presumably carried out at European room temperature.

Table III gives densities of zinc sulfate solutions at selected molalities, supplementing those available in the literature.

TABLE III

m	2.003	1.512	0.5041	0.2498	0.09836
d^{25}_{4}	1.2973	1.2268	1.0772	1.0374	1.0134

Discussion

The curve of cation transference numbers plotted against $\sqrt{m}$ shows that in concentrated solution the transference numbers follow a normal trend, and there is no evidence to support the existence of negatively charged zinc complex ions. From the Onsager conductivity equation it can be shown that the theoretical limiting slope[8] for zinc sulfate at 25° is $(\mathrm{d}t_+/\mathrm{d}\sqrt{m})_{m\to 0} = -0.184$. In the figure this gradient is shown dotted, passing through the point $\sqrt{m} = 0$, $t_+ = 0.398$. The gradient of the curve approaches the limiting slope from above as $m \to 0$.

We have calculated the values of E corresponding to the tabulated values of E_t given by Wolten and King[1] and have plotted E_t as a function of E. The experimental points in the present work lie on a smooth curve while the data of Wolten and King are scattered and show a mean deviation from the present values of the order of 5 mv. Their data would be difficult to fit to an analytical expression and it is clear that the calculation of the differential coefficients by the method of Rutledge would be equally inapplicable as this method requires a smooth function.

It would appear that the experimental work of Wolten and King was inaccurate and the mathematical treatment of their experimental data unsound.

NEDLANDS, WESTERN AUSTRALIA RECEIVED MAY 3, 1951

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[8] Reference 6, pp. 162, 172, 151.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE COLLEGE]

Organic Compounds of Titanium. II. Association of Organic Titanates in Benzene Solution

BY C. N. CAUGHLAN, H. S. SMITH, WALTER KATZ, WM. HODGSON AND R. W. CROWE

Molecular weight determinations of ethyl, propyl and butyl titanates and monochlorotriethoxytitanium indicate association numbers in dilute benzene solutions to about three. This association is attributed to the fact that the coördination number of titanium is 6, thus allowing additional oxygens to surround the central titanium.

In the course of an investigation to determine the electric moments of some alkyl orthotitanates and related halogen compounds[1] it was necessary to determine molecular weights of these compounds in benzene solution. It was found that although the molecular weight of the solutes approached the calculated molecular weight in very dilute solutions, association apparently took place in more concentrated solutions. This appeared to have little or no effect upon the calculated electric moment since polarizations were calculated at infinite dilution. The existence of the ethyl orthotitanate as a solid and the peculiar manner in which the solid formed suggested the possibility of some abnormal phenomenon. Likewise, the high viscosity and peculiar behavior of the monochlorotriethoxytitanium upon exposure to moist air suggest the possibility of association. The action of the orthotitanates as waterproofing agents described by Speer and Carmody[2] suggests the possibility of association or polymerization. Consequently, a more detailed study has been made of the molecular weights of some of these substances in benzene solution. Ethyl orthotitanate, propyl orthotitanate, butyl orthotitanate and monochlorotriethoxytitanium have been found to be associated in benzene solution.

Preparation of Materials and Methods of Determining Molecular Weights.—The ethyl orthotitanate and monochlorotriethoxytitanium were prepared and purified as described by Crowe and Caughlan.[1] Propyl and butyl orthotitanates were prepared and purified essentially by the same method as the ethyl compound. In each case satisfactory purity was indicated by analysis of the compound. The benzene used for the determinations was Merck and Co., Inc., C.P. benzene, thiophene-free. This was kept over sodium until ready for use and then distilled in the absence of moisture. Reproducible results were obtained easily for the three alkyl orthotitanates. Reproducible results were extremely difficult to obtain for the monochlorotriethoxytitanium. Acceptable results were finally obtained by distilling both solute and solvent directly into the apparatus used for the molecular weight determination. Solute and solvent were weighed immediately after collection without opening to the air. Any adjusting necessary was carried out in a dry-box in which phosphorus pentoxide and sulfuric acid reduced the moisture content to a minimum.

Molecular weights were determined by the Beckmann freezing point-lowering method, assuming the solutions dilute enough to be essentially ideal in behavior.

