text{CH}_2\text{Cl})_2 \text{ X Type Complex (X: Ethylacetate)}$

(f) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}} (C'\sigma_1 + C\sigma_2 + C\sigma_3)$
	$5d_{z^2}$	$\frac{1}{\sqrt{2}} (\sigma_4 + C'\sigma_5)$
e'	$5d_{xy}, 5d_{x^2-y^2}$	$\frac{1}{\sqrt{3}} (2C'\sigma_1 - C\sigma_2 - C\sigma_3),$ $\frac{1}{\sqrt{2}} (C\sigma_2 - C\sigma_3)$
a_2''	$5p_z$	$\frac{1}{\sqrt{2}} (\sigma_4 - C'\sigma_5)$

(g) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}} (C\sigma_1 + C'\sigma_2 + C'\sigma_3)$
	$5d_{z^2}$	$\frac{1}{\sqrt{2}} (\sigma_4 + C\sigma_5)$
e'	$5d_{xy}, 5d_{x^2-y^2}$	$\frac{1}{\sqrt{2}} (C'\sigma_2 - C'\sigma_3),$ $\frac{1}{\sqrt{6}} (2C\sigma_1 - C'\sigma_2 - C'\sigma_3)$
a_2''	$5p_z$	$\frac{1}{\sqrt{2}} (\sigma_4 - C\sigma_5)$

(h) Isomer (3)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}} (\sigma_1 + C'\sigma_2 + C\sigma_3)$
	$5d_{z^2}$	$\frac{1}{\sqrt{2}} (C\sigma_4 + C'\sigma_5)$
e'	$5d_{xy}, 5d_{x^2-y^2}$	$\frac{1}{\sqrt{2}} (C'\sigma_2 - C\sigma_3),$ $\frac{1}{\sqrt{6}} (2\sigma_1 - C'\sigma_2 - C\sigma_3)$
a_2''	$5p_z$	$\frac{1}{\sqrt{2}} (C\sigma_4 - C'\sigma_5)$

(D) $\text{ClSn (IV)} (\text{CH}_2\text{Cl})_3 \text{ X Type Complex (X: Ethylacetate)}$

(i) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}} C' (\sigma_1 + \sigma_2 + \sigma_3)$
	$5d_{z^2}$	$\frac{1}{\sqrt{2}} (\sigma_4 + C\sigma_5)$
e'	$5d_{xy}, 5d_{x^2-y^2}$	$\frac{1}{\sqrt{2}} C' (\sigma_2 - \sigma_3),$ $\frac{1}{\sqrt{6}} C' (2\sigma_1 - \sigma_2 - \sigma_3)$
a_2''	$5p_z$	$\frac{1}{\sqrt{2}} (\sigma_4 - C\sigma_5)$

(j) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1'	5s	$\frac{1}{\sqrt{3}} (C\sigma_1 + C\sigma_2 + C'\sigma_3)$
	$5d_{z^2}$	$\frac{1}{\sqrt{2}} (\sigma_4 + C'\sigma_5)$

$$e' \quad 5d_{xy}, 5d_{x^2-y^2} \quad \frac{1}{\sqrt{2}} (C'\sigma_2 - C'\sigma_3),$$

$$\frac{1}{\sqrt{6}} (2C\sigma_1 - C'\sigma_2 - C'\sigma_3)$$

$$a_2'' \quad 5p_z \quad \frac{1}{\sqrt{2}} (\sigma_4 - C'\sigma_5)$$

Where $C = \frac{\text{Electronegativity of Cl}}{\text{Electronegativity of O}} = 0.8524$

$C' = \frac{\text{Electronegativity of C}}{\text{Electronegativity of O}} = 0.7530$

TABLE 3: Orbital Transformation Schemes for Octahedral $\text{Cl}_n\text{Sn(IV)} (\text{CH}_2\text{Cl})_{6-n} \text{ 2X Type Complexes}$ (A) $\text{Sn (IV)} \text{Cl}_4 \text{ 2X Type Complex (X: Dioxane)}$

(a) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}} (C\sigma_1 + C\sigma_2 + C\sigma_3 + C\sigma_4 + \sigma_5 + \sigma_6)$
e	$5d_{z^2}$	$\frac{1}{\sqrt{12}} (2\sigma_5 + 2\sigma_6 - C\sigma_1 - C\sigma_2 - C\sigma_3 - C\sigma_4)$
	$5d_{x^2-y^2}$	$\frac{1}{2} C (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
t_1	$5p_x$	$\frac{1}{\sqrt{2}} C (\sigma_1 - \sigma_3)$
	$5p_y$	$\frac{1}{\sqrt{2}} C (\sigma_2 - \sigma_4)$
	$5p_z$	$\frac{1}{\sqrt{2}} (\sigma_5 - \sigma_6)$

(b) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}} (\sigma_1 + C\sigma_2 + C\sigma_3 + C\sigma_4 + \sigma_5 + C\sigma_6)$
e	$5d_{z^2}$	$\frac{1}{\sqrt{12}} (2\sigma_5 + 2C\sigma_6 - C\sigma_1 - C\sigma_2 - C\sigma_3 - C\sigma_4)$
	$5d_{x^2-y^2}$	$\frac{1}{2} (\sigma_1 - C\sigma_2 + C\sigma_3 - C\sigma_4)$
t_1	$5p_x$	$\frac{1}{\sqrt{2}} (\sigma_1 - C\sigma_3)$
	$5p_y$	$\frac{1}{\sqrt{2}} C (\sigma_2 - \sigma_4)$
	$5p_z$	$\frac{1}{\sqrt{2}} (\sigma_5 - C\sigma_6)$

(B) $\text{Cl}_3\text{Sn(IV)} (\text{CH}_2\text{Cl})_2 \text{ 2X Type Complex (X: Ethylacetate)}$

(c) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}} (C\sigma_1 + C'\sigma_2 + C\sigma_3 + C\sigma_4 + \sigma_5 + \sigma_6)$
e	$5d_{z^2}$	$\frac{1}{\sqrt{12}} (2\sigma_5 + 2\sigma_6 - C\sigma_1 - C'\sigma_2 - C\sigma_3 - C\sigma_4)$
	$5d_{x^2-y^2}$	$\frac{1}{2} (C\sigma_1 - C'\sigma_2 + C\sigma_3 - C\sigma_4)$
t_1	$5p_x$	$\frac{1}{\sqrt{2}} C (\sigma_1 - \sigma_3)$
	$5p_y$	$\frac{1}{\sqrt{2}} (C'\sigma_2 - \sigma_4)$
	$5p_z$	$\frac{1}{\sqrt{2}} (\sigma_5 - \sigma_6)$

(d) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(\sigma_1 + C\sigma_2 + C\sigma_3 + C\sigma_4 + \sigma_5 + C'\sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2C'\sigma_6 - \sigma_1 - C\sigma_2 - C\sigma_3 - C\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(\sigma_1 - C\sigma_2 + C\sigma_3 - C\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}(\sigma_1 - C\sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}C(\sigma_2 - \sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - C'\sigma_6)$

