



Structural studies of titanium alkoxides  
by Robert Dale Witters

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry  
Montana State University  
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Abstract:

Dipole moments of four alkyl titanates were determined in n-heptane solution by the method Halverstadt and Kumler. It was found that the values obtained for the ethyl, n-propyl, and n-butyl orthoesters were for the trimers, but those found for tert-butyl titanate were for the monomers. Variations of the dipole moments of these compounds with temperature change indicate the potential energy barrier to rotation of the alkoxy groups is of magnitude  $kT$ .

The crystal and molecular structures of monomethyltriethyl titanate was determined by x-ray diffraction techniques. Crystal data obtained are:  $a = 12.14 \text{ \AA}$   $\alpha = 76^\circ 56'$  density (meas.) = 1.244 g/cc  $b = 12.13$   $\beta = 77^\circ 2'$  density (calc.) = 1.236 g/cc  $c = 16.93$   $\gamma = 74^\circ 15'$   $Z = 8$  Space Group P1 In the solid state the molecules are linked together to form tetramer units. In the tetramers the four titanium atoms form a planar diamond shape, sharing oxygen atoms so that each titanium atom has a coordination number of six.

A preliminary investigation of an hydrolysis product of tetraethyl titanate was carried out. The unit cell of this crystal contains approximately 60 titanium atoms. Due to the complexity of this crystal and also to the fact that the molecular formula of the compound is uncertain, the structure determination was not completed. Crystal data obtained for this compound are:  $a = 27.92 \text{ \AA}$  density = 1.305 g/cc  $b = 22.40$  space group P21/a  $c = 23.30$   $\beta = 117^\circ 15'$

STRUCTURAL STUDIES OF TITANIUM ALKOXIDES

by

ROBERT DALE WITTERS

A thesis submitted to the Graduate Faculty in partial  
fulfillment of the requirements for the degree

of

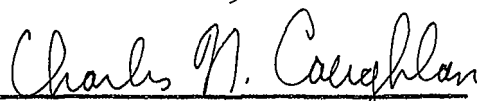
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## TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
INTRODUCTION	x
PART I. DIELECTRIC STUDIES OF TETRAETHYL TITANATES	5
Theory and Discussion of Methods	5
Preparation of Compounds	9
Dielectric Constant Apparatus	9
Density Apparatus	9
Temperature Control and Measurement	10
Data and Results	12
PART II. PRELIMINARY INVESTIGATION OF THE HYDROLYSIS PRODUCT OF TETRAETHYL TITANATE	47
Preparation of Crystals	47
Analysis of Crystals	49
Density Determination of the Hydrolysis Product	50
Collection of X-Ray Data	50
Space Group	52
Cell Dimensions	53
Choosing the Axes	54
Indexing Weissenberg Photographs of Monoclinic Crystals	59
Attempt to Determine Structure	63

## TABLE OF CONTENTS (cont.)

	Page
PART III. THE CRYSTAL STRUCTURE OF MONOMETHYLTRIETHYL TITANATE	72
Preparation of Crystals	72
Density Determination of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	72
Experimental: X-Ray Apparatus and Intensity Measurements	72
Space Group	23
Cell Dimensions and Choice of Axes	75
Indexing Weissenberg Photographs of Triclinic Crystals	81
Determination of the Structure	87
Review of Structure	118
DISCUSSION	119
SUMMARY	122
APPENDIX	123
A. Derivation of Formula. Calculation of Axial Length from a Rotation Picture	124
B. Derivation of a Method for the Determination of Interaxial Angles from Weissenberg Photographs Derivation for a Monoclinic Crystal Derivation for a Triclinic Crystal	128
C. Table of Structure Factors for $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	141
LITERATURE CITED	175