Results.—The results are indicated in Figs. 1, 2 and 3 in which association number, *i.e.*, the apparent molecular weight divided by the molecular weight of an unassociated molecule, is plotted against the mole fraction solute. Figure 4 indicates the effect of small amounts of water upon the association of monochlorotriethoxytitanium. The addition of water was accomplished by adding drops of benzene saturated with water. The amounts of water can be considered only approximate in this case since they were calculated from the solubility of water in benzene, *i.e.*, 0.057 weight per cent. at 20°.[3]

Discussion.—The association of these orthotitanates appears to be due to the fact that titan-

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[1] R. W. Crowe and C. N. Caughlan, THIS JOURNAL, **72**, 1694 (1950).

[2] R. J. Speer and D. R. Carmody, "Tetraalkyl Orthotitanates, New Water-proofing Agents," presented at A. C. S. Meeting, Atlantic City, N. J., 1949.

[3] "International Critical Tables," Vol. III, First Edition, McGraw-Hill Book Co., Inc., New York, N.Y., 1928, p. 389.

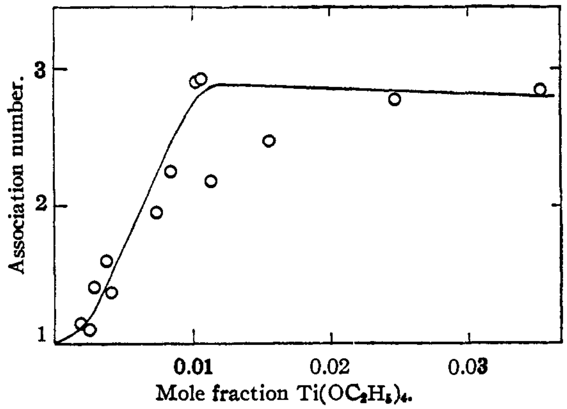

Fig. 1.—Association number of solute plotted against mole fraction $Ti(OC_2H_5)_4$ in benzene solution.

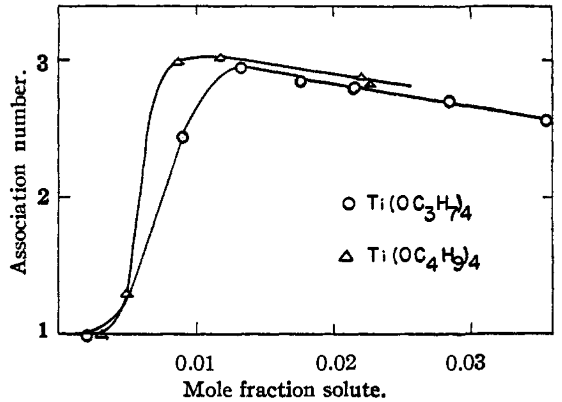

Fig. 2.—Association number of solute plotted against mole fraction solute in benzene solution.

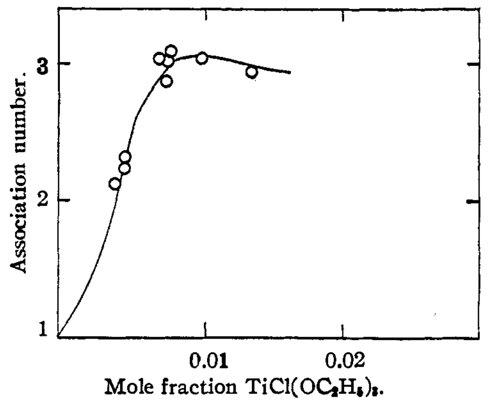

Fig. 3.—Association number of solute plotted against mole fraction $TiCl(OC_2H_5)_3$ in benzene solution.

ium has a coördination number of six while in the orthotitanates and monochlorotriethoxytitanium there are only four atoms surrounding the central titanium atom. It is probable that there is a change from the tetrahedral bond angles of the four oxygen atoms surrounding the titanium to an angle of ninety degrees when there are six oxygen atoms surrounding the titanium atom. Rutile has six equally spaced oxygen atoms surrounding each titanium. This is apparently a very stable configuration and accordingly a somewhat similar structure is probable here. Figure 5 shows a possible structure for the trimer of ethyl orthotitanate. According to this structure, each outside titanium is bound to the central titanium atom of the trimer through three coördinate valences. Additional coördination of the trimer to other titanium atoms from monomers could occur but would be less stable due to the fact that there are only two bonds possible. Thus the trimer would appear to be the most stable in structures.