(e) Isomer (3)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(\sigma_1 + C\sigma_2 + C\sigma_3 + C'\sigma_4 + \sigma_5 + C\sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2C\sigma_6 - \sigma_1 - C\sigma_2 - C\sigma_3 - C'\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(\sigma_1 - C\sigma_2 - C\sigma_3 - C'\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}(\sigma_1 - C\sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}(\sigma_2 - C'\sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - C\sigma_6)$

(C) Cl₂Sn (IV) (CH₂Cl)₂ 2X type Complex (X: Ethylacetate)

(f) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(C'\sigma_1 + C\sigma_2 + C\sigma_3 + C'\sigma_4 + \sigma_5 + \sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2\sigma_6 - C'\sigma_1 - C\sigma_2 - C\sigma_3 - C'\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(C'\sigma_1 - C\sigma_2 + C\sigma_3 - C'\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}(C'\sigma_1 - C\sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}(C\sigma_2 - C'\sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6)$

(g) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(C'\sigma_1 + C\sigma_2 + \sigma_3 + C'\sigma_4 + \sigma_5 + C\sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2C\sigma_6 - C'\sigma_1 - C\sigma_2 - \sigma_3 - C'\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(C'\sigma_1 - C\sigma_2 + \sigma_3 - C'\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}(C'\sigma_1 - \sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}(C\sigma_2 - C'\sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - C\sigma_6)$

(h) Isomer (3)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(C'\sigma_1 + C\sigma_2 + \sigma_3 + \sigma_4 + C\sigma_5 + C'\sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2C\sigma_5 + 2C'\sigma_6 - C'\sigma_1 - C\sigma_2 - \sigma_3 - \sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(C'\sigma_1 - C\sigma_2 + \sigma_3 - \sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}(C'\sigma_1 - \sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}(C\sigma_2 - \sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(C\sigma_5 - C'\sigma_6)$

(D) ClSn (IV) (CH₂Cl)₃ 2X Type Complex (X: Ethylacetate)

(i) Isomer (1)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(C'\sigma_1 + C\sigma_2 + C'\sigma_3 + C'\sigma_4 + \sigma_5 + \sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2\sigma_6 - C'\sigma_1 - C\sigma_2 - C'\sigma_3 - C'\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(C'\sigma_1 - C\sigma_2 + C'\sigma_3 - C'\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}C'(\sigma_1 - \sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}(C\sigma_2 - C'\sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6)$

(j) Isomer (2)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(\sigma_1 + C'\sigma_2 + C'\sigma_3 + C'\sigma_4 + \sigma_5 + C\sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2C\sigma_6 - \sigma_1 - C'\sigma_2 - C'\sigma_3 - C'\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(\sigma_1 - C'\sigma_2 + C'\sigma_3 - C'\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}(\sigma_1 - C'\sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}C'(\sigma_2 - \sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - C\sigma_6)$

(k) Isomer (3)

Irreducible representation	Metal orbital	Ligand orbitals
a_1	5s	$\frac{1}{\sqrt{6}}(C'\sigma_1 + \sigma_2 + C'\sigma_3 + C\sigma_4 + \sigma_5 + C'\sigma_6)$
e	5d _{z²}	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2C'\sigma_6 - C'\sigma_1 - \sigma_2 - C'\sigma_3 - C\sigma_4)$
	5d _{x²-y²}	$\frac{1}{2}(C'\sigma_1 - \sigma_2 + C'\sigma_3 - C\sigma_4)$
t_1	5p _x	$\frac{1}{\sqrt{2}}C'(\sigma_1 - \sigma_3)$
	5p _y	$\frac{1}{\sqrt{2}}(\sigma_2 - C\sigma_4)$
	5p _z	$\frac{1}{\sqrt{2}}(\sigma_5 - C'\sigma_6)$

Where $C = \frac{\text{Electronegativity of Cl}}{\text{Electronegativity of O}} = 0.8524$

$C' = \frac{\text{Electronegativity of C}}{\text{Electronegativity of O}} = 0.7530$

2. EHT Calculation of the Dipole Moments

For organotin(IV) complexes, it was reported that four coordinate compounds have the tetrahedral structure and five coordinate Sn(IV) compounds the trigonal bipyramidal structure.²⁴ We therefore choose tetrahedral $\text{Cl}_n\text{Sn(IV)}-(\text{CH}_2\text{Cl})_{4-n}$, trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}2\text{X}$ type complexes to calculate the dipole moments for organotin(IV) complexes (X: ethylacetate or dioxane).

It was also reported that for organotin(IV) chelate complexes β -ketoenolate ligand exchange very rapidly at room temperature¹⁶ and complexes of tin(IV) halides and organotin(IV) halides with organic sulfides and selenides undergo the pyramidal atomic inversion about sulfur and selenium.¹⁷ A trigonal bipyramidal molecule with five different ligands was found to exist as 20 different geometric isomers and octahedral molecule, such as occurs throughout transition metal chemistry, with six different ligands as 30 different geometrical isomers.^{24a} Such experimental facts indicated that rearrangements between different ligands are possible providing that energetics permits. we therefore choose two or three geometrical isomers for trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)}-(\text{CH}_2\text{Cl})_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}2\text{X}$ type complexes to investigate the effect of solvent on the dipole moments. The geometric structures of these organotin(IV) complexes are represented in Figure 1, 2 and 3, respectively.

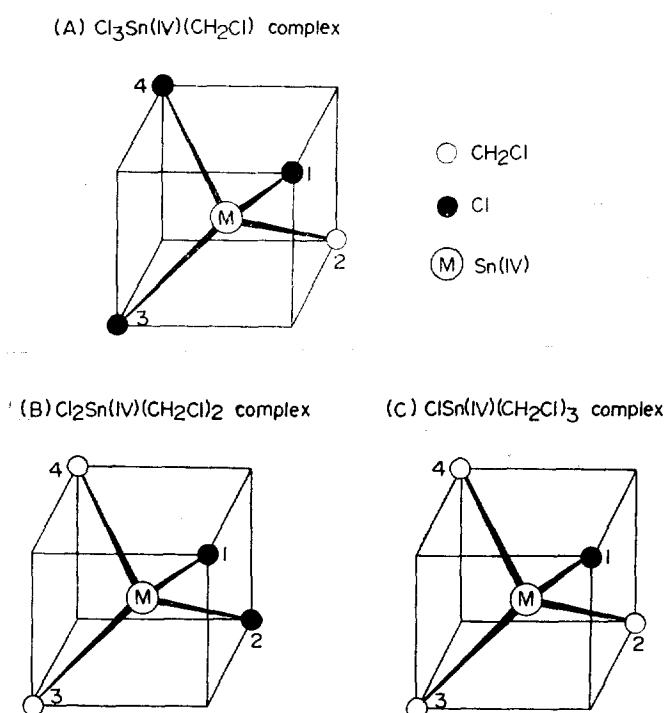


Figure 1. Coordinate systems for tetrahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}$ type complexes.