## LIST OF TABLES

PART I. Variation of Dielectric Constant and Specific Volume with Concentration for n-Heptane Solutions of Tetraalkyl Titanates		Page
TABLE I	Tetraethyl Titanate, 50°C	14
TABLE II	Tetraethyl Titanate, 25°C	15
TABLE III	Tetraethyl Titanate, 0°C	16
TABLE IV	Tetrapropyl Titanate, 50°C	17
TABLE V	Tetrapropyl Titanate, 25°C	18
TABLE VI	Tetrapropyl Titanate, 0°C	19
TABLE VII	Tetra-n-butyl Titanate, 50°C	20
TABLE VIII	Tetra-n-butyl Titanate, 25°C	21
TABLE IX	Tetra-n-butyl Titanate, 0°C	22
TABLE X	Tetra-tert-butyl Titanate, 25°C	23
TABLE XI	Results of Dielectric Studies	45
TABLE XII	Densities and Refractive Indices for Pure Liquids	46
PART II.		
TABLE XIII	Determination of c from Rotation Film	55
TABLE XIV	Determination of $a \cdot \sin \beta$ and b from Weissenberg Film	56
TABLE XV	Summary of Crystal Data for Hydrolysis Product	57
PART III.		
TABLE XVI	Determination of Cell Edge b from Rotation Film	76
TABLE XVII	Determination of Interplanar Spacings from Weissenberg Film	77

LIST OF TABLES  
(continued)

		Page
TABLE XVII	Summary of Crystal Data $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	77
TABLE XVIII	Summary of Crystal Data $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	83
TABLE XIX	Patterson Peaks Used and Predicted	91
TABLE XX	Bond Distances	100
TABLE XXI	Atom Parameters	106
TABLE XXII	O - Ti - O Bond Angles	115
APPENDIX C	Table of Structure Factors for $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	141

## LIST OF FIGURES

INTRODUCTION			Page
Figure 1.	Proposed Structures for Trimeric Tetraethyl Titanate		4
PART I			
Figure 2.	Pycnometer Variation of Dielectric Constant and Specific Volume with Concentration for Tetraalkyl Titanates		11
Figure 3.	$Ti(OC_2H_5)_4$	Specific Volume	0°C 24
Figure 4.	$Ti(OC_2H_5)_4$	Dielectric Constant	0°C 25
Figure 5.	$Ti(OC_2H_5)_4$	Specific Volume	25°C 26
Figure 6.	$Ti(OC_2H_5)_4$	Dielectric Constant	25°C 27
Figure 7.	$Ti(OC_2H_5)_4$	Specific Volume	50°C 28
Figure 8.	$Ti(OC_2H_5)_4$	Dielectric Constant	50°C 29
Figure 9.	$Ti(OC_3H_7^n)_4$	Specific Volume	50°C 30
Figure 10.	$Ti(OC_3H_7^n)_4$	Dielectric Constant	50°C 31
Figure 11.	$Ti(OC_3H_7^n)_4$	Specific Volume	25°C 32
Figure 12.	$Ti(OC_3H_7^n)_4$	Dielectric Constant	25°C 33
Figure 13.	$Ti(OC_3H_7^n)_4$	Specific Volume	0°C 34
Figure 14.	$Ti(OC_3H_7^n)_4$	Dielectric Constant	0°C 35
Figure 15.	$Ti(OC_4H_9^n)_4$	Specific Volume	50°C 36
Figure 16.	$Ti(OC_4H_9^n)_4$	Dielectric Constant	50°C 37
Figure 17.	$Ti(OC_4H_9^n)_4$	Specific Volume	25°C 38
Figure 18.	$Ti(OC_4H_9^n)_4$	Dielectric Constant	25°C 39
Figure 19.	$Ti(OC_4H_9^n)_4$	Specific Volume	0°C 40
Figure 20.	$Ti(OC_4H_9^n)_4$	Dielectric Constant	0°C 41



LIST OF FIGURES  
(continued)

