



The dielectric properties of some esters of titanium tetrachloride containing organic groups  
by Robert W Crowe

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry  
Montana State University  
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Abstract:

Several derivatives of  $TiCl_4$  containing organic groups, have been prepared and, the dielectric properties of some of these studied. The compounds prepared were: titanium tetraethylate,  $Ti(OC_2H_5)_4$  monochloro-tri-ethoxy-titanium,  $TiCl(OC_2H_5)_3$ ; trichloro-phenoxy-titanium,  $TiCl_3OC_6H_5$ ; di-chloro-diethoxy-titanium,  $TiCl_2(OC_2H_5)_2$ ; and compounds formed by the reaction of  $TiCl_4$  with ethylene glycol and hexamethylene glycol.

The dielectric constants of  $Ti(OC_2H_5)_4$ ,  $TiCl(OC_2H_5)_3$  and  $TiCl_3OC_6H_5$  have been measured in dilute solution in benzene at  $25^\circ C$  and their molar polarizations, calculated by an equation derived from the Debye-Clausius-Mossotti equation, have been found to be 108, 222 and 250 ml. respectively. The molar refraction of  $Ti(OC_2H_5)_4$  has been calculated from measurements of its refractive index and density in the pure state. The value obtained was 64.4 ml. The molar refractions of  $TiCl(OC_2H_5)_3$  and  $TiCl_3OC_6H_5$  were calculated from measurements of their refractive indices and densities in dilute solution in benzene. The values obtained here were 66.6 ml. respectively. The electric moments for  $Ti(OC_2H_5)_4$ ,  $TiCl(OC_2H_5)_3$  and  $TiCl_3OC_6H_5$  have been found to be 1.4, 2.83 and 2.97 Debye units respectively. Several unsuccessful attempts have been made to purify the other compounds prepared.

$Ti(OC_2H_5)_4$  previously reported as a liquid, has been found to exist as a white solid, stable below  $34^\circ C$ . The dielectric constant of this compound has been measured through its melting point to determine the effect of solidification on the rotation of the molecule.

The apparatus used for all measurements has been described and an attempt made to explain the experimental results.

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I. ABSTRACT

Several derivatives of  $TiCl_4$ , containing organic groups, have been prepared and the dielectric properties of some of these studied. The compounds prepared were: titanium tetraethylate,  $Ti(OC_2H_5)_4$ ; monochloro-triethoxy-titanium,  $TiCl(OC_2H_5)_3$ ; trichloro-phenoxy-titanium,  $TiCl_3OC_6H_5$ ; dichloro-diethoxy-titanium,  $TiCl_2(OC_2H_5)_2$ ; and compounds formed by the reaction of  $TiCl_4$  with ethylene glycol and hexamethylene glycol.

The dielectric constants of  $Ti(OC_2H_5)_4$ ,  $TiCl(OC_2H_5)_3$  and  $TiCl_3OC_6H_5$ , have been measured in dilute solution in benzene at  $25^\circ C$  and their molar polarizations, calculated by an equation derived from the Debye-Clausius-Mossotti equation, have been found to be 108, 222 and 250 ml. respectively. The molar refraction of  $Ti(OC_2H_5)_4$  has been calculated from measurements of its refractive index and density in the pure state. The value obtained was 64.4 ml. The molar refractions of  $TiCl(OC_2H_5)_3$  and  $TiCl_3OC_6H_5$  were calculated from measurements of their refractive indices and densities in dilute solution in benzene. The values obtained here were 54.8 and 66.6 ml. respectively. The electric moments for  $Ti(OC_2H_5)_4$ ,  $TiCl(OC_2H_5)_3$  and  $TiCl_3OC_6H_5$  have been found to be 1.4, 2.83 and 2.97 Debye units respectively. Several unsuccessful attempts have been made to purify the other compounds prepared.

$Ti(OC_2H_5)_4$ , previously reported as a liquid, has been found to exist as a white solid, stable below  $34^\circ C$ . The dielectric constant of this compound has been measured through its melting point to determine the effect of solidification on the rotation of the molecule.

The apparatus used for all measurements has been described and an attempt made to explain the experimental results.

## II. INTRODUCTION

Titanium dioxide and several other inorganic compounds of titanium have been known for some time to possess an abnormally high dielectric constant. As a result they have been used quite extensively as dielectric materials in electrical condensers. From this fact, it seemed that perhaps some organo titanium compounds might also exhibit abnormal behavior, and that their other properties might make them even more useful as dielectrics than titanium dioxide.

With these possibilities in mind, it was desired to attempt the preparation and purification of some derivatives of  $TiCl_4$  containing organic groups, and study their dielectric properties. In addition, a study of these properties will add valuable information regarding the nature and structure of the compounds and the bonds involved.

Several polymer-like compounds of questionable structure and composition have been prepared by the reaction of  $TiCl_4$  with poly-hydroxy alcohols such as glycol and glycerol. These compounds alone, if stable, should make a very interesting study.