Here we assume that the O , T_d and D_{3h} symmetries are still maintained for octahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}2\text{X}$, tetrahed-

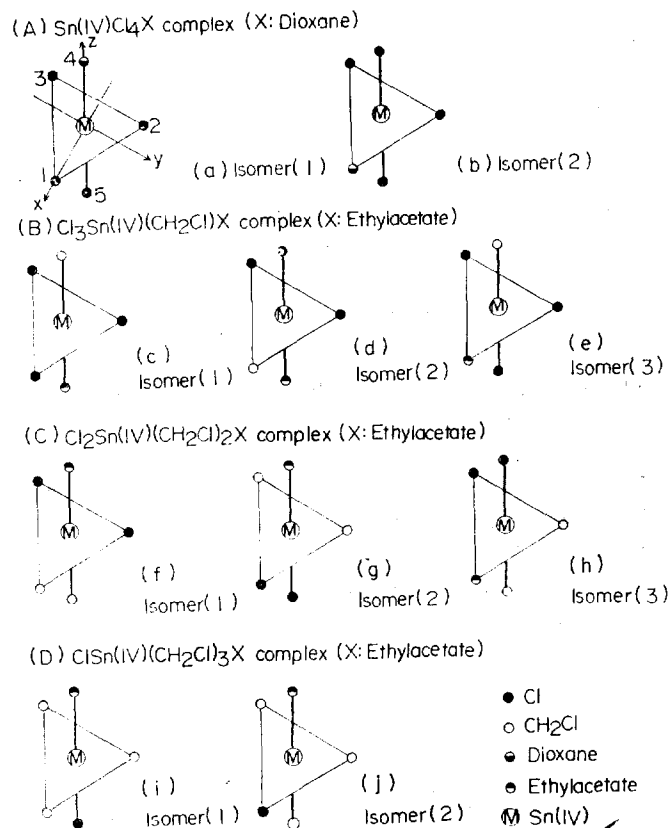


Figure 2. Coordinate systems for trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}\text{X}$ type complexes.

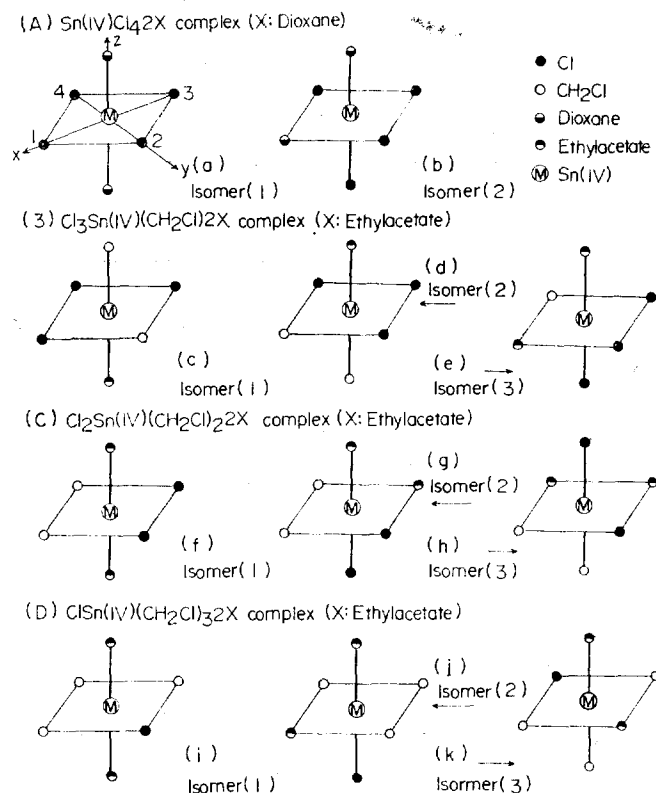


Figure 3. Coordinate systems for octahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}2\text{X}$ type complexes.

ral $\text{Cl}_2\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}$ and trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)}-(\text{CH}_2\text{Cl})_{4-n}\text{X}$ type complexes although $(4-n)$ chlorine atoms have been replaced to form cis complexes by carbon atoms of CH_2Cl . It is necessary to stress that only σ -bonds are assumed to be formed between Sn(IV) atom and ligands because the bonding in most Sn(IV) compounds was reported to be largely covalent and the properties of these complexes could be explained most satisfactorily by covalent arguments,²⁵ and tin-oxygen (ligand atom) bonds are of a simple polar type lacking $(p \rightarrow d)\pi$ character, no appreciable fraction of the ligands was found to be unbound.¹⁶

We thus adopt the modified approximate molecular orbitals of tetrahedral, trigonal bipyramidal and octahedral complexes. We also adopt the σ bonding orbitals as a linear combination of ns and np_z orbitals of ligands as follows ($n=2$ or 3)

$$\sigma(l) = \sin \theta(ns) \pm \cos \theta(np_z) \quad (1)$$

The degree of hybridization is estimated after the manner of Ballhausen and Gray²⁶ by minimizing the quantity $\text{VSIP}(\theta)/S(\theta)$, where $S(\theta)$ is the overlap integrals of the atomic orbitals for Sn(IV) with ligand hybrid orbital of varying values θ , while $\text{VSIP}(\theta)$ is the valence state ionization potential of the same ligand hybrid orbital. The angle at which the minimum occurred are listed in Table 4.

The molecular orbitals may be approximated as

$$\begin{aligned} \phi_i(\text{MO}) &= N_i \{ \alpha_i \Gamma_i(\text{M}) + \beta_i \Gamma_i(l) + \gamma_i \Gamma'_i(l) \} \\ \phi_i^*(\text{MO}) &= N_i^* \{ \alpha_i^* \Gamma_i(\text{M}) + \beta_i^* \Gamma_i(l) + \gamma_i^* \Gamma'_i(l) \} \end{aligned} \quad (2)$$

Where N_i and N_i^* are normalization constants for bonding and antibonding molecular orbitals given by

$$\begin{aligned} N_i &= \{ \alpha_i^2 + 2\alpha_i\beta_i \langle \Gamma_i(\text{M}) | \Gamma_i(l) \rangle + 2\alpha_i\gamma_i \langle \Gamma_i(\text{M}) | \Gamma'_i(l) \rangle \\ &\quad + \beta_i^2 \langle \Gamma_i(l) | \Gamma_i(l) \rangle + \gamma_i^2 \langle \Gamma'_i(l) | \Gamma'_i(l) \rangle \}^{-\frac{1}{2}} \\ N_i^* &= \{ \alpha_i^{*2} + 2\alpha_i^*\beta_i^* \langle \Gamma_i(\text{M}) | \Gamma_i(l) \rangle \\ &\quad + 2\alpha_i^*\gamma_i^* \langle \Gamma_i(\text{M}) | \Gamma'_i(l) \rangle \\ &\quad + \beta_i^{*2} \langle \Gamma_i(l) | \Gamma_i(l) \rangle + \gamma_i^{*2} \langle \Gamma'_i(l) | \Gamma'_i(l) \rangle \}^{-\frac{1}{2}} \end{aligned} \quad (3)$$

The molecular orbital energies and the corresponding-

eigenvectors are obtained by solving the following secular equation.²⁷

$$(H_{ij} - G_{ij}E) = 0 \quad (4)$$

Where G_{ij} is the group overlap integral. In equation (4), the diagonal matrix elements for the central orbitals, H_{ii} , are estimated as the negative of the valence state ionization potential (VSIP) of tin atom.^{28,29}

$$H_{ij} = -\text{VSIP of Sn atom} \quad (5)$$

and off-diagonal matrix elements are calculated by using Wolfberg and Helmholtz approximation.³⁰

$$H_{ij} = \frac{1}{2}FG(H_{ii} + H_{jj}) \quad (6)$$

Where $F=1.75$. Since we choose the σ bonding orbitals for

TABLE 4: Degree of Hybridization

(A) Degree of hybridization for $\text{Cl}_n\text{Sn(IV)}\text{X}_{4-n}$ Complexes (X: CH_2Cl)