			Page
Figure 21.	$\text{Ti}(\text{OC}_4\text{H}_9^t)_4$	Specific Volume	25°C 42
Figure 22.	$\text{Ti}(\text{OC}_4\text{H}_9^t)_4$	Dielectric Constant	25°C 43
Figure 23.	Temperature Variation of Dipole Moment		44
PART II			
Figure 24.	Crystal Growing Apparatus		48
Figure 25.	Apparatus for Growing Crystals for Analysis		51
Figure 26.	Choosing Axes on a*c* Net		58
Figure 27.	Relationship Between the Precession and Weissenberg Films		60
Figure 28.	Arrangement in Reciprocal Space for Upper Level Weissenberg Films		62
Figure 29.	Appearance of b* Axial Lines (Festoons) on 4th Level Weissenberg Films		64
Figure 30.	Indication of Subcells from Weighted a*b* Net		70
PART III			
Figure 31.	Chart for Intensity Correction		74
Figure 32.	Arrangement of Axes on Weissenberg and Precession Films		80
Figure 33.	Arrangement of Reciprocal Axes for Upper Level Weissenberg Films		82
Figure 34.	Reciprocal Axes Arrangement		85
Figure 35.	Comparison of 3d and 4th Level Weissenberg Films		88
Figure 36.	Structure of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer		111
Figure 37.	$\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer		112
Figure 38.	Bond Distances. $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer Unit #1		113
Figure 39.	Bond Distances. $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer Unit #2		114

LIST OF FIGURES  
(Continued)

Page

## APPENDIX

Figure 40.	Sphere of Reflection and X-Ray Camera	125
Figure 41.	Reciprocal Lattice Setting for an Equi-Inclination Weissenberg Picture when Crystal is Mounted on c Axis, for a Monoclinic Crystal	129
Figure 42.	Reciprocal Lattice Setting for an Equi-Inclination Weissenberg Picture when Crystal is Mounted on c Axis, for a Triclinic Crystal	132
Figure 43.	Relationship Between Reciprocal Lattice Axes and c Axis, for a Triclinic Crystal	133
Figure 44a.	First and Second Settings for $b^*$ Axis	136
Figure 44b.	First and Second Settings for $a^*$ Axis	137

## ABSTRACT

Dipole moments of four alkyl titanates were determined in n-heptane solution by the method Halverstadt and Kumler. It was found that the values obtained for the ethyl, n-propyl, and n-butyl orthoesters were for the trimers, but those found for tert-butyl titanate were for the monomers. Variations of the dipole moments of these compounds with temperature change indicate the potential energy barrier to rotation of the alkoxy groups is of magnitude  $kT$ .

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Space Group  $P1$

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A preliminary investigation of an hydrolysis product of tetraethyl titanate was carried out. The unit cell of this crystal contains approximately 60 titanium atoms. Due to the complexity of this crystal and also to the fact that the molecular formula of the compound is uncertain, the structure determination was not completed. Crystal data obtained for this compound are:

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$c = 23.30$	
$\beta = 117^{\circ}15'$	

## INTRODUCTION

The chemistry of organic compounds of titanium has been of interest for a number of years. In many ways the organic titanates exhibit unusual properties, some of which have lead to industrial uses in the paint and the electrical industries. To a large extent, however, understanding of their chemistry has been limited because the structures were not known. Only in very recent years have attempts been made to determine their structures by any of the various methods now used. The research reported in this dissertation is an attempt to provide some of the first accurate structural information about these compounds. Before describing the methods and results a brief review of the knowledge available at present will be given.

Gilman and Jones<sup>(24)</sup> have summarized early attempts to prepare organic titanium compounds. In 1875 Demarcay<sup>(21)</sup> reported the first preparation of an alkyl titanate, but later investigators<sup>(31)</sup> were unable to duplicate his work and showed that his compounds were probably a mixture of oxy-ethyl titanates. Probably the first preparation of a pure alkyl titanate was carried out in 1923 by Bischoff and Adkins<sup>(1)</sup>. They reported obtaining the tetraethyl, tetraisopropyl, and tetramethyl titanates.

