Nachod[8] measured the rate of ionization of methylacetylacetone at 25° by a photometric method. He made the error of assuming that the ionization was acid catalyzed in 0.1 N hydrobromic acid. His results, however, can be recalculated to give a rate constant of 0.0046 min.$^{-1}$ in good agreement with the value given here. No acid catalysis has ever been observed for acids of the strength of those measured here.[9]

Table III presents a compilation of the rates of ionization of a number of pseudo acids collected from the literature, together with the acid ionization constants where known. The general trend evidently is for the rate of ionization to increase as the acidity increases. The effect of an alkyl group is generally acid weakening and rate retarding. The effect of a bromine atom is generally acid strengthening (no accurate data are known) and rate increasing.

TABLE III

RATES OF IONIZATION OF PSEUDO ACIDS AT 25°: HA +
$$H_2O \longrightarrow H_3O^+ + A^-$$

Compound	k_1, min.$^{-1}$	K_{ion}
Acetoacetic ester	1.29×10^{-3a}	2.09×10^{-11c}
α-Bromoacetoacetic ester	1.59×10^{-2a}	$\sim 10^{-7}$
α-Ethylacetoacetic ester	4.53×10^{-4}	1.84×10^{-13d}
Acetylacetone	6.8×10^{-1b}	1.17×10^{-9c}
Methylacetylacetone	4.97×10^{-3}	1.52×10^{-11d}
Malonic ester	1.80×10^{-3}	5×10^{-14d}
Bromomalonic ester	8.6×10^{-3}	$\sim 10^{-9}$
Ethylmalonic ester	2×10^{-5}	$\sim 10^{-15}$

[a] Pedersen, reference 9a. [b] Bell and Lidwell, Proc. Roy. Soc. (London), A176, 88 (1940). [c] Eidinoff, THIS JOURNAL, 67, 2072 (1945). [d] Mills and Pearson, unpublished results.

(8) Nachod, Z. physik. Chem., A182, 193 (1938).

(9) (a) Pedersen, J. Phys. Chem., 37, 751 (1933); (b) Junell, Z. physik. Chem., A141, 89 (1929).

(10) Schwarzenbach and Felder, Helv. Chem. Acta, 27, 1701 (1944).

Table IV shows values of the rate constant k_2 for the recombination of the ions calculated from the data in Table III. There is a trend again for the weakest acids to have the highest rates of recombination of ions. Table IV also shows the heats and entropies of activation for the forward and reverse processes of equation (1) as calculated from the transition state theory of reaction rates for those compounds where the activation energy for ionization and the heat of ionization are known. The entropies of activation for the process of ionization are always fairly large and negative and the entropies for the recombination of ions are either positive or small and negative. An explanation of this effect in terms of electrostriction of the solvent has been discussed in the first paper of this series.

TABLE IV

RATE CONSTANTS FOR THE RECOMBINATION OF IONS AT
25°: $H_3O^+ + A^- \longrightarrow HA + H_2O$

Compound	k_2, 1./mole·min.	ΔH_2,‡ kcal.	ΔS_2,‡ E. U.	ΔH_2,‡ kcal.	ΔS_2,‡ E. U.
Acetoacetic ester	6.17×10^7	13.6	−34.4	7.2	−6.8
α-Ethylacetoacetic ester	2.46×10^9	14.9	−31.6	7.2	1.0
Acetylacetone	5.81×10^8	..	....	...	...
Methylacetylacetone	3.27×10^8	17.4	−16	9.2	6
Malonic ester	4×10^{10}	..	....	...	...

Summary

The rates of ionization in water of several pseudo acids have been measured. The rates of ionization and ion recombination are correlated with ionization constants for a number of pseudo acids.

EVANSTON, ILLINOIS   RECEIVED JUNE 3, 1949

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MONTANA STATE COLLEGE]

The Electric Moments of Tetraethoxytitanium, Monochlorotriethoxytitanium and Trichlorophenoxytitanium in Benzene Solutions. I

BY ROBERT W. CROWE AND C. N. CAUGHLAN

Although a number of studies have been made on the dielectric properties of inorganic titanates[1] little is known about any of the physical properties of the derivatives of titanium tetrachloride containing organic groups. It has appeared worthwhile and interesting to make a somewhat detailed study of the dielectric properties of these compounds in order (a) to learn more about their structures, and (b) to find out if any of these compounds exhibit interesting and important dielectric properties. This paper represents the

(1) Von Hippel, Brechenridge, Chesley and Tiszo, Ind. Eng. Chem., 38, 1097 (1946).

first report of a more extended research on the physical properties of such derivatives of titanium tetrachloride. In this work the electric moments of $Ti(OC_2H_5)_4$, $TiCl(OC_2H_5)_3$, and $TiCl_3OC_6H_5$ have been determined in benzene solution.