Representation	$\sin \theta$	$\cos \theta$	θ
a_1	0	1	0
$t_1(p)$	0	1	0
$t_2(d)$	1	0	90

(B) Degree of hybridization for $\text{Cl}_n\text{Sn(V)}\text{X}_{4-n}\text{Y}$ Complexes (X: CH_2Cl , Y: Dioxane or Ethylacetate)

Representation	$\sin \theta$	$\cos \theta$	θ
$a_1'(s)$	0	1	0
$a_1'(d)$	1	0	90
e'	1	0	90
a_2''	0	1	0

(C) Degree of hybridization for $\text{Cl}_n\text{Sn(IV)}\text{X}_{4-n}2\text{Y}$ Complexes (X: CH_2Cl , Y: Ethylacetate)

Representation	$\sin \theta$	$\cos \theta$	θ
a_1	0	1	0
e	1	0	90
t_1	0	1	0

(θ : Degree)

TABLE 5: The Group Overlap Integrals and Molecular Orbital Energies for Tetrahedral Complexes

(A) $\text{Cl}_3\text{Sn(IV)}(\text{CH}_2\text{Cl})$ Complex

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.3337	-20.84	0.8156	0.6783	-7.34	-0.3673	0.9952
t_1	0.2704	-17.76	0.6807	0.7846	-5.14	0.9394	-0.4432
	0.2704	-17.76	0.6807	0.7846	-5.14	0.9394	-0.4432

(B) $\text{Cl}_2\text{Sn(IV)}(\text{CH}_2\text{Cl})_2$ Complex

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2575	-20.54	0.6968	0.7638	-7.03	-0.5599	0.8601
t_1	0.2164	-14.68	0.6518	0.7901	-5.56	0.9124	-0.4654
	0.2164	-14.68	0.6518	0.7901	-5.56	0.9124	-0.4654

(C) $\text{ClSn(IV)}(\text{CH}_2\text{Cl})_3$ Complex

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.1814	-16.80	0.7920	0.6377	-7.53	-0.4835	0.8946
t_1	0.1624	-12.05	0.6383	0.7872	-5.94	0.8804	-0.5020
	0.1624	-12.05	0.6383	0.7872	-5.94	0.8804	-0.5020

TABLE 6: Group Overlap Integrals and Molecular Orbital Energies for Trigonal Bipyramidal Complexes

(A) $\text{Sn(IV)Cl}_4\text{X}$ Type Complex (X: Dioxane)

(a) Isomer (1)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1'(s)$		0.3025	-21.76	0.7068	0.7753		-6.01	-0.5252	0.9082	
$a_1'(d_{x^2})$	0.4193		-40.03	0.6836	0.8663		-1.78	1.0707	-0.2535	
e'	0.1013		-23.33	0.1569	-0.7639	0.6702	-2.27	0.9659	-0.0958	-0.1113
	0.0585		-15.73	0.1021	0.8212	0.5988				
a_2''		0.3199	-20.27	0.7269	0.7653		-4.69	0.9576	-0.4439	

(b) Isomer (2)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1'(s)$		0.2802	-22.31	0.6600	0.8060		-7.02	-0.5888	0.8594	
$a_1'(d_{x^2})$	0.4193		-26.86	0.7171	0.8361		-2.09	1.0597	-0.3005	
e'	0.3241		-28.82	0.4609	-0.5658	0.7965	-1.56	1.0181	-0.1337	0.2410
	0.0702		-25.35	0.1553	0.8832	0.4669				
a_2''		0.3387	-17.74	0.8048	0.6941		-4.17	0.9257	-0.5222	

(B) $\text{Cl}_3\text{Sn(IV)}(\text{CH}_2\text{Cl})\text{X}$ Type Complex (X: Ethylacetate)

(c) Isomer (1)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1'(s)$		0.3025	-21.76	0.7068	0.7753		-6.01	-0.5252	0.9082	
$a_1'(dz^2)$	0.1206		-23.44	0.3002	0.9616		-3.27	0.9908	-0.1820	
e'	0.1013		-18.90	0.1698	-0.3287	0.9276	-2.42	0.9933	-0.0506	-0.0897
	0.0585		-16.67	0.0352	0.9722	0.2944				
a_2''		0.2072	-14.35	0.6429	0.7948		-5.65	0.9107	-0.4643	

(d) Isomer (2)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1'(s)$		0.3008	-20.89	0.7366	0.7462		-5.62	-0.4901	0.9270	
$a_1'(dz^2)$	0.4193		-39.88	0.6813	0.8655		-1.88	1.0714	-0.2556	
e'	0.1152		-19.77	0.2010	-0.1287	0.9705	-2.38	0.9939	-0.0487	-0.0925
	0.0665		-13.02	0.0103	1.0155	0.0841				
a_2''		0.3387	-17.74	0.8049	0.6941		-4.16	0.9256	-0.5222	

(e) Isomer (3)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1'(s)$		0.2802	-22.31	0.6600	0.8060		-7.02	-0.5888	0.8594	
$a_1'(dz^2)$	0.3973		-23.73	0.6984	0.8365		-2.25	1.0451	-0.3086	
e'	0.3178		-28.61	0.4453	-0.5948	0.7451	-1.59	1.0151	-0.1360	-0.2417
	0.0701		-25.29	0.1635	0.8654	0.4967				
a_2''		0.2259	-12.42	0.7685	0.6805		-4.92	0.8366	-0.5949	

(C) $\text{Cl}_2\text{Sn(IV)}(\text{CH}_2\text{Cl})_2\cdot\text{X}$ Type Complex (X: Ethylacetate)

(f) Isomer (1)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{V})$	α_i^*	β_i^*	γ_i^*
$a_1'(s)$		0.3154	-20.46	0.7696	0.7199		-4.81	-0.4404	0.9574	
$a_1'(d_{z^2})$	0.1206		-23.44	0.3002	0.9616		-3.27	0.9908	-0.1820	
e'	0.1152		-19.77	0.2010	-0.1287	0.9702	-2.38	0.9939	-0.0487	-0.0925
	0.0665		-13.02	0.0103	1.0155	0.0841				
a_2''		0.2702	-14.35	0.6429	0.7948		-5.65	0.9107	-0.4643	

(g) Isomer (2)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1(s)$		0.1785	-15.72	0.8704	0.5247		-6.11	-0.3609	0.9501	
$a_1'(d_{z^2})$	0.4193		-39.88	0.6813	0.8655		-1.88	1.0714	-0.2556	
e'	0.1577		-13.72	0.2346	-0.6634	0.7205	-2.29	0.9865	-0.0907	-0.1816
	0.0673		-12.51	0.1332	0.7963	0.6165				
a_2''		0.3200	-20.27	0.7685	0.6805		-4.69	0.8366	-0.5949	