### III. LITERATURE SURVEY

Many important advances have recently been made from dielectric studies concerning the structure and configuration of molecules. In this connection, the electric moment concept is of considerable value, since it can be used to determine the electrical asymmetry of molecules.

Both Debye (3) and Smyth (10) have given a comprehensive treatise on dielectric properties in general. A more detailed treatment of a portion of their work is given in the next section. Their work and the work of numerous other investigators in this field has done a great deal to advance our knowledge of polar molecules and the relation of dielectric constants to molecular structure.

Titanium dioxide possesses, perhaps, some of the most unusual dielectric properties. Most solids have dielectric constants from 1 to 10, while there are a few inorganic solids with dielectric constants of 15 to 30. The most common form of  $\text{TiO}_2$  (Rutile), however, has been found to have a mean dielectric constant of 11.4 (1) which is essentially constant with frequency. Because of this abnormality, it has recently found use as a dielectric in high frequency electrical capacitors.

The dielectric properties of a few organo-metallic compounds have been studied (11), but very little has been done with such compounds containing titanium. Ulich, Hertel and Hespital (12) have measured the total polarizations and dipole moments of a few additional compounds of  $\text{TiCl}_4$  such as  $\text{TiCl}_4 \cdot \text{C}_2\text{H}_5\text{CN}$ ,  $\text{TiCl}_4 \cdot 2\text{C}_2\text{H}_5\text{CN}$ ,  $\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{CN}$ , and  $\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{NO}_2$ . In the present investigation, however, the main interest was centered around deriva-

tives of  $TiCl_4$  containing organic groups. Several of these compounds have been prepared previously. Compounds of the type,  $Ti(OR)_4$ , have been prepared by Bischoff and Adkins (2). Jennings, Wardlaw and Way (7) have also prepared several chloro-esters of the type  $TiCl(OR)_3$  and  $TiCl_2(OR)_2$ . In addition, polymer-like compounds of questionable structure have been prepared with  $TiCl_4$  and poly-hydroxy alcohols such as glycol and glycerol (5). As far as can be determined, however, no dielectric studies have been made or attempted on any of these compounds.

#### IV. THEORY AND POSSIBILITIES

When two charges of electricity are separated by a definite distance, there is a force acting between them. The magnitude of this force is determined by a property called the dielectric constant of the medium in which the charges are present. It is a well known physical fact that the force acting between two charges is proportional to the product of the charges divided by the square of the distance between them. Therefore, if two charges,  $e_1$  and  $e_2$ , are separated by a distance  $d$ , the resulting force is given by the relationship  $f = e_1 e_2 / d^2 \epsilon$ , where  $\epsilon$  is called the dielectric constant.

The dielectric constant is also familiar as a quantity to which the capacitance of a condenser is proportional. In other words,  $C = \epsilon C_0$ , where  $C_0$  is the capacity of the condenser with a vacuum between its plates. However, when measuring by this method, the dielectric constant of substances having a constant considerably greater than one, very little error is introduced by using  $C_0$  as the capacity with air between the plates, since it has a dielectric constant very close to unity. This is the most common method by which the dielectric constant may be determined experimentally.

In order to visualize better the concept of dielectrics, it is necessary to consider a single molecule of a compound or substance. Every molecule, though electrically neutral, contains both positive and negative electricity. In a few types of molecules the centers of positive and negative electricity coincide, while in most molecules, due to configuration, they are separated by a definite distance. Molecules of this type are called polar, since they possess a permanent dipole moment,  $m = ed$ . HCl is



a convenient example of a polar molecule. Since the chlorine atom has a greater attraction for electrons than the hydrogen atom, it tends to shift the center of negative electricity in its direction. The center of positive electricity is thus shifted toward the hydrogen atom. In a molecule of  $\text{CCl}_4$ , however, it can be seen that any resulting shift of electrons to the chlorine atoms would be cancelled, since the four carbon bonds are tetrahedral. This molecule, then, is non-polar.

The electrons and nuclei in any molecule are, to some extent, mobile and so when the molecule, whether it is polar or non-polar, is placed in an electric field there will be a small displacement of the electrical centers with the result that a dipole, in addition to one which may already be present, will be induced in the molecule. The dielectric constant depends upon the extent of this displacement, the permanent displacement and the number of molecules per unit volume or density of the compound.

If the strength of a uniform electric field produced by two charged plates is  $E_0$ ; then in a non-polar medium the field strength is reduced to  $E$  because the dipoles induced in the molecules act in opposition to the applied field. The ratio  $E_0/E$  is the dielectric constant of the medium. It has been shown by electrostatics that  $E_0 = E + 4\pi I$ , where  $I$  is the induced electric moment per unit volume.