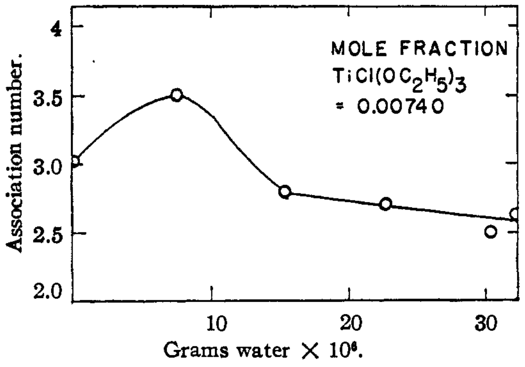

Fig. 4.—Association number $TiCl(OC_2H_5)_3$ against grams of water added in benzene solution of mole fraction 0.00740 solute.

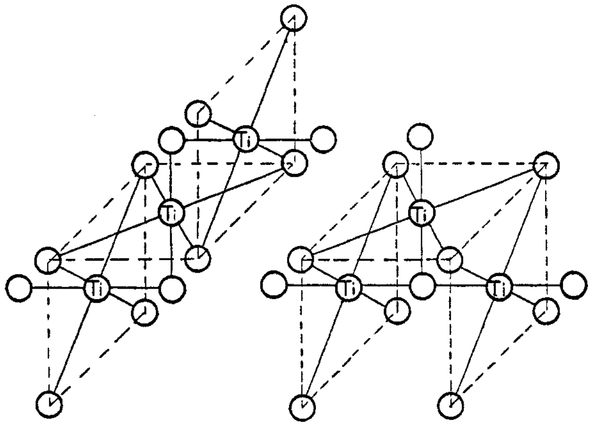

Fig. 5.—Proposed structure of $[Ti(OR)_4]_3$. The R groups are not included.

Solidification of the ethyl orthotitanate takes place only very slowly or under rather peculiar circumstances. Solid ethyl orthotitanate appears after several weeks along the sides and at the bottom of a sealed tube containing freshly distilled liquid, if this is kept at room temperature. On the other hand if the liquid is suddenly cooled to Dry Ice temperatures, the liquid becomes extremely viscous but does not appear to change. However, upon allowing to come to the room temperature, the liquid becomes cloudy and gradually, over a period of about three hours, becomes an opaque white solid. It is probable that during this change, as well as the much slower one in which the liquid is allowed to stand at room temperature, larger units than the trimer are being formed, which eventually cause complete solidification of the substance. Attempts are being made in this Laboratory to confirm this by X-ray diffraction studies.

Acknowledgment.—The authors wish to thank the Research Corporation for a grant which has made this investigation possible.

BOZEMAN, MONTANA RECEIVED APRIL 14, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE COLLEGE]

Organic Titanium Compound. III. The Electric Moments of Tetraethoxytitanium, Monochlorotriethoxytitanium, Tetrapropoxytitanium, Tetrabutoxytitanium and Ethyl Orthoformate in Hexane Solution

BY C. N. CAUGHLAN, WALTER KATZ, WILLIAM HODGSON

Measurements show (a) electric dipole moments of 1.50, 1.20, 1.15 for $Ti(OEt)_4$, $Ti(OPr)_4$ $Ti(OBu)_4$; 2.51 for $TiCl(OC_2H_5)_3$. and 0.76 for $HC(OC_2H_5)_3$. (b) Both restriction of rotation and an incorrect oxygen valence angle probably account for the difference in experimental and theoretical moment for $Ti(OR)_4$. (c) An estimation of Ti–Cl bond moment is 4.3 based upon Ti–O bond moment of 1.6 *D*.

I. Introduction

In a previous paper[1] the electric moments of $Ti(OC_2H_5)_4$, $TiCl(OC_2H_5)_3$ and $TiCl_3(OC_6H_5)$ have been reported, respectively, as 1.41, 2.87 and 2.97 *D* in benzene solution. Theoretical calculations of the moments for $Ti(OC_2H_5)_4$ using Eyring's equation[2] and assuming free rotation of the ethylate groups, the normal valence angle of 105° for oxygen, and 1.1 as the sum of C–O and C–H bond moments, yielded a result of 2.11 *D*. The reasons for the difference in experimental and theoretical values is probably due to (a) restricted rotation and (b) larger oxygen valence angle. There is probably some solvent effect in benzene, but this would tend to increase the moment rather than decrease it. Theoretical calculation of the moments for the other compounds was not possible due to the lack of knowledge of bond moments of Ti–O and Ti–Cl.