(h) Isomer (3)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1(s)$		0.2879	-21.38	0.7030	0.7721		-6.34	-0.5371	0.8955	
$a_1'(d_{z^2})$	0.3973		-23.73	0.6984	0.8365		-2.25	1.0451	-0.3086	
e'	0.1501		-16.05	0.2175	-0.1625	0.9633	-2.34	0.9916	-0.0557	-0.1229
	0.0719		-12.87	0.0349	1.0042	0.1233				
a_2''		0.3004	-14.57	0.7685	0.6805		-4.20	0.8366	-0.5949	

(D) $\text{ClSn(IV)}(\text{CH}_2\text{Cl})_3\text{X}$ type Complex (X: Ethylacetate)

(i) Isomer (1)

MO symmetry	G_{ij}	G_{kj}	$E_i(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1(s)$		0.3184	-19.51	-0.8109	0.6747		-3.98	-0.3815	0.9835	
$a_1'(d_{z^2})$	0.4194		-39.88	0.6813	0.8655		-1.88	1.0714	-0.2556	
e'	0.0556		-10.14	-0.0491	0.9012	-0.4320	-2.48	0.9878	0.0118	-0.0739
	0.0080		-9.99	0.1398	0.4247	0.8841				
a_2''		0.3247	-22.54	0.7041	0.7888		-4.77	0.9747	-0.4098	

(j) Isomer (2)

MO symmetry	G_{ij}	G_{kj}	$E_j(\text{eV})$	α_i	β_i	γ_i	$E_i^*(\text{eV})$	α_i^*	β_i^*	γ_i^*
$a_1(s)$		0.3154	-20.46	0.7696	0.7199		-4.81	-0.4404	0.9574	
$a_1'(d_{z^2})$	0.3973		-23.73	0.6984	0.8365		-2.25	1.0451	-0.3086	
e'	0.1430		-22.16	-0.0931	0.9898	-0.1663	-2.50	1.0602	0.0144	-0.1565
	0.0278		-15.10	0.4033	0.1440	0.9825				
a_2''		0.3469	-16.16	0.8541	0.6382		-3.78	0.8949	-0.5797	

ligands as a hybridized atomic orbital of ns and np_z , the corresponding diagonal matrix elements are then estimated from³¹

$$H_{ij} = -\{\sin^2 \theta (\text{VSIP of } ns) + \cos^2 \theta (\text{VSIP of } np_z)\} \quad (7)$$

Group overlap integrals and molecular orbital energies for tetrahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}$, trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}\text{X}_2$ type complexes are listed in Tables 5, 6 and 7, respectively. Energy level diagrams for those complexes are listed in Figure 4 and 5, respectively.

The general formulas of the dipole moment matrix elements for the bonding and antibonding molecular orbitals are

$$\langle \phi_i(\text{MO}) | \mathbf{r} | \phi_i(\text{MO}) \rangle = N_i^2 \{ 2\alpha_i \beta_i \langle \Gamma_i(M) | \mathbf{r} | \Gamma_i(L) \rangle$$

$$+ 2\alpha_i \gamma_i \langle \Gamma_i(M) | \mathbf{r} | \Gamma_i'(L) \rangle + \beta_i^2 \langle \Gamma_i(L) | \mathbf{r} | \Gamma_i(L) \rangle + \gamma_i^2 \langle \Gamma_i'(L) | \mathbf{r} | \Gamma_i'(L) \rangle \}$$

$$\begin{aligned} & \langle \phi_i^*(\text{MO}) | \mathbf{r} | \phi_i^*(\text{MO}) \rangle \\ &= N_i^{*2} \{ 2\alpha_i^* \beta_i^* \langle \Gamma_i(M) | \mathbf{r} | \Gamma_i(L) \rangle \\ &+ 2\alpha_i^* \gamma_i^* \langle \Gamma_i(M) | \mathbf{r} | \Gamma_i'(L) \rangle \\ &+ \beta_i^{*2} \langle \Gamma_i(L) | \mathbf{r} | \Gamma_i(L) \rangle + \gamma_i^{*2} \langle \Gamma_i'(L) | \mathbf{r} | \Gamma_i'(L) \rangle \} \end{aligned} \quad (8)$$

Applying the coordinate transformation schemes for tetrahedral²¹, trigonal bipyramidal²³ and octahedral²² complexes, we evaluate the dipole moment matrix elements and then calculate the dipole moments for tetrahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}$, trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)}(\text{CH}_2\text{Cl})_{4-n}\text{X}_2$ type complexes. The

TABLE 7: The Group Overlap Integrals and Molecular Orbital Energies for Octahedral Complexes

(A) $\text{Sn(IV)Cl}_4\text{2X}$ Type Complex (X: Dioxane)

(a) Isomer (1)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.3963	-29.00	0.6245	0.8923	-5.40	-0.5718	0.9270
e	z^2	0.4846	-49.66	0.7712	0.8439	-1.32	1.1119
	x^2-y^2	0.4267	-29.80	0.7046	0.8521	-1.68	1.0713
t_1	x	0.3387	-17.74	0.8049	0.6941	-4.16	0.9256
	y	0.3387	-17.74	0.8049	0.6941	-4.16	0.9256
	z	0.3013	-22.80	0.6592	0.8156	-5.06	0.9763

(b) Isomer (2)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.3963	-29.00	0.6245	0.8923	-5.40	-0.5718	0.9270
e	z^2	0.4175	-36.38	0.6855	0.8605	-1.96	1.0658
	x^2-y^2	0.3417	-29.83	0.5705	0.8982	-2.12	1.0391
t_1	x	0.3200	-20.27	0.7269	0.7653	-4.69	0.9576
	y	0.3387	-17.74	0.8049	0.6941	-4.16	0.9256
	z	0.3200	-20.27	0.7269	0.7653	-4.69	0.9576

(B) $\text{Cl}_3\text{Sn(IV)}(\text{CH}_2\text{Cl})_2\text{X}$ Type Complex (X: Ethylacetate)

(c) Isomer (1)

MO Symmetry	G_{ij}	$E_i(\text{Ve})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.3433	-25.01	0.6558	0.8388	-5.91	-0.5627	0.9038
e	z^2	0.3042	-34.62	0.5112	0.9169	-2.68	1.0290
	x^2-y^2	0.3350	-22.82	0.5859	0.8849	-2.21	1.0301
t_1	x	0.3387	-17.74	0.8049	0.6941	-4.16	0.9256
	y	0.3242	-18.22	0.7701	0.7242	-4.43	0.9347
	z	0.3013	-22.80	0.6592	0.8157	-5.08	0.9763

(d) Isomer (2)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_{ii}^*	β_i^*
a_1	0.3433	-25.01	0.6558	0.8388	-5.91	-0.5627	0.9038
e	z^2	0.4465	-45.80	0.7148	0.8590	-1.62	1.0878
	x^2-y^2	0.3417	-29.83	0.5705	0.8982	-2.12	1.0391
t_1	x	0.3200	-20.27	0.7269	0.7653	-4.69	0.9576
	y	0.3387	-17.74	0.8049	0.6941	-4.19	0.9256
	z	0.3432	-18.22	0.7701	0.7242	-4.43	0.9347