Assuming that the actual intensity  $F$ , acting upon one molecule, causes it to assume an electric moment  $m$ , then  $m = \alpha F$ , where  $\alpha$  is called the polarizability of the molecule. This intensity or force is calculated by supposing a unit charge to be enclosed in a small spherical cavity which is

relatively large as compared with a molecule, but small in comparison with the distance between the charged plates, as shown in Figure 1. It con-

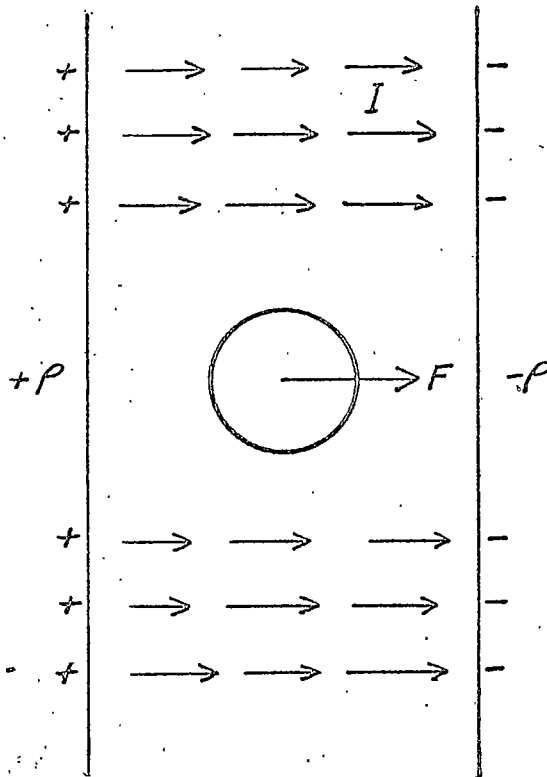


Figure 1

sists of three parts,  $F = F_1 + F_2 + F_3$  (3).  $F_1$  is the force which results from the electric charges on the two plates having a surface density charge  $\rho$ . Thus,  $F_1 = 4\pi\rho = E_0$ . The second force  $F_2$  is due to the presence of the dielectric and consists of two parts, one caused by the induced charges on the surface of the dielectric in contact with the plates, and the other by the induced charge on the surface of the spherical cavity which surrounds the molecule. This force is given by the expression,  $F_2 = -4\pi I + 4\pi I/3$ .

Finally, the component  $F_3$  is the contribution to the force by the atoms inside the sphere. It has been shown that in cubical crystals  $F_3$  is actually zero. This result is also applicable in the case of liquids and gases which are non-associated. By assuming  $F_3 = 0$  the total force  $F = E_0 - 4\pi I + 4\pi I/3$  is applicable only to gases and liquids in which the molecules move independently of one another. Therefore, since  $E_0 = E + 4\pi I$ ,  $F = E + 4\pi I/3$ .

Since by definition,  $I$  is the electric moment per unit volume of the dielectric,  $I = nm = n\alpha F = n\alpha(E + 4\pi I/3)$ , where  $n$  is the number of molecules per unit volume. Using this relationship, and the fact that  $E_0 = \epsilon E$ , the following equation may be derived:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3} \pi n \alpha$$

and since  $n = Nd/M$ , where  $M$  is the molecular weight,  $N$  Avogadro's number, and  $d$  the density, the equation reduces to the form:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4}{3} \pi N \alpha$$

The above equation is known as the Clausius-Mossotti equation where  $P$  is the molar polarization. Since it was derived on the assumption that there is no interaction between the molecules in the dielectric, it is useful only for gases in which the molecules are relatively far apart.

According to Maxwell's Law,  $\epsilon = r^2$  for a non-polar substance where  $r$  is the index of refraction. Hence, the following equation holds (3):

$$\frac{r^2 - 1}{r^2 + 2} \cdot \frac{M}{d} = \frac{4}{3} \pi N \alpha$$

According to the equation derived for the molar polarization, its value should not change with temperature. However, it has been noted that this is

not always the case. The polarization for polar molecules does change with temperature. Debye (3) has shown mathematically that the polarizability  $\epsilon$ , is not always constant as was previously thought. He has developed the following equation for this quantity:  $\epsilon = \epsilon_0 + \frac{2}{3} \frac{N\mu^2}{kT}$ , where  $\mu$  is the permanent electric moment of the molecule,  $k$  the Boltzmann constant and  $T$  the absolute temperature. According to this,  $\epsilon$  will be constant only for non-polar molecules with no permanent electric moment. By introducing these results into the original Clausius-Mossotti equation, the following relationship was obtained:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N_0}{3} \frac{4\pi N \mu^2}{9kT}$$

This equation is known as the Debye formula for total molar polarization. It has been used extensively, since its derivation, for determining dipole moments of gaseous molecules. This, however, is sometimes not convenient, especially with compounds which are difficult to vaporize. Consequently, a similar equation has been developed for calculating polarization by dissolving the compound to be studied in a non-polar solvent. If the solutions are dilute enough the dissolved particles will be far apart and the only interaction of importance will be between the polar molecules and the surrounding non-polar molecules of the solvent. For this method, the following equation has been found to be applicable (10):

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

where  $c$  is the mole fraction. The subscripts 1 and 2 indicate solvent and solute, respectively. By determining the molar polarization  $P_2$  at several concentrations and plotting these values against mole fraction solute  $c_2$ ,

a curve will result which may be extrapolated to infinite dilution. The extrapolated value gives the polarization of the solute in a solution of infinite dilution where there would be no interaction between molecules of the solute.