Since the early 1940's chemists have become concerned with the structures of these compounds and the mechanisms of their reactions, particularly with water. All of the alkyl titanates react with water, the rate of reaction generally increasing with decreasing molecular weight of the compound.

Much of the work carried on in this laboratory and described in this dissertation began with the investigation of tetraethyl titanate, as this

is probably the most unusual of this group. For several years it was reported in the literature to be a liquid at room temperature; however in 1950 Caughlan and Crowe<sup>(15)</sup> showed that its normal state is solid. The pure compound is obtained as a liquid by distillation. If the liquid is allowed to stand for a considerable length of time, usually several months, small crystals form on the sides of the container, and eventually the entire liquid solidifies.

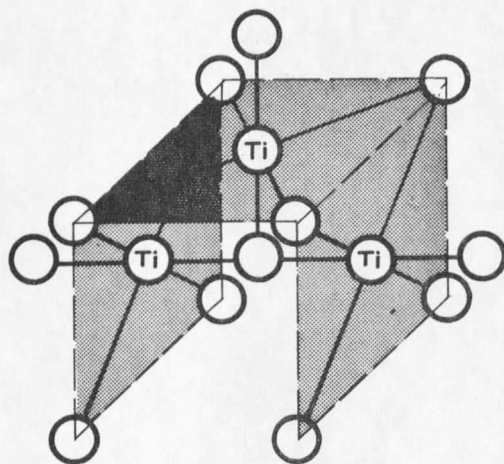
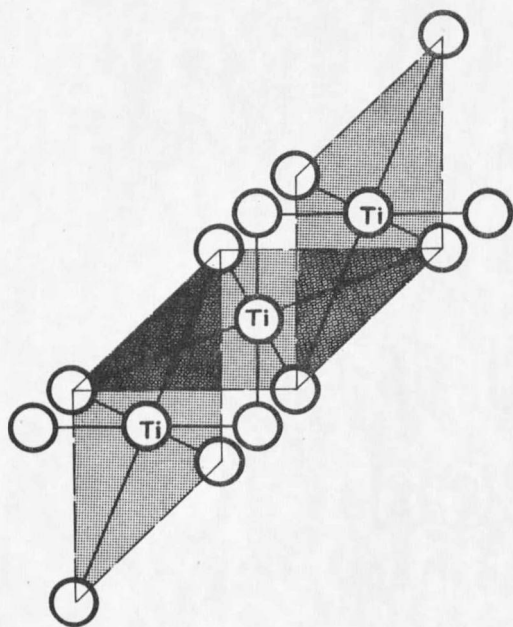
In this laboratory research on organic titanates started with a study of the dielectric properties of these compounds and the molecular weights in solution. Results of the molecular weight investigations showed that all of the orthoesters studied had an association number of three<sup>(13)</sup>. This association is not surprising when one considers the fact that the coordination number of titanium is six, whereas its primary valence number in the monomeric titanate is only four. To satisfy the coordination number of six, oxygens from surrounding titanate molecules must be used. The structures proposed for the trimer are shown in Figure 1; the linear structure in Figure 1a is the one that most generally has been accepted.

As already mentioned most of the alkyl titanates react readily with water. For small amounts of water the major products of the reaction are polymers, the size of the polymer depending on the amount of water added. D. C. Bradley and his associates have made a very thorough investigation of the hydrolysis of  $Ti(OC_2H_5)_4$  and, based on the trimer structure proposed by Caughlan, have proposed a set of reactions for the hydrolysis and structures for the hydrolysis products (2), (3), (4).

In order to confirm the trimeric structure of the alkyl titanates it was decided to determine the structure of the tetraethyl titanate by single crystal x-ray diffraction techniques. Crystals were obtained from an ethanol solution, and cell dimensions were determined from x-ray data. It was apparent in the early stages of this investigation that the crystals were not of the tetraethylate but of one of the hydrolysis products. Since good crystals of the hydrolysis product were now on hand, it was decided to continue the x-ray structure determination of this compound.