(e) Isomer (3)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.3433	-25.01	0.6558	0.8388	-5.91	-0.5627	0.9038
e	z^2	0.4867	-43.11	0.7841	0.8340	-1.45	1.0249
	x^2-y^2	0.2500	-23.88	0.4409	0.9340	-2.66	1.0145
t_1	x	0.3200	-20.27	0.7269	0.7653	-4.69	0.9576
	y	0.3242	-18.22	0.7701	0.7242	-4.43	0.9347
	z	0.3200	-20.27	0.7229	0.7653	-4.69	0.9576

(C) $\text{Cl}_2\text{Sn(IV)}(\text{CH}_2\text{Cl})_2\text{X}$ Type Complex (X: Ethylacetate)

(f) Isomer (1)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2812	-22.28	0.7205	0.7528	-6.71	-0.5198	0.9032
e	z^2	0.1984	-29.50	0.3507	0.9585	-3.35	1.0089
	x^2-y^2	0.2433	-17.65	0.4591	0.9231	-2.71	1.0071

t_1	x	0.3429	-15.82	0.8561	0.5327	-3.78	0.8879	-0.5873
	y	0.3429	-15.82	0.8561	0.6327	-3.78	0.8879	-0.5873
	z	0.3013	-22.80	0.6952	0.8157	-5.08	0.9763	-0.3828

(g) Isomer (2)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2812	-22.28	0.7205	0.7528	-6.71	-0.5198	0.9032
e	z^2	0.3759	-22.54	0.6458	-2.33	1.0439	-0.2735
	x^2-y^2	0.1583	-19.60	0.2979	-3.08	1.0029	-0.1409
t_1	x	0.3242	-18.22	0.7701	-4.43	0.9347	-0.4937
	y	0.3429	-15.82	0.8561	-3.78	0.8879	-0.5873
	z	0.3200	-20.27	0.7269	-4.69	0.9576	-0.4439

(h) Isomer (3)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2812	-22.28	0.7205	0.7528	-6.71	-0.5198	0.9032
e	z^2	0.2575	-21.56	0.4771	-3.06	1.0102	-0.1409
	x^2-y^2	0.1651	-25.26	0.2936	-3.04	1.0056	-0.1294
t_1	x	0.3242	-18.22	0.7701	-4.43	0.9337	-0.4937
	y	0.3200	-20.27	0.7269	-4.69	0.9576	-0.4439
	z	0.3429	-15.82	0.8561	-3.78	0.8879	-0.3828

(D) $\text{ClSn(IV)(CH}_2\text{Cl)}_3\text{X}$ Type Complex (X: Ethylacetate)

(i) Isomer (1)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2373	-19.92	0.7651	0.6886	-7.05	-0.4874	0.9067
e	z^2	0.1984	-28.83	0.3511	-3.35	1.0086	-0.1541
	x^2-y^2	0.1519	-13.91	0.3272	-3.11	0.9976	-0.1679
t_1	x	0.2269	-10.16	0.7239	-4.16	-0.5449	0.8702
	y	0.3429	-15.82	0.8561	-3.78	0.8879	-0.5873
	z	0.3013	-22.80	0.6592	-5.08	0.9763	-0.3828

(j) Isomer (2)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2373	-19.92	0.7651	0.6886	-7.05	-0.4874	0.9067
e	z^2	0.2870	-28.13	0.4999	-2.85	1.0214	-0.2158
	x^2-y^2	0.1333	-13.69	0.2853	-3.16	0.9972	-0.1537
t_1	x	0.3242	-18.22	0.7701	-4.43	0.9347	-0.4937
	y	0.2269	-10.76	0.7239	-4.16	-0.5449	0.8702
	z	0.3200	-20.27	0.7269	-4.69	0.9576	-0.4439

(k) Isomer (3)

MO symmetry	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
a_1	0.2373	-19.92	0.7651	0.6886	-7.05	-0.4874	0.9067
e	z^2	0.1546	-22.04	0.2932	-3.58	1.0025	-0.1398
	x^2-y^2	0.1583	-19.60	0.2979	-3.08	1.0029	-0.1409
t_1	x	0.2269	-10.76	0.7239	-4.16	-0.5449	0.8702
	y	0.3200	-20.27	0.7269	-4.69	0.9576	-0.4439
	z	0.3242	-18.22	0.7701	-4.43	0.9347	-0.4937

dipole moments are listed in Table 8, 9 and 10, respectively.

3. Results and Discussion

The calculated dipole moments for tetrahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$ type complexes are very close to the experimental values in benzene solutions except for $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$.

The calculated dipole moment for $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$, 6.161D, is almost double to the experimental value, 3.17D. This calculated result for $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ may suggest that there exists an equilibrium between the cis and trans tetrahedral $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ complex in benzene solution. Such an equilibrium may cause the calculated dipole moment for this

complex to deviate greatly from the experimental value.

In the case of Sn(IV)Cl_4 in dioxane solution, the calculated dipole moment for the trigonal bipyramidal $\text{Sn(IV)Cl}_4\text{X}$ (Isomer(b)), 3.675 D, is close to the experimental value, 3.82D, than that for the octahedral $\text{Sn(IV)Cl}_4\text{X}$ complex, 5.105 D. Such a result indicates that Sn(IV)Cl_4 in dioxane solution may have the trigonal bipyramidal structure [Isomer(b)].

The calculated dipole moment for the octahedral $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)2X}$ type complex [Isomer(d)], 7.802, is closer to the measured value of the dipole moment for $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)}$ complex, 8.36, in ethylacetate solution than other isomers involved in the dipole moment calculation. The calculated dipole moments for octahedral $\text{ClSn(IV)(CH}_2\text{Cl)}_3\text{2X}$ [Isomer(k)], 8.335D, and $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2\text{2X}$ [Isomer(h)], 9.461, are also closer to the experimental values than those of other isomers for octahedral and trigonal bipyramidal complexes. Such facts suggest that $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ and $\text{ClSn(IV)(CH}_2\text{Cl)}_3$ in ethylacetate solution may have octahedral structures, Isomer(h) and Isomer(k), as represented in Figure 3C and 3D, respectively.

We describe the differences in the calculated dipole moments for trigonal bipyramidal $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{X}$ and octahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{2X}$ type complexes in ethylacetate solution and $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$ in benzene solution in Table 11.

As shown in Table 11, the calculated difference in the dipole moment between Sn(IV)Cl_4 and the trigonal bipyramidal $\text{Sn(IV)Cl}_4\text{X}$ type complex [Isomer (b)] is close to the experimental difference in the dipole moment. The calculated differences in the dipole moments between $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$ and octahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}\text{2X}$ are however close to the experimental differences in the dipole moments except for $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ type complex which we are assumed to exist equilibrium mixture of the cis and *trans* forms. The calculated results in Table 11 also indicate that Sn(IV)Cl_4 may have the trigonal bipyramidal structure [Isomer(b)] in dioxane solution, while $\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)}$ and $\text{ClSn(IV)(CH}_2\text{Cl)}_3$ in ethylacetate solution the octahedral structures, Isomer(d) and Isomer(k), respectively.