Two methods exist for determining the permanent dipole moment  $\mu$  from the above equations. It can be seen from the Debye equation, derived above, that if a molecule has a permanent dipole moment its molar polarization will be a linear function of the reciprocal of the absolute temperature. By plotting polarizations at infinite dilution against  $1/T$ , the dipole moment may be determined from the slope  $b$  of the curve,  $\mu = 0.0127 \times 10^{-18} \sqrt{b}$  electrostatic units.

The second method for determining the permanent dipole moment is derived from the fact that the total polarization consists of three parts. These are (1) the electronic polarization  $P_e$ , (2) the atomic polarization  $P_a$ , and (3) the orientation polarization  $P_o$ , where  $P_a + P_e = 4\pi N\alpha_0/3$  and  $P_o = 4\pi N\mu^2/9kT$ . Since the square of the refractive index of a non-polar compound is essentially the same as the dielectric constant,  $P_a + P_e$  may be determined from refractive index and density measurements. The total polarization  $P$  may be determined from dielectric constant and density data. The permanent dipole moment, then, may be calculated from the relationship:

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P - P_e - P_a) T}$$

Dipole moments have been very useful in determining structures and configurations of many molecules. Since the dipole moment is due to the

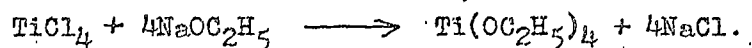
difference in the electronegativity of two atoms connected by a chemical bond, it is evident that it should be possible to associate a dipole moment with every linkage. The resultant dipole moment of a molecule is, then, the vector sum of the individual bond moments since each acts along the line connecting the centers of the atoms forming the bond. This view is in harmony with the fact that symmetrical molecules like  $\text{CCl}_4$  have no moment although each carbon-chlorine bond has an appreciable moment. The four bond moments are directed tetrahedrally and their vector sum is zero. Many bond moments have been determined by the measurement of various compounds. By the vector addition of these bond moments the resultant dipole moments of various other substances have been found to be in agreement with the observed values. Bond angles may also be estimated from dipole moment measurements.

Another interesting aspect of the question of orientation polarization is that in the solid state the molecules remain almost rigidly fixed in the space lattice so that no orientation in the direction of the electric field is possible. Under these conditions even a polar molecule will show no orientation polarization. This should result in a marked difference between the total polarization and dielectric constant in the liquid and solid states. For a non-polar substance, however, there is no orientation polarization in any case, so the difference in the two states should be small.

V. PREPARATION OF COMPOUNDS USED

The compounds prepared for study have all been prepared before by other investigators. However, little is known regarding many of their properties.

Titanium Tetraethylate -  $Ti(OC_2H_5)_4$ : This compound was prepared according to Bischoff and Adkins (2) by the reaction,



750 ml. of absolute ethyl alcohol were placed in a three-necked, round bottom flask equipped with a reflux condenser and a mechanical stirrer. To this was added 50 grams of sodium metal in rather large pieces. The reaction was cooled by means of an ice-water bath. After the reaction had subsided, the bath was removed and heat applied slowly until the sodium was entirely dissolved.

After the reaction mass had cooled, 58.5 ml. of  $TiCl_4$  were added dropwise by means of a dropping funnel over a period of three hours with continuous stirring. Again an ice-water bath was placed around the reaction flask since the reaction between  $TiCl_4$  and sodium ethoxide is quite exothermic. Through the entire addition, large amounts of smoke were produced in the reaction flask, and the mixture assumed a chalky appearance.

The mixture was then transferred to a centrifuge in order to separate the sodium chloride and other solids formed in the reaction, from the alcoholic solution containing the  $Ti(OC_2H_5)_4$ . The liquid was decanted from the centrifuge bottles and the excess alcohol removed by distillation with a water bath at  $100^\circ C$ .

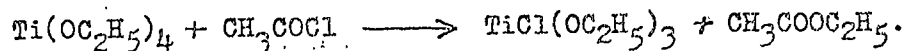
The residue which was a clear, viscous, yellow liquid, was transferred

to a small Claisen flask and distilled under reduced pressure. The product distilled at 158°C at 20 mm. pressure. It was distilled three times to insure complete purification.

The final product was a colorless, viscous liquid which hydrolyzed rapidly when exposed to air. Its general properties checked closely with those recorded in the literature. Although reported as a colorless liquid, it was found that this compound also exists as a white solid at room temperature if cooled to considerably below zero and gradually warmed. Upon warming, the viscous liquid was gradually transformed into a white solid, stable in this state below 34°C. The solidification process required between three and four hours.

In order to verify the composition of the  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  prepared, two analytical determinations were made. A Carius halogen determination showed an absence of chlorine in the molecule. Titanium determinations were made by hydrolyzing samples with water and igniting in a porcelain crucible over a Meker burner. The residue was assumed to be  $\text{TiO}_2$ . The results showed: 20.96, 20.88, 21.09, and 21.00% titanium. The theoretical value is 21.05%. The compound was therefore assumed to be reasonably pure.