Experimental

Tetraethoxytitanium.—This compound was easily prepared by addition of titanium tetrachloride to sodium ethoxide as described by Bischoff and Adkins.[2] The product obtained after removal of excess alcohol was purified by several distillations under reduced pressure. It is a colorless, oily liquid, d_{25} 1.1066, $n^{25}D$ 1.5082, b. p. 133–

(2) Bischoff and Adkins, THIS JOURNAL, 46, 27 (1924).

135° at 5 mm. pressure. The dielectric constant at 25°, was found to be 3.68, using the cell and instrument described below. It is easily hydrolyzed in moist air forming ethyl alcohol and hydrated TiO_2. It gave, on ignition, 21.04% Ti; 21.05% is the theoretical amount. This compound is evidently a supercooled liquid at room temperature, since it can be transformed into a white solid when cooled to considerably below zero, and gradually warmed. The actual transition required about three hours. The density of the solid form at 25°, determined by measuring the change in volume on changing to the liquid was 1.23.

Monochlorotriethoxytitanium.—This compound was prepared according to the method of Jenning, Wardlow and Way[3] by adding acetyl chloride to $Ti(OC_2H_5)_4$. It was also purified by distillation under reduced pressure. It is a pale yellow, viscous liquid, b. p. 170° at 15 mm. pressure. On analysis, it gave 21.77% Ti and 16.37% Cl; 21.90% Ti and 16.22% Cl are required.

Trichlorophenoxytitanium.—This compound was prepared according to the method of Lutschinsky and Altmann.[4] Titanium tetrachloride and phenol were both diluted in a mixture of dry petroleum ether and chloroform, and mixed slowly in the cold. The solvent was distilled until dark red crystals began to separate and then the mixture was cooled and filtered. Fractional crystallization was used to purify the crystals. Analysis showed 19.58 and 19.35% Ti, whereas the theoretical amount is 19.37%. It forms dark red solutions in non-polar solvents.

Benzene.—Redistilled Merck C.P. benzene (thiophene free) was used for the measurements. This was kept over sodium wire or phosphorus pentoxide and carefully distilled just before using.

Apparatus.—The measurements reported here were made at 4.6 mc. The electrical circuit used for the measurements was a rebuilt aircraft radio transmitter Type CHY-52209, and is shown in Fig. 1. It consists of an electron coupled oscillator using a 1626 tube, a 4.6 mc. crystal and electric eye tube. The frequency over a small range is controlled by the standard capacitance. As an indicating device the standard crystal and electric eye tube 1629 were used. Quite precise capacitance measurements can be made with this apparatus, a capacitance change of 0.01 $\mu\mu$f. being indicated by 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 150–200 $\mu\mu$f., thus giving a greater percentage error than in circuits where a large standard capacitor can be used. The precision condenser is a General Radio Type 722-D. Figure 2 shows schematically the cell used. Satisfactory temperature control was provided by circulating thermostated water through the external brass jacket. This cell was plugged directly into the precision condenser, the capacitance being indicated by the required change in the standard to re-open the electric eye. The cell constant was 25.50 $\mu\mu$f.

The refractive indices were determined for the pure substances and their solutions with a dipping refractometer and the density determinations were made with an ordinary Ostwald type pycnometer.