We may guess that for the case of $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$ complex, an appreciable fraction of this complex exists as

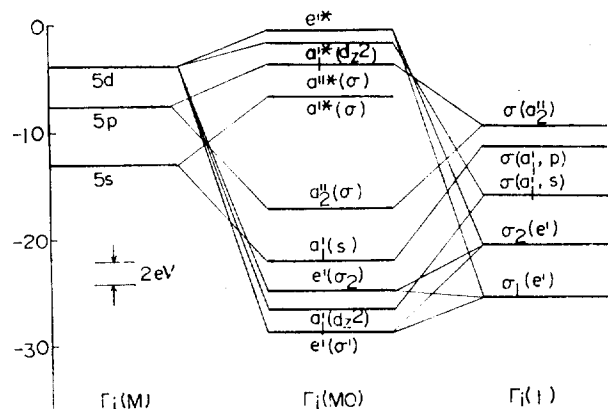


Figure 4. Energy level diagram for trigonal bipyramidal Sn(IV)-ClX , Isomer (b).

the *trans* form in benzene solution. However, when this complex dissolves in ethylacetate, the *trans* complex transforms to cis form and only cis form exists in ethylacetate solution.

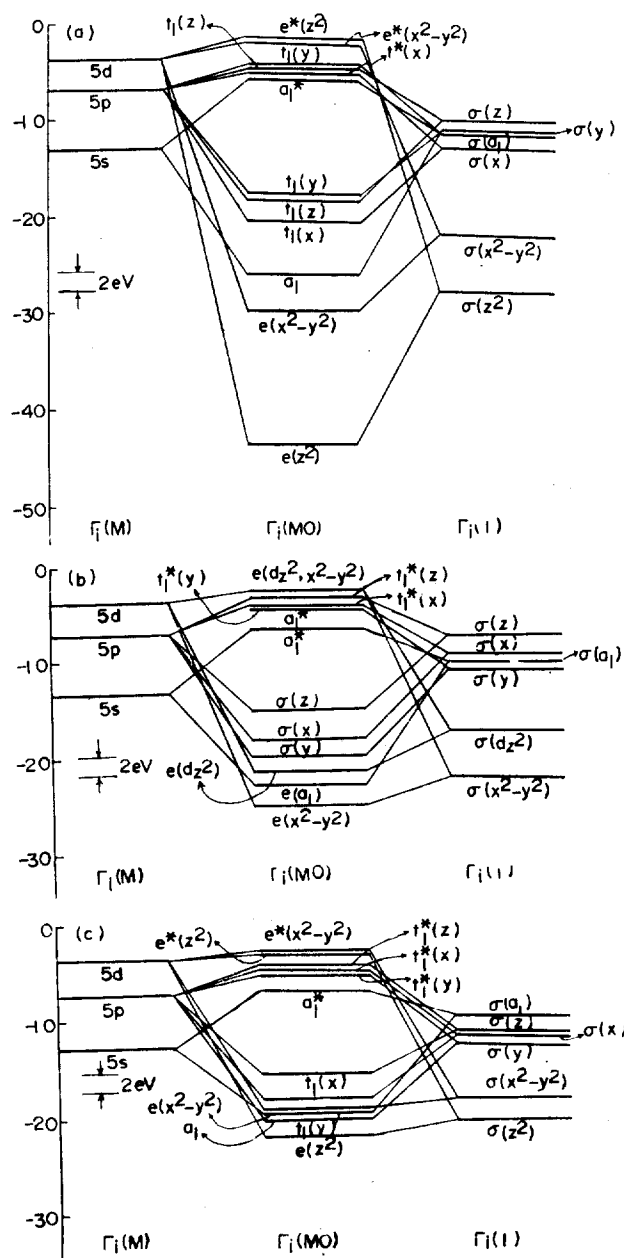


Figure 5. (a). Energy level diagram for octahedral $\text{Cl}_3\text{Sn(IV)-(CH}_2\text{Cl)}$, Isomer (d); (b). Energy level diagram for octahedral $\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$, Isomer (h). (c). Energy diagram for octahedral $\text{ClSn(IV)(CH}_2\text{Cl)}_3$, Isomer (k).

TABLE 8: The Calculated Dipole Moments for Tetrahedral $\text{Cl}_n\text{Sn(IV)(CH}_2\text{Cl)}_{4-n}$ Type Complexes

Complex	R	R'	μ (Debye)	Exp. value
Sn(IV)Cl_4	2.36	0	0	0
$\text{Cl}_3\text{Sn(IV)(CH}_2\text{Cl)}$	2.36	2.21	3.316	3.67
$\text{Cl}_2\text{Sn(IV)(CH}_2\text{Cl)}_2$	2.36	2.21	6.161	3.17
$\text{ClSn(IV)(CH}_2\text{Cl)}_3$	2.36	2.21	3.465	3.11

Where R : the bond length between Sn (IV) and chlorine atom;
R' : the bond length between Sn(IV) and carbon atom.

TABLE 9: The Calculated Dipole Moments for Trigonal Bipyramidal $\text{Cl}_n\text{Sn(IV)} (\text{CH}_2\text{Cl})_{4-n}\text{X}$ Type Complexes**(A) $\text{Sn(IV)Cl}_4\text{X}$ Complex (X: Dioxane)**

Exp. value: 3. 82 D

Complex	R	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.18	0	0	2.287	2.287
Isomer (2)	2.36	2.18	3.675	0	0	3.675

(B) $\text{Cl}_3\text{Sn(IV)} (\text{CH}_2\text{Cl})\text{X}$ Complex (X: Ethylacetate)

Exp. value: 8. 36 D.

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	0.	0	6.138	6.138
Isomer (2)	2.36	2.21	2.18	6.181	0	1.944	6.479
Isomer (3)	2.36	2.21	2.18	2.488	0	2.658	3.641

(C) $\text{Cl}_2\text{Sn(IV)} (\text{CH}_2\text{Cl})_2\text{X}$ Complex (X: Ethylacetate)

Exp. value: 8. 32 D

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	0.965	0	5.660	5.742
Isomer (2)	2.36	2.21	2.18	5.974	0	2.748	6.576
Isomer (3)	2.36	2.21	2.18	2.600	0	3.693	4.516

(D) $\text{ClSn(IV)} (\text{CH}_2\text{Cl})_3\text{X}$ Complex (X: Ethylacetate)

Exp. value: 7.94 D

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	0	0	1.882	1.882
Isomer (2)	2.36	2.21	2.18	7.634	0	6.367	9.941

Where R: the bond length between Sn(IV) and chlorine atom; R': the bond length between Sn(IV) and carbon atom; R'': the bond length between Sn(IV) and oxygen atom.

TABLE 10: The Calculated Dipole Moments for Octahedral $\text{Cl}_n\text{Sn(IV)} (\text{CH}_2\text{Cl})_{6-n}\text{X}$ Type Complexes**(A) $\text{Sn(IV)Cl}_6\text{X}$ complex (X: Dioxane)**

Exp. value: 3. 82 D

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	0	0	0	0
Isomer (2)	2.36	2.21	2.18	3.801	0	3.408	5.105

(B) $\text{Cl}_5\text{Sn(IV)} (\text{CH}_2\text{Cl})\text{X}$ Complex (X: Ethylacetate)

Exp. value: 8.36 D.

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	0.	4.130	0.	4.130
Isomer (2)	2.36	2.21	2.18	3.880	0	6.769	7.802
Isomer (3)	2.36	2.21	2.18	4.313	3.433	3.223	6.385

(C) $\text{Cl}_4\text{Sn(IV)} (\text{CH}_2\text{Cl})_2\text{X}$ Complex (X: Ethylacetate)

Exp. value: 8. 32 D.