Monochloro-triethoxy-titanium -  $\text{TiCl}(\text{OC}_2\text{H}_5)_3$ : This compound was prepared according to Jennings, Wardlaw and Way (7) by the reaction:

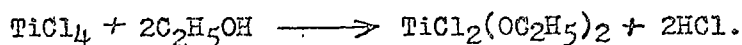


18 grams of acetyl chloride were added dropwise to 52 grams of titanium tetraethylate, cooled by means of an ice-water bath. After the addition, the mixture was refluxed for two hours and the ethyl acetate distilled off. The yellow, viscous residue was then distilled under reduced pressure.

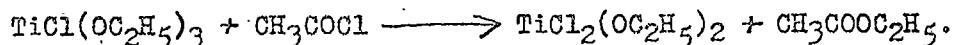


The distillate, a pale yellow, extremely viscous liquid, boiled at 170°C at 15 mm. pressure. The product was redistilled several times to insure purification. Since it hydrolyzes rapidly in air, it was necessary to store it in a sealed flask.

Dichloro-diethoxy-titanium -  $TiCl_2(OC_2H_5)_2$ : Jennings, Wardlaw and Way (7) have indicated two methods for the preparation of this compound. The first method consists in the reaction of  $TiCl_4$  with ethyl alcohol according to the equation:



The second consists of the reaction of acetyl chloride with  $TiCl(OC_2H_5)_3$ :



Both of these methods were used, but several difficulties were encountered in each case.

In the first method, 100 grams of  $TiCl_4$  were added dropwise to 100 grams of absolute ethyl alcohol in a three-necked round-bottom flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel. HCl was evolved in the reaction and the mixture turned yellow and became quite viscous. After refluxing at 100°C for two hours, the mixture was fractionally distilled under reduced pressure. At 70°C/15 mm. a white sublimate began to form in the neck of the distilling flask. From 100°C to 140°C, a yellow liquid distilled over and set to a yellow solid immediately on cooling. The yield was very small and the product had a strong odor of HCl even after redistillation. According to the literature,  $TiCl_2(OC_2H_5)_2$  should boil at 142°C/18 mm. The reaction was repeated several times with equally poor results.

In the second method, 31 grams of acetyl chloride were added dropwise to 84 grams of  $\text{TiCl}(\text{OC}_2\text{H}_5)_3$ , and the mixture refluxed for two hours. The ethyl acetate was distilled off and the yellow, viscous residue distilled under reduced pressure. Here again a white sublimate began to form at  $70^\circ\text{C}/15\text{ mm.}$ , and a pale yellow liquid was collected between  $100^\circ\text{C}$  and  $140^\circ\text{C}$ . This liquid also set to a solid after cooling, and possessed the same properties as that prepared by the first method. The yield was again low, and the product gave off  $\text{HCl}$  when melted.

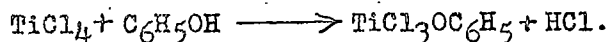
In order to verify the composition of this compound, an ignition was run to determine the titanium content. The experimental value was 19.8%, while the calculated value was 22.97%. From this analysis, it was concluded that the compound was partially decomposed at the temperature necessary for distillation. This conclusion is supported by the fact that the compound fumes considerably when warmed to  $100^\circ\text{C}$ .

Jennings, Wardlaw and Way (7) have also found that, when  $\text{TiCl}_2(\text{OC}_2\text{H}_5)_2$  is added to a minimum amount of warm ethyl alcohol, colorless needles separate out on cooling. There has been some controversy concerning the structure of this compound. According to Jennings, Wardlaw and Way, it has the formula  $\text{TiCl}_2(\text{OC}_2\text{H}_5)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ . However, according to Gardner and Bielouss (5), the compound formed is  $\text{TiCl}(\text{OC}_2\text{H}_5)_3 \cdot \text{HCl}$ . The former structure seems to be the most probable since  $\text{TiCl}(\text{OC}_2\text{H}_5)_3$  also adds an alcohol of crystallization when dissolved in ethyl alcohol (7). A titanium analysis showed 18.65% titanium while the required value is 18.82%. This at first seemed a good method for purifying the compound, but in order to remove the

alcohol of crystallization, enough heat was required to cause fuming, thus introducing impurities.

It was finally decided to abandon any further attempts to purify the compound, since a high degree of purity is required for dielectric measurements.

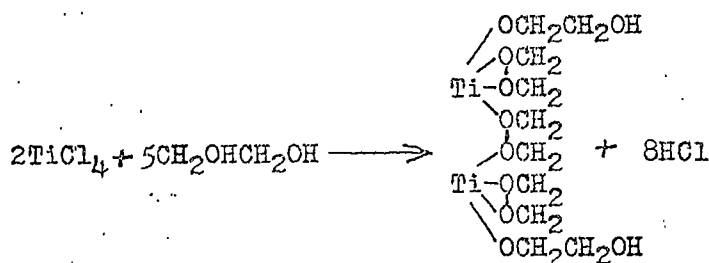
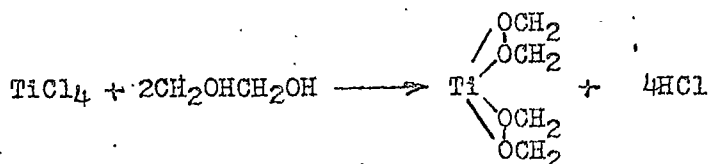
Trichloro-phenoxy-titanium -  $\text{TiCl}_3\text{OC}_6\text{H}_5$ : This compound was prepared according to Lutschinsky and Altmann (8) by the reaction:



