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

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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).

TABLE II

SUMMARY OF ELECTRIC MOMENT DETERMINATIONS

Compound	A	ϵ_1	B	V_1, cc./g.	P_∞	P_e	μ
$Ti(OC_2H_5)_4$	2.6739	1.9240	−1.6082	1.4612	111.4	64.4	1.50
$Ti(OC_3H_7)_4$	2.4882	1.9266	−2.0371	1.4681	118.4	82.3	1.20
$Ti(OC_4H_9)_4$	2.6444	1.9227	−2.5789	1.4617	129.7	102.0	1.15
$TiCl(OC_2H_5)_3$	7.1230	1.9210	−2.0815	1.4652	185.1	54.9	2.51
$HC(OC_2H_5)_3$	0.02515	1.9237	−0.06378	1.4655	51.74	39.4	0.76

TABLE III

THEORETICAL AND MEASURED ELECTRIC MOMENTS IN DEBYE UNITS

Compound	Measured electric moment In hexane	In benzene	Theoretical moment
$Ti(OC_2H_5)_4$	1.50	1.41[1]	2.11
$Ti(OC_3H_7)_4$	1.20		2.11
$Ti(OC_4H_9)_4$	1.15		2.11
$TiCl(OC_2H_5)_3$	2.51	2.87[1]	
$HC(OC_2H_5)_3$	0.76		2.0
$CCl(OC_2H_5)_3$			2.14
$C(OC_2H_5)_4$[4]		1.1	
$TiCl_3OC_6H_5$[1]		2.97	
$Si(OC_2H\ )_4$[5]		1.70	2.11
$C(OCH_3)_4$[6]		0.80	

bonds, thus lowering the moment. On the other hand increased size resulting in less restriction of rotation would increase the moment. The results of this paper thus would indicate, on the basis of comparison of the molecular moments, considerable ionic character to the oxygen bonds and a valence angle somewhat greater than the 105° used.

However, greater restriction of rotation should occur with larger alkyl groups. It can be seen in Table III that for $Ti(OC_2H_5)_4$, $Ti(OC_3H_7)_4$ and $Ti(OC_4H_9)_4$ the moments decrease in this order indicating greater restriction of rotation with the larger alkyl groups.

Any attempt to calculate bond moments must be considered extremely speculative inasmuch as there is considerable deviation of experimental from theoretical values. Consideration of a spacial model $TiCl_3OC_6H_5$, however, indicates very little restriction of rotation of the O–Ph group and little or no influence of rotation on the electric moment. Thus, as far as this is concerned, the calculated and experimental values should be in close agreement. There are, however, two unknown bond moments, *i.e.*, Ti–O and Ti–Cl. If we assume a value of 1.6 for the Ti–O, a value of 4.3 for the Ti–Cl yields a moment for the compound of 3.0. The choice of 1.6 for Ti–O is based upon consideration of the electronegativity scale. C–O, on the same basis, yields 1.0, while the bond moment is 0.8; H–O is 1.4 and the observed moment is 1.51. The bond moment from the electronegativity scale for Ti–Cl would be about 1.4, while our value here is 4.3. This is rather typical of comparison of most of the metal–halogen bond moments calculated from electronegativities. For example, C–Cl from electronegativities is 0.5, while the observed is 1.5. C–Br = 0.3, observed = 1.4; As–Cl = 1, observed is 1.64; Sb–Cl = 1.2, observed is 2.6.

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