(3) Jenning, Wardlow and Way, J. Chem. Soc., Part I 637 (1936).
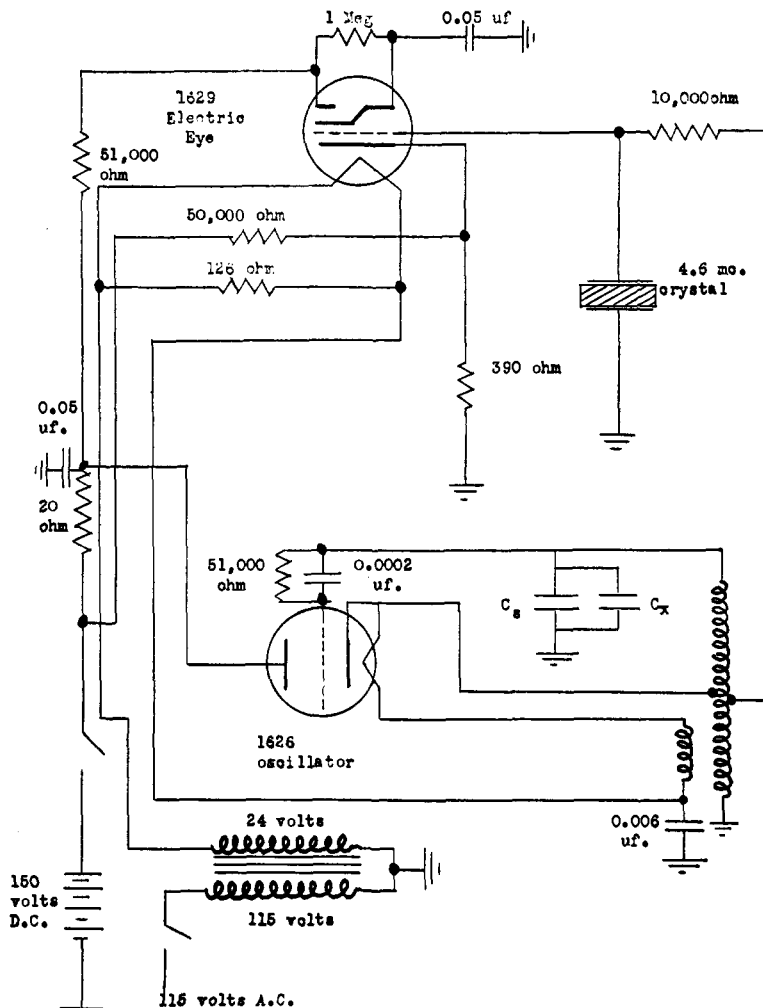(4) Lutschinsky and Altmann, Z. anorg. allgem. Chem., 225, 321 (1935).

Fig. 1.—Electrical circuit used for dielectric constant measurements.

Experimental Results

Polarizations were determined in benzene solution by measuring the dielectric constant and density of the solution. Calculation of the polarizations was accomplished by the method of Halverstadt and Kumler.[5] As derived by these authors

$$P_\infty = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}(M_2 V_1 + M_1 B) + \frac{3 A v_1 M_1}{(\epsilon_1 + 2)^2} \quad (1)$$

where ϵ_1 is the dielectric constant of the pure solvent found by extrapolating $\epsilon_{12} = \epsilon_1 + Ac_2$ to infinite dilution and v_1 is the specific volume of the solvent found in the same way. A and B are the slopes of ϵ_{12} and v_{12} plotted against concentration, and M_1 and M_2 are the molecular weights of solvent and solute, respectively.

Table I summarizes the data by giving the intercepts, ϵ_1 and v_1 and the corresponding slopes, A and B, for the straight lines obtained by plotting dielectric constants and specific volumes of solutions against the mole fractions.

The average deviations of the experimental points from the straight lines indicated in Table I are: for tetraethoxytitanium at 10, 25, 35

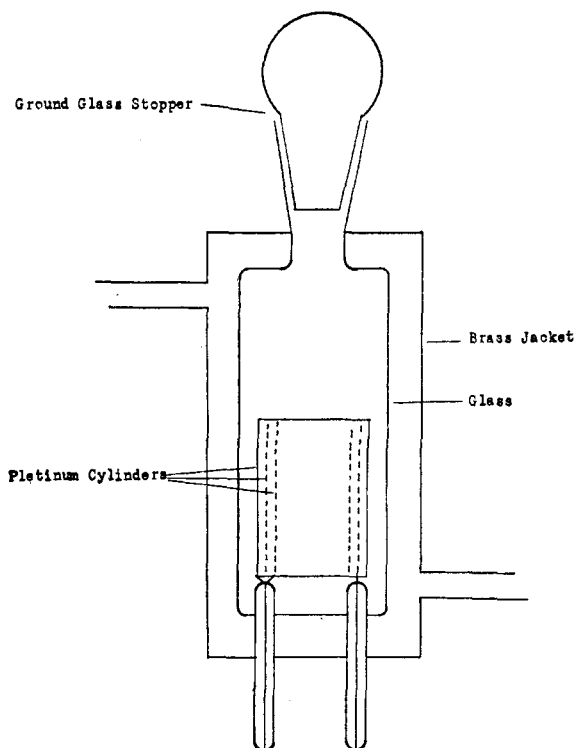(5) Halverstadt and Kumler, THIS JOURNAL, 64, 2988 (1942).