Two solutions, one containing 9.5 grams of  $\text{TiCl}_4$  in a mixture of dry petroleum ether and chloroform and the other containing 4.7 grams of phenol in the same solvent, were mixed together slowly in the cold. The mixture turned dark red immediately with the evolution of HCl gas. After the reaction was complete, the solvent was distilled off until dark red crystals began to separate. At this point the mixture was cooled with ice and filtered. The crystals were washed carefully with more solvent and dried in a vacuum dessicator over  $\text{P}_2\text{O}_5$ . The compound dissolved in  $\text{CCl}_4$  and benzene giving a deep red solution. When it was dissolved in ethyl alcohol, a reaction took place giving a yellow solution. It decomposed instantly in water giving a colorless solution. When exposed to moist air, the compound gave off HCl slowly and gradually assumed a light red color.

In order to verify the composition and purity of the compound, a titanium analysis was made. The results showed 19.58 and 19.35% titanium. The required value is 19.37%. From this analysis, it was assumed that the compound was sufficiently pure for dielectric measurement.

Titanium Tetrachloride-ethylene glycol Compound: A very interesting compound formed by the reaction of  $TiCl_4$  with ethylene glycol has been reported by Gardner and Bielouss (5), but these investigators have been unable to verify any definite structure for it. They have, however, offered the following possibilities:



For the present work,  $TiCl_4$  was added dropwise to the glycol. The mixture became very viscous and evolved  $HCl$ . After the reaction was complete, most of the excess glycol was removed by distillation under reduced pressure. The residue remaining was a transparent, viscous, brown substance which hardened to a glassy material on cooling. It could be removed only by breaking the flask. It was found to be soluble in ethyl alcohol and water but not in ether or benzene. The titanium content found by ignition was 17.47, 18.14 and 18.38%. The lack of agreement in these results was probably due to the fact that the substance was not entirely homogeneous.

A qualitative test for halogen was next run on the compound by means of sodium fusion, and chlorine was found to be present. A Carius halogen

determination was then attempted, but the Carius tube exploded each time. A sample was then placed in a small round-bottom flask equipped with a reflux condenser. 100 ml. of ethyl alcohol and 10 grams of sodium metal were added. The mixture was allowed to reflux until all of the sodium was dissolved. This treatment will decompose many organic compounds. About 40 ml. of distilled water was added and the alcohol distilled off. The remaining mixture was then filtered, made acid with  $\text{HNO}_3$ , and treated with a small amount of  $\text{AgNO}_3$  to precipitate the  $\text{AgCl}$ .  $\text{NH}_4\text{OH}$  solution was then added until the halide had completely dissolved. At this point the titanium precipitated out as the hydroxide. The mixture was filtered and made acid again with  $\text{HNO}_3$  to precipitate the  $\text{AgCl}$ . It was then filtered through a Gooch crucible. The precipitate was dried and weighed, and the chlorine content determined by calculation. The results showed 11.73, 11.71 and 12.29% chlorine in the compound.

A purification of this polymer-like compound was attempted by precipitation of its alcoholic solution with dry ether. A white precipitate appeared as soon as the ether was added. This was filtered and redissolved in ethyl alcohol. However, while warming, a white powdery precipitate formed which was found to be insoluble in all of the organic solvents. It did, however, burn on ignition, indicating that it was still organic in nature. Even when allowed to stand in a dessicator over  $\text{P}_2\text{O}_5$  for several hours, after only one precipitation, the compound was found to be insoluble in ethyl alcohol.

After several unsuccessful attempts at purification, the idea of tak-

ing any dielectric measurements on it was abandoned for the present.