In the present work the electric moments of $Ti(OC_2H_5)_4$, $Ti(OC_3H_7)_4$, $Ti(OC_4H_9)_4$ and $TiCl(OC_2H_5)_3$ as well as some similar compounds of carbon, have been determined in hexane solution. In addition, an attempt has been made to estimate the Ti–Cl bond moment from the previously measured moment of $TiCl_3(OC_6H_5)$.

Experimental

Tetraethoxytitanium was prepared and purified as described in the previous paper[1] and the other orthotitanates were prepared in the same manner using sodium propylate or butylate in place of the sodium ethylate. Table I gives results of analysis for each compound.

TABLE I

Compound	Titanium, % Found	Titanium, % Theoretical	Chlorine, % Found	Chlorine, % Theoretical
$Ti(OC_2H_5)_4$	21.06	21.05		
$Ti(OC_3H_7)_4$	16.69	16.84		
$Ti(OC_4H_9)_4$	14.02	14.08		
$TiCl(OC_2H_5)_3$	21.77	21.97	16.37	16.22

Monochlorotriethoxytitanium was prepared and purified as described by Crowe and Caughlan.[1] Ethyl orthoformate was obtained from Eastman Kodak Company. Purification was accomplished by distillation and the purity checked by refractive index: refr. index found = 1.3923; accepted refr. index 1.3922.

Two grades of hexane were used, Eastman Kodak Co. technical grade (from petroleum) and Phillip's pure hexane 99 mole %. The physical properties were considerably different and in the case of the technical grade hexane, the density, dielectric constant and refractive index of each different sample would differ slightly. However, since the method of calculation effectively eliminates error due to the slight differences in solvent, it was felt that little error was introduced by use of the technical grade hexane. The hexane was kept over sodium and carefully distilled in the absence of moisture immediately before taking a series of measurements.

The apparatus used for the measurements at 25° has been described previously.[1] Deviations of the experimental points from the straight lines are of the same order as those reported by Crowe and Caughlan.[1]

Calculations and Results

Polarizations at infinite dilution were calculated according to the method of Halverstadt and Kumler.[3] For each compound the dielectric constants and specific volume of the solution were linear functions of the concentrations. Slopes and intercepts of dielectric constants and specific volume plotted against concentration were calculated by the method of least squares. Small differences appear in the intercepts indicating slight differences in the samples of hexane used. Table II shows the intercepts ϵ_1 and V_1, and slopes A and B for the straight lines obtained by plotting dielectric constants and specific volume against the mole fraction as well as the total polarization P_∞, electronic polarization P_e (*i.e*, molar refraction) and the electric moment μ, calculated by the Debye equation. Table III lists the measured moments in hexane for the compounds studied in this paper, moments for some of the compounds in benzene from previous results, as well as electric moments from other workers and some theoretically calculated moments.

Discussion

The theoretical moments for the compounds of the type $Ti(OR)_4$ can be calculated from the Eyring equation[2] which assumes free rotation for all groups. For compounds of the type $Me(OR)_4$ this equation reduces to $\mu^2 = 4m^2 \sin^2 \phi$ where m is the O–R bond moment and ϕ is oxygen valence angle. Thus $C(OC_2H_5)_4$, $Si(OC_2H_5)_4$ and $Ti(OC_2H_5)_4$ should all have the same moment. Measured values for these are seen to be 1.1, 1.7 and 1.4, respectively. If the deviation from the theoretical value is considered due to restriction of rotation alone, it would be expected that the moments would increase in the order C, Si, Ti, due to the increasing size of the central atom. However, electronegativities for these atoms are; C = 2.5, Si = 1.8 and Ti = 1.6 while that for oxygen is 3.5. This would tend to produce bonds of greater ionic character, *i.e.* less directive

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[1] R. W. Crowe and C. N. Caughlan, THIS JOURNAL, **72**, 1694 (1950).

[2] H. Eyring, *Phys. Rev.*, **39**, 747 (1932).

[3] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).