Fig. 2.—Cell used for measuring dielectric constants of solutions.

and 45°, respectively; $\Delta\epsilon_{12}$ = 0.0006, 0.0005, 0.0004, 0.0005; v_{12} = 0.0001, 0.0005, 0.0001, 0.0001; for monochlorotriethoxytitanium at 25° $\Delta\epsilon_{12}$ = 0.0019 and v_{12} = 0.0002; for trichlorophenoxytitanium at 25° $\Delta\epsilon_{12}$ = 0.0006 and v_{12} = 0.00004. Concentrations extended to about 0.01 mole fraction solute in all cases.

Also included in Table I are the molar refractions and molar polarizations. The molar refraction of tetraethoxytitanium was calculated from the refractive index and density of the pure compound. Molar refractions for the other two compounds were calculated from data on solutions by use of equation (1), replacing ϵ_1 with n_1^2. Values of n_1^2 were obtained by plotting the square of the refractive index of the solutions against the mole fraction and determining slopes and intercepts of the straight lines. For monochlorotriethoxytitanium n_1^2 was found to be 2.24204 and the slope of the straight line was

TABLE I
REFRACTIONS, POLARIZATIONS AND OTHER DATA FOR MOLECULES STUDIED

	Temp., °C.	A	B	ϵ_1	v_1 cc./g.	MR	$P\infty$
Ti(OC₂H₅)₄	10	3.5061	−0.6516	2.3042	1.1254		112
	25	3.2257	−0.7726	2.2757	1.1466	64.4	109
	35	3.0903	−0.6663	2.2530	1.1595		109
	45	3.0803	−0.6491	2.2363	1.1742		107
TiCl· (OC₂H₅)₃	25	11.5398	−0.9645	2.2718	1.1456	54.9	222
TiCl₃OC₆H₅	25	13.6577	−1.5186	2.2690	1.1457	66.6	250

0.24197; and for trichlorophenoxytitanium n_1^2 was found to be 2.2436 and the slope was found to be 1.2305. The average deviation of the experimental points from the straight lines are, respectively, 0.00004 and 0.00016. Refractive indices of solutions up to concentrations of about 0.01 mole fraction were measured.

The electric moment for tetraethoxytitanium was calculated directly from the Debye equation using the molar refraction and molar polarization at 25°. This method gave the value 1.43 D. By plotting $P\infty$ for the various temperatures against $1/T$ and using the slope of the resulting curve, the value 1.41 D, was obtained. By using the pure liquid value of the dielectric constant 3.68 at 25° in the Onsager equation[6]

$$P_0 = \frac{M}{d} \frac{(\epsilon - N^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} = \frac{4\pi N\mu^2}{9kT} \quad (2)$$

the electric moment was calculated again to be 1.41 D. It can be seen that excellent agreement was obtained from the three methods. The values for the electric moments of monochlorotriethoxytitanium and trichlorophenoxytitanium, calculated from the data at 25°, were 2.87 D and 2.97 D, respectively.

Discussion

The existence of an electric moment for tetraethoxytitanium is of considerable interest. With the assumptions (a) that the oxygen atoms are arranged around the titanium atom at the corners of a regular tetrahedron,[7] and (b) that the C₂H₅–O groups are free to rotate about the Ti–O axis, the equation derived by Eyring[8] was used to calculate the theoretical moment for this compound. Because of the tetrahedral structure, Ti–O bond moments will cancel and the equation reduces to $\mu^2 = 4m^2 \sin^2 \phi$, where m is the O–R bond moment and ϕ the oxygen valence angle. Assuming m as the sum 1.1 of the H–C and C–O bond moments and ϕ as 105°, the theoretical moment for the molecule is 2.11 D, a much higher value than that obtained experimentally. Svirbely and Lander[9] have measured the moment for ethyl orthosilicate in benzene and obtained the value 1.70 D for that compound, while the moment obtained for ethyl orthocarbonate has been found to be 1.1 D.[10] These three molecules, due to their tetrahedral structure should have the same resultant moment. However, the difference in the size of the central atom may have an effect on the oxygen valence angle as well as the freedom of rotation of the O–R groups. By placing the observed moment 1.41 D for Ti(OC₂H₅)₄ in the

(6) Onsager, THIS JOURNAL, **58**, 1486 (1936).