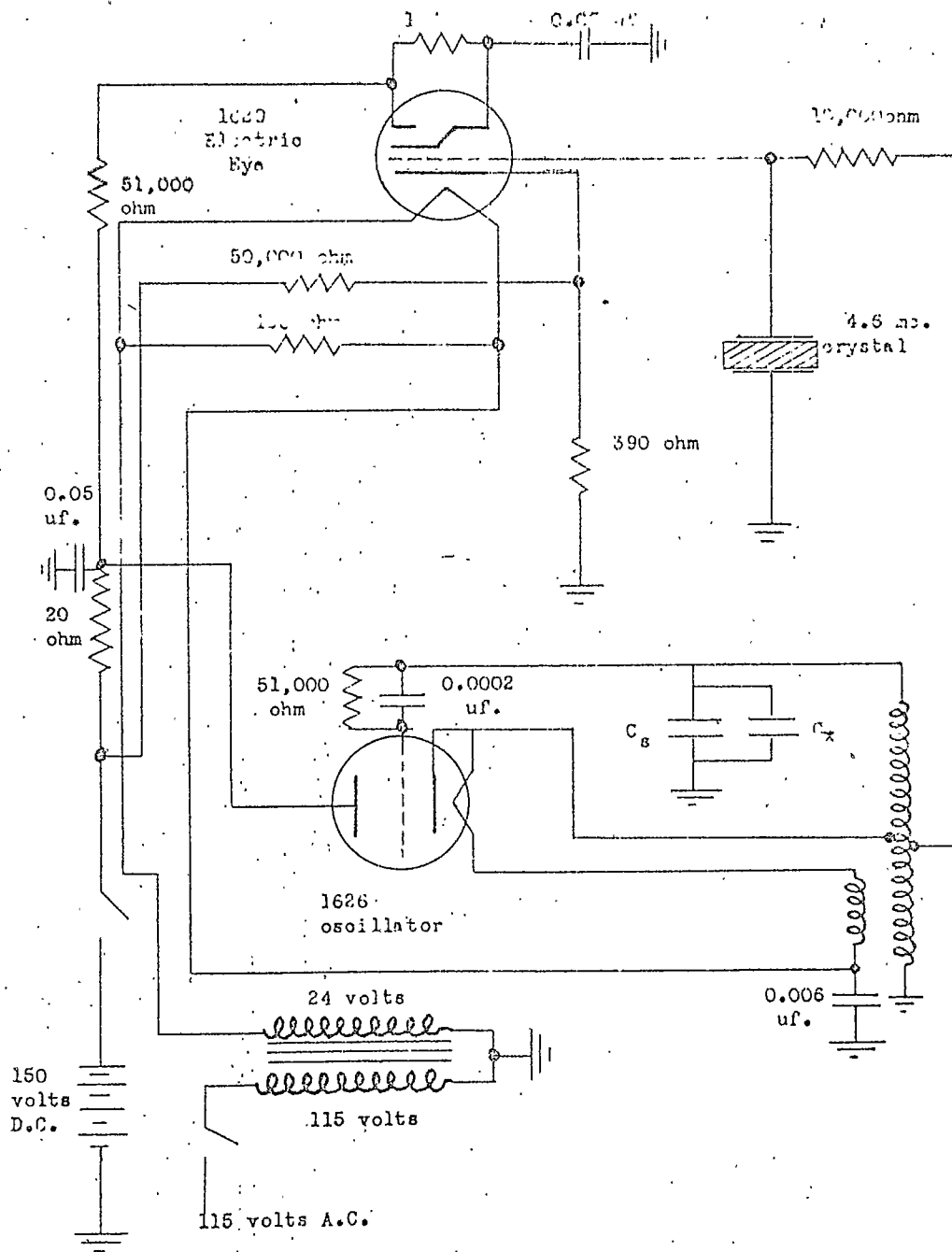
A similar compound was prepared using hexamethylene glycol instead of ethylene glycol. It seemed to have properties similar to those of the ethylene glycol compound and was not purified.

#### VI. ELECTRIC MOMENT MEASUREMENTS

The electric moments of  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{TiCl}(\text{OC}_2\text{H}_5)_3$  and  $\text{TiCl}_3\text{OC}_6\text{H}_5$  have been determined. For these determinations it was required to measure the dielectric constants of several dilute solutions of these compounds using a convenient non-polar solvent. In this case, benzene was used. The densities of these solutions were also measured. With this data it was possible to calculate the molar polarizations of the compounds.

For the molar refraction calculations, it was necessary to determine either the refractive index and density of the pure compounds or those of the same dilute solutions described above. From the polarization and refraction, it was possible to calculate the permanent electric moments of the molecules in question. A more detailed treatment of the mathematical equations used will be discussed later in this section.

Apparatus used for Measurements: The electrical circuit used for the measurements of dielectric constants was a made-over aircraft transmitter, Type CBY-52209. A schematic diagram of the circuit is shown in Figure 2. It consists of an electron coupled oscillator using the tube 1626, and a crystal and detecting device. The frequency over a small range is controlled by a General Radio 722-D standard precision condenser. As an indicating device, the standard crystal and electric eye tube 1629 were used.



CIRCUIT USED FOR MEASURING DIELECTRIC CONSTANTS OF SOLUTIONS

Figure 2

When the frequency of the oscillator is exactly that of the crystal, 4.6 megacycles in this case, the grid of the electric eye tube is essentially shorted to ground causing the eye to open.

This piece of apparatus proved to be quite accurate and sensitive, capacitance changes of 0.01  $\mu\text{mf}$ . being indicated by a narrowing of the electric eye. The limiting factor in the accuracy of the circuit is the fact that the capacitance of the standard condenser cannot be much greater than 150 to 200  $\mu\text{mf}$ . The percentage error was thus greater than in circuits where larger standard capacitors can be used. This is a precise and easily constructed piece of equipment if such a war surplus transmitter is available.

The cell constructed for measurements was of the Smyth type (10) and is shown in Figure 3. Three concentric platinum cylinders were first constructed. These were held rigid by the insertion of small glass spacers. The outside and inside cylinders were connected together and grounded.