Crystals of monomethyltriethyl titanate were obtained by the method described by Varma and Mehrotra<sup>(34)</sup>. Since this compound is also trimeric in solution, determination of this structure would serve to verify that proposed for the trimers. Accordingly, a major portion of this research is on the structure of  $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ .

In addition to the x-ray examination of the two crystals mentioned, the dielectric properties of tetraethyl titanate, tetra-n-propyl titanate, tetra-tert-butyl titanate, and tetra-n-butyl titanate have been measured in n-heptane at 0°, 25°, and 50°C.



Proposed Structures for Trimeric Titanium Tetraethylate

(Carbons not Shown)

Figure 1

## PART I

### Dielectric Studies of Alkyl Titanates

The dipole moment of a compound is determined by its molecular structure. Aside from translational or rotational motion of the molecule as a whole, its atoms are not in fixed locations; they are in constant vibration about an average point, and atoms or groups of atoms may rotate about some bond in the molecule. Greater vibrations of the atoms at increased temperatures generally have little effect on the dipole moment since the average positions of the atoms are not changed. The degree to which an atom or group of atoms rotate about an axis may be affected by temperature, however, thus changing the dipole moment of the molecule. Comparison of measured and theoretically calculated dipole moments for alkyl titanates has indicated restriction of rotation of the alkoxy groups.

This dielectric study of the titanates was therefore undertaken to learn how the dipole moments are affected by temperature. From this, insight into the degree of restriction of rotation of the groups and to the energy barrier to rotation may be obtained.

#### Theory and Discussion of Methods

A detailed review of the theory of dielectric constants, polarization, and dipole moment may be found in the references (14), (20), and (29). However a brief discussion of the general theory will be given here.

Molecules, although neutral, possess small centers of negative and positive charges. In polar molecules there is a finite distance of separation between the centers of the negative and positive charges, and the



polarity of a molecule becomes less as these centers approach each other. When placed in an electric field a polar molecule will tend to orient itself, the charges lining up in the direction of the field. The force required to orient the molecule depends on the magnitude of the charges and on the distance between them. The dipole moment is a measure of these two quantities; it is the product of either charge  $e$  by the distance between them:  $\mu = er$ . It serves as a useful quantitative measure of the extent to which a molecule is polar. Thus dipole, or dielectric, studies provide some information concerning the shape of a molecule.

The dielectric constant of a substance is related to its degree of polarization in an electric field. Polarization is determined in this research by determining the extent to which the substance in the dissolved state in a solution of a nonpolar solvent contributes to the dielectric constant of the solution. By extrapolating the measurements of dielectric constant to infinite dilution, a value is obtained which corresponds to a situation in which the molecules are so far apart that they do not induce charges in each other.

The molar polarization of a substance can be calculated from the dielectric constant  $\epsilon$  using a formula developed by Clausius and Mosotti on the basis of theories of electric charges induced by electric field:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d}$$

where  $P$  is the molar polarization,  $M$  the molecular weight, and  $d$  the density.

For a binary solution the equation can be written as

$$P_{12} = c_1 P_1 + c_2 P_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{c_1 M_1 + c_2 M_2}{d_{12}}$$

where  $P$  is the molar polarization,  $\epsilon$  the dielectric constant,  $d$  the density,  $c$  the concentration, and  $M$  molecular weight. The subscripts 1, 2, and 12 refer to solvent, solute, and solution, resp.

Assuming the dielectric constant and the specific volume of a binary solution to be linear functions of concentration, Halverstadt and Kumler<sup>(25)</sup> arrived at the following equation:

$$P_{\infty} = \frac{\epsilon_1}{\epsilon_1} \frac{-1}{+2} (M_2 v_1 + M_1 B) + \frac{3Av_1 M_1}{(\epsilon_1 + 2)^2},$$

where the meanings of the symbols are as follows:

$P_{\infty}$  is the molar polarization of solute at infinite dilution

$\epsilon_1$  is the dielectric constant of solution at infinite dilution (intercept)

$v_1$  is the specific volume of solution at infinite dilution (intercept)

$M_1$  and  $M_2$  are the molecular weights of solvent and solute, resp.