(7) This is true for TiCl₄, A. F. Wells, "Structural Inorganic Chemistry," Oxford Press, 1945, p. 282.

(8) Eyring, Phys. Rev., **39**, 746 (1932).

(9) Svirbely and Lander, THIS JOURNAL, **70**, 4121 (1948).

(10) Eisenschitz and Hartel, Z. physik. Chem., **B1**, 94 (1928); calculated from data given by these authors from equation μ = $0.0127 \sqrt{(P - P_0)T}$. $P - P_0$ according to their data is 24 cc. in benzene solution.

above equation, it can be seen that the oxygen valence angle will have to be about 140° to satisfy the conditions. This rather large value is possible when one considers the relatively larger size of the Ti atom compared with carbon and the possible ionic character of the Ti–O bond. For example, in H_2O the oxygen valence angle is 105°, while in Cl_2O it is 115°.[11]

The ionic character also tends to reduce the directive nature of the bond. Sauer and Mead[12] have calculated the Si–O–Si valence angle and found it to be 160 ± 15°, which would indicate considerable ionic character for the Si–O bond in hexamethyldisiloxane. For ethyl orthosilicate, the required oxygen valence angle, assuming free rotation, would have to be about 128°. Similarly, the oxygen valence angles in ethyl orthocarbonate would have to be still larger, which is obviously not the case. However, in this compound, hindered rotation might well be expected. Thus, 140° for C–O–Ti bond angle cannot be disregarded without some consideration.

It is difficult to say whether free rotation would be possible, even for tetraethoxytitanium. Figure 3 shows spacial arrangement of $O–C_2H_5$ groups for several possible orientations of $–C_2H_5$ groups, assuming the normal oxygen valence angle of 105°. According to this diagram, rotation would certainly be hindered. However, an increase of oxygen valence angle would tend to promote free rotation.

There may also be some solvent effect. To check this, measurements made on hexane solutions will be published in a later paper.

Due to a lack of knowledge of the bond moments for Ti–O and Ti–Cl bonds, the theoretical moments for the monochlorotriethoxytitanium and trichlorophenoxytitanium cannot be calculated at this time. Equations can be set up in terms of these moments, but since the observed moments for tetraethoxytitanium is much lower than the theoretical value, the observed moments for these molecules will probably not agree with the calculated values.

(11) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 79.
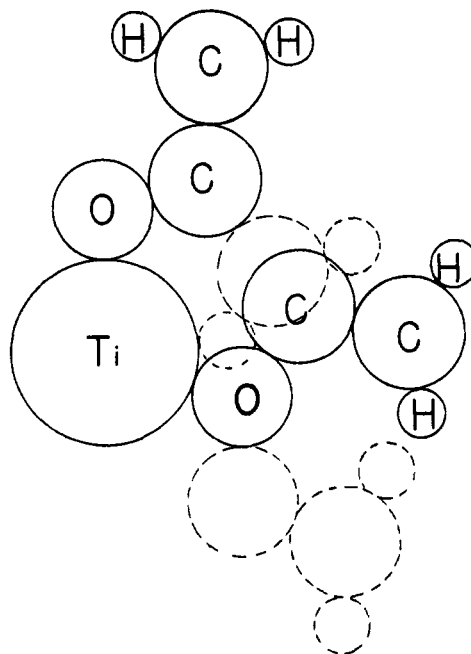
(12) Sauer and Mead, THIS JOURNAL, 68, 1794 (1946).

Fig. 3.—Special arrangement of $= Ti(OC_2H_5)_2$ for several possible orientations of $–C_2H_5$.

Summary

1. The electric moments of tetraethoxytitanium, monochlorotriethoxytitanium, and trichlorophenoxytitanium, have been determined in benzene solution from the dielectric constants, densities, and refractive indices of these solutions and have been found to be, respectively, 1.41, 2.87 and 2.97 debye units.

2. The theoretical electric moment for tetraethoxytitanium has been calculated, assuming free rotation of the $O–C_2H_5$ groups and is found to be 2.11 debye units. An attempt has been made to explain the low experimental value for this compound and for analogous compounds of silicon and carbon.