The cylinders were then placed in a glass cell of about 20 ml. capacity and the platinum leads sealed through the bottom. A brass jacket was then placed around the entire cell for use as a temperature controlling device. Water from a rigidly controlled constant temperature bath was circulated through this jacket. The external leads were rigid, terminating in small "banana" plugs so that the entire cell could be plugged directly into the precision condenser. In this position it is in parallel with the standard condenser as shown in Figure 1. The capacitance of the



CELL USED FOR MEASURING DIELECTRIC CONSTANTS OF SOLUTIONS

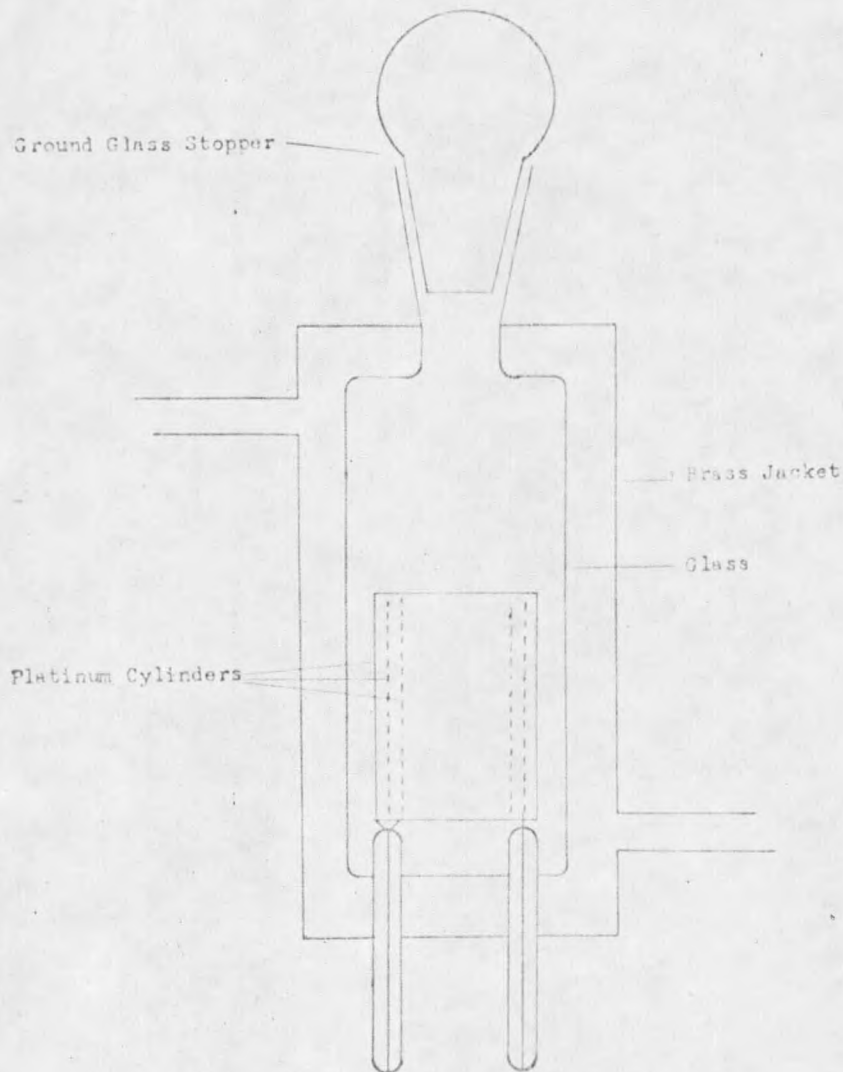


Figure 3

cell can therefore be measured by measuring the capacitance of the standard condenser alone and then with the cell in the circuit. The difference in the two readings gives the total cell capacitance.

Calibration of the cell was accomplished in the following manner. The total capacitance of the cell empty is equal to the sum of the lead capacitance and the product of the dielectric constant of air and the capacitance between the fixed plates, viz.  $C_a = C_0 + \epsilon_a C$ .  $C$  is often referred to as the cell constant. However, if a liquid of known dielectric constant is placed in the cell, the total capacitance is equal to the sum of the lead capacitance and the product of the dielectric constant of the known liquid and the cell constant. Thus:  $C_x = C_0 + \epsilon_x C$ . By solving these two equations simultaneously, it will be noted that  $C = (C_x - C_a) / (\epsilon_x - \epsilon_a)$  and  $\epsilon_x = (C_x - C_a + \epsilon_a C) / C$ . Using pure benzene with a known dielectric constant of 2.273 at 25°C, the cell constant was calculated. The results are shown in Table I. This constant was checked several times throughout the work and was found to remain sensibly constant.

TABLE I

Trial No.	$C_a$	$C_x$	$C$	Average
1	34.02	67.79	26.53	26.50
2	34.01	67.71	26.47	
3	34.00	67.74	26.50	
4	33.98	67.72	26.50	
5	33.98	67.72	26.50	
6	34.02	67.77	26.51	













































