$A$  is the slope of the dielectric constant-concentration curve

$B$  is the slope of the specific volume-concentration curve.

The method of Halverstadt and Kumler takes into account the fact that the dielectric constant of the solvent may be considerably different from the measured dielectric constant of the pure solvent. This may be due partially to the absorption of water. This solvent polarization error is essentially eliminated by obtaining the dielectric constant of the pure solvent from extrapolation to infinite dilution. These authors point out that solvents with a low dielectric constant must be used.

The molar polarization determined by this method is the total polarization and is the sum of the orientation polarization, the atomic polarization, and the electronic polarization. The dipole moment of a

molecule can be calculated from the orientation polarization. Thus the atomic and electronic polarizations must be determined and subtracted from  $P_{\infty}$ . Hence,  $P_{\mu} = P_{\infty} - P_e - P_a$  where  $P_{\mu}$ ,  $P_{\infty}$ ,  $P_e$ , and  $P_a$  are the orientation, total, electronic, and atomic polarizations, resp.

The electronic polarization and molar refraction of a compound theoretically are the same for a high frequency oscillating electric field. According to Maxwell's relation,  $\epsilon = n^2$  for a non-polar substance, where  $n$  is the refractive index. Thus  $n^2$  is really a measure of the dielectric constant with the effects of the permanent dipoles and atomic effects removed. The reason for this is that the frequencies of optical light are so great that the dipoles of the molecules are unable to orient themselves fast enough, and only the effects due to electronic polarization are manifest. Thus by determining the refractive index of a substance, and its density, the electronic polarization may be determined. The molar refraction  $R$  is given by the relation  $R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$ .

The atomic polarization is not so easily determined. This contribution to the total polarization is usually quite small and is frequently omitted from calculations; sometimes it is assumed to be about 5% of the electronic polarization. In this work on titanium alkoxides the effect due to the atomic polarization has been neglected. Thus in this case the orientation polarization is calculated by subtracting the molar refraction from  $P_{\infty}$ :  $P_{\mu} = P_{\infty} - R - P_a$  where it is assumed that  $P_a \approx 0$ .

The dipole moment of a compound can be calculated from the orientation polarization by the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{P_{\mu} T} \text{ e.s.u.} = \sqrt{P_{\mu} T} \text{ Debye.}$$

#### A. Preparation of Compounds

The tetraethyl and tetra-n-propyl titanates were prepared by the sodium alkoxide method.<sup>(1)(31)</sup> Tetra-tert-butyl titanate was prepared by the pyridine-ammonia method,<sup>(5)(19)</sup> while the n-butyl ester was obtained from E. I. duPont de Nemours and Co., Inc.

#### B. Dielectric Constant Apparatus

The electric circuit, the precision condenser, and the dielectric cell have been described before.<sup>(14)(15)</sup> The dielectric cell was modified slightly by placing a thermostated reservoir on top of the cell, increasing the effective volume of the unit from 10 ml to about 25 ml. An opening in the top of the reservoir permitted inserting a metal thermister directly into the dielectric cell for accurate temperature measurement. A second opening permitted addition of solute to the solution in the cell. Both openings in the reservoir were sealed with ground glass stoppers so no evaporation of solvent nor absorption of water could take place except during the brief periods when solute was being added.

#### C. Density Apparatus

Densities of the solutions at 25° and at 50°C were obtained by the Westphal balance method. An analytic balance was modified for this purpose. A plummet of 15.65 ml capacity was made by sealing several grams of mercury into a glass tube. The solutions were placed in a thermostated container (80 ml) for the readings. Additional solute was easily added to this, the mixture being stirred by moving the bob up and down. A cork stopper sealed the solution from contact with air except for a small hole for the wire leading from the balance to the plummet.



























































































































































































































































































































































