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	8.008	8.008	0	11.325
Isomer (2)	2.36	2.21	2.18	7.625	3.536	5.245	9.907
Isomer (3)	2.36	2.21	2.18	7.660	4.788	2.814	9.461

(D) $\text{Cl}_3\text{Sn(IV)} (\text{CH}_2\text{Cl})_3\text{X}$ Complex (X: Ethylacetate)

Exp. value: 7.94 D.

Complex	R	R'	R''	μ_x	μ_y	μ_z	μ
Isomer (1)	2.36	2.21	2.18	0	5.055	0.	5.055
Isomer (2)	2.36	2.21	2.18	4.884	0	3.590	6.061
Isomer (3)	2.36	2.21	2.18	0	5.206	6.509	8.335

Where R: the bond length between Sn(IV) and Chlorine atom; R': the bond length between Sn(IV) and Carbon atom; R'': the bond length between Sn(IV) and Oxygen atom.

TABLE 11: The Differences of the Calculated Dipole Moments for $\text{Cl}_n\text{Sn(IV)} (\text{CH}_2\text{Cl})_{4-n}$ in Benzene and Ethylacetate Solutions

(A) Trigonal Bipyramidal Complexes			
Complexes		$\Delta\mu$	$\Delta\mu(\text{Exp.})$
$\text{Cl}_3\text{Sn(IV)} (\text{CH}_2\text{Cl})_2\text{X}$	Isomer (1)	2.822	4.69
	Isomer (2)	3.163	4.69
	Isomer (3)	0.325	4.69
$\text{Cl}_2\text{Sn(IV)} (\text{CH}_2\text{Cl})_2\text{X}$	Isomer (1)	-0.419	5.15
	Isomer (2)	0.415	5.15
	Isomer (3)	-1.645	5.15
$\text{ClSn(IV)} (\text{CH}_2\text{Cl})_3\text{X}$	Isomer (1)	-1.583	4.83
	Isomer (2)	6.476	4.83
$\text{Sn(IV)} \text{Cl}_4\text{X} (\text{X: Dioxane})$	Isomer (1)	2.287	3.82
	Isomer (2)	3.675	3.82
(B) Octahedral Complexes			
Complexes		$\Delta\mu$	$\Delta\mu(\text{Exp.})$
$\text{Cl}_3\text{Sn(IV)} (\text{CH}_2\text{Cl})_2\text{X}$	Isomer (1)	0.814	4.69
	Isomer (2)	4.486	4.69
	Isomer (3)	3.069	4.69
$\text{Cl}_2\text{Sn(IV)} (\text{CH}_2\text{Cl})_2\text{X}$	Isomer (1)	-1.106	5.15
	Isomer (2)	-0.100	5.15
	Isomer (3)	2.174	5.15
$\text{ClSn(IV)} (\text{CH}_2\text{Cl})_3\text{X}$	Isomer (1)	7.860	4.83
	Isomer (2)	6.442	4.83
	Isomer (3)	5.996	4.83
$\text{Sn(IV)}\text{Cl}_4\text{X} (\text{X: Dioxane})$	Isomer (1)	0	3.82
	Isomer (2)	5.105	3.82

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Study of the Kinetics and Mechanisms of Alkoxy Radical Reactions in the Gas Phase (I). Arrhenius Parameters for *t*-Butoxy Radical Reactions with Isobutane and Cyclohexane

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The relative Arrhenius parameters for *t*-butoxy radical decomposition ($\log A_d, E_d$) and hydrogen abstraction of *t*-butoxy radical from hydrogen donor ($\log A_a, E_a$) by competitive method were obtained as follows: for cyclohexane; $\log A_d/A_a = -4.17$ mole/l and $E_d - E_a = 9.01$ kcal/mole, for isobutane; $\log A_d/A_a = -5.70$ mole/l and $E_d - E_a = 11.0$ kcal/mole. From the reported Arrhenius parameters for *t*-Butoxy radical decomposition reactions the parameters for *t*-Butoxy radical reactions with isobutane and cyclohexane are estimated to be $\log A$ (l/mol·sec) = 8.4, $E_a = 4.3$ kcal/mol and $\log A$ (l/mol·sec) = 9.9, $E_a = 6.3$ kcal/mol, respectively.

1. Introduction

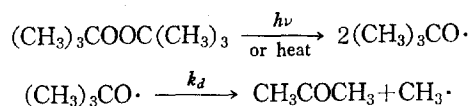
Alkoxy radicals are known to be very important intermediate species in combustion,¹ biological,² and atmospheric chemistry.³ Alkoxy radicals are obtained either by the pyrolyses of peroxides and alkyl nitrites⁴ or by the photolyses of peroxides⁵ and esters.⁶ Alkoxy radicals, once generated, can either decompose to give ketone and alkyl radicals or react with hydrogen donor to give corresponding alcohol. The relative rate constants for the reaction of alkoxy radicals usually determine the distribution of final products.

Most of alkoxy radical reactions have been studied by a competition method. The relative rate constants for the decomposition (k_d) versus hydrogen abstraction reaction (k_a) of alkoxy radicals in liquid phase were extensively studied by Walling and co-workers.^{7,8} The solvent polarity was found to be affecting the activation energies for the decomposition reactions.⁷ Only very recently a direct measurement of absolute rate constant at low temperatures for *t*-butoxy radical reactions with various hydrogen donors by ESR and laser photolysis techniques was reported.^{9,10}

The gas phase decomposition of alkoxy radicals have also been studied by competition method, either with NO reaction,¹¹⁻¹⁴ i.e., $\text{RO}\cdot + \text{NO} \longrightarrow \text{RONO}$ vs. $\text{RO}\cdot \longrightarrow$ decomposition, or with hydrogen abstraction reaction i.e., $\text{RO}\cdot + \text{R}'\text{H} \longrightarrow \text{ROH} + \text{R}'\cdot$ vs. $\text{RO}\cdot \longrightarrow$ decomposition. Due to the inaccuracies in the rate constants of reference reac-

tions and the narrow temperature ranges, large discrepancies in Arrhenius parameters have been noticed.^{15,16} Baldwin *et al.* and Batt and coworkers attempted to design a systematic scheme for the estimation of Arrhenius parameters for the alkoxy radical reactions. However, their estimated A factor appears to be too high, so as the activation energies. Recently, Choo and Benson have made a systematic approach on the evaluation of Arrhenius parameters for the alkoxy radical decomposition reactions by a tight transition state model.¹⁷ They showed that the estimated Arrhenius parameters ($\log A = 14.1$ sec⁻¹, $E_a = 15.3$ kcal/mole) for *t*-butoxy radical decomposition reactions gave reasonably self-consistent results for the rate constants reported at different laboratories and in different environments.

In this work the ratios of the rate constant of *t*-butoxy radical decomposition versus the rate constant of hydrogen abstraction of *t*-butoxy radical from cyclohexane or isobutane is measured. The basic mechanism of di-*t*-butyl peroxide decomposition is well known,



t-butoxy radicals are decomposed to acetone and methyl radical by β -scission cleavage. When hydrogen donor such as cyclohexane or isobutane is added,