$Sn(ClO_4)_2$ to $[(CH_3)_2SnCl]^+$ in 9 *M* HCl. This relatively small decrease may be a result of the rather high electronegativity of chlorine.[45]

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The Polymeric Nature of Titanium Tetraethoxide in Solution.
I. Cryoscopic Studies in Benzene

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In carefully dried benzene the molecular weight of $Ti(OC_2H_5)_4$ is independent of concentration over the range 2.0–100.2 × 10^{-3} *m*. The number average degree of polymerization of 2.82 suggests that a single trimeric species is present in solution, contrary to the tetrameric nature of the crystalline solid. No evidence for a time-dependent depolymerization was found and it is suggested that early reports of such behavior and of a concentration dependence of molecular weight resulted from hydrolysis. Experiments with slightly wet benzene (4 × 10^{-3} *m* water) demonstrated that hydrolysis causes an apparent decrease in molecular weight with decrease in concentration.

Although several workers have studied the colligative properties of titanium tetraethoxide in organic solvents, certain features of these results demanded further investigation.

For example, Caughlan, *et al.*,[1] found by cryoscopy in benzene that the degree of polymerization was concentration dependent, increasing from unity at low concentration to a maximum of three.

On the other hand, Bradley, *et al.*,[2] found that the degree of polymerization was constant at 2.4 over a reasonable concentration range in boiling benzene. Recently, Ibers[3] has reported preliminary details of the crystal structure of $Ti(OC_2H_5)_4$ as determined by X-ray diffraction with the very interesting conclusion that the substance is tetrameric in the solid state. At the same time Martin and Winter[4] reported cryoscopic molecular weight measurements over a wide concentration range in benzene and confirmed the concentration dependence of the degree of polymerization at low concentrations. Although their data appear to indicate a trimeric ceiling at higher concentrations, they claim that the results are not adequately described by a monomer–trimer equilibrium but need the presence of a tetrameric species too.

Perhaps the most remarkable results are those due to Nesmeyanov, *et al.*,[5] who presented evidence suggesting that the degree of polymerization of titanium tetraethoxide and other titanium alkoxides determined cryoscopically in benzene solution slowly decreased with time until the monomeric state was reached. Moreover they claimed that the rate of depolymerization increased with increase in temperature and they deduced an "activation energy of dissociation" of 8.0 kcal./mole for titanium tetraethoxide.

We were skeptical of these results and in checking the behavior of titanium ethoxide in benzene solution have found some interesting results which we hope will now clarify the situation.

Experimental

The main purpose of this investigation was to perform cryoscopic measurements on benzene solutions of $Ti(OC_2H_5)_4$ with rigorous precautions to prevent hydrolysis. The cryoscopic method is particularly vulnerable to this source of contamination because atmospheric moisture is readily condensed into the solution when the freezing point determinations are made. If a positive pressure of say dry nitrogen is used to prevent the ingress of moisture considerable errors can be caused by evaporation of the solvent. We used an all-glass double-walled vessel containing a Sargent S-81630 thermistor sealed-in with Fisher Sealit, and a glass-covered magnetic stirrer. The temperature of the system was measured using a thermistor bridge and a Philips PR4069M/04 recorder.

The pure solvent and solute were introduced through the thermistor joint which was then sealed. These filling operations were conducted in an atmosphere of dry nitrogen in a drybox.

Benzene was dried first azeotropically with ethanol and then over Molecular Sieve 4A which had been freshly dried by heating at 200° *in vacuo* for about 4 hr. Titanium tetraethoxide prepared by the usual method[2] was distilled *in vacuo* and the supercooled liquid was added from a special weight pipet. Although this method may not completely exclude moisture due to the filling procedure, sealing of the apparatus must prevent progressive hydrolysis.

The thermistor was calibrated by determining the freezing points of solutions of known concentrations of fluorene in benzene in

[1] C. N. Caughlan, H. S. Smith, W. Katz, W. Hodgson, and R. W. Crowe, *J. Am. Chem. Soc.*, **73**, 5652 (1951).

[2] D. C. Bradley, R. C. Mehrotra, J. D. Swanwick, and W. Wardlaw, *J. Chem. Soc.*, 2025 (1953).

[3] J. A. Ibers, *Nature*, **197**, 686 (1963).

[4] R. L. Martin and G. Winter, *ibid.*, **197**, 687 (1963).

[5] A. N. Nesmeyanov, O. V. Nogina, and V. A. Dubovitskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 8 (1959); 127 (1959).

the range 1.57–5.60 × 10^{-3} m. The coefficient of variation for these measurements was ±4.4% with a most probable error of a single measurement of ±3%. The thermistor was found to give a linear response to temperature over the range 0.01–0.5° by comparison with a Beckmann thermometer. As a further check on the accuracy of cryoscopic molecular weight determinations on solutes at the lowest concentration (*ca.* 2 × 10^{-3} m) some measurements were made on compounds having molecular weights in the 250–400 range; for example: 1,3-hexachlorobutadiene, calcd. 261; found 261, 275; cholesterol, calcd. 386; found 380, 400.

A number of experiments were carried out at different initial concentrations of titanium tetraethoxide, and measurements of the depression of the freezing point were made in a given experiment at various intervals of time, the solution being kept meanwhile at 25° in a thermostat. A sample of pure benzene was kept permanently sealed in a second apparatus as a reference for the freezing point of the pure solvent.

Results and Discussion

No change in molecular weight at a given concentration was found over a period as long as 48 hr. starting with initial determinations within 20 min. of preparing the solution. This lack of time dependence was verified at the concentrations indicated in Table I, which records the results obtained in series 1 using the same batch of benzene. However, these data do show the previously reported increase in molecular weight with concentration and in particular are very similar to the results of Martin and Winter.[4] Unfortunately we cannot assess the reliability of the work of Nesmeyanov, *et al.*,[5] because no experimental details were given. A plausible explanation of their results can be given in terms of hydrolysis. Hydrolysis of titanium ethoxide produces polymeric titanium oxide ethoxides[6] and ethanol as shown in eq. 1, with a net increase in the number of osmotic particles and a consequent *decrease* in apparent molecular weight of the titanium compound. If a small quantity of water is incorporated with each measurement of the freezing point in a series of measurements made at various intervals, it is obvious that an apparent time-dependent depolymerization will be found.

$$n[\mathrm{Ti_3(OC_2H_5)_{12}}] + 4x\mathrm{H_2O} \longrightarrow [\mathrm{Ti_{3(x+1)}O_{4x}(OC_2H_5)_{4(x+3)}}] + 8x\mathrm{C_2H_5OH} + [n - (x+1)][\mathrm{Ti_3(OC_2H_5)_{12}}] \quad (1)$$

TABLE I

MOLECULAR WEIGHTS OF $\mathrm{Ti(OC_2H_5)_4}$ IN BENZENE (SERIES 1)

$\mathrm{Ti(OC_2H_5)_4}$ concn.				
g./100 g. of $\mathrm{C_6H_6}$	m × 10^2	Time at 25°, hr.	Mol. wt.	Deg. of polymerization (n)
0.160	0.702	48	310	1.36
0.250	1.097	..	372	1.63
0.450	1.987	..	429	1.88
0.565	2.480	24	460	2.02
1.130	4.95	4	562	2.46
1.420	6.23	4	594	2.60
1.770	7.76	..	608	2.66
2.285	10.02	48	630	2.76

TABLE II

MOLECULAR WEIGHTS OF $\mathrm{Ti(OC_2H_5)_4}$ IN BENZENE (SERIES 2)

$\mathrm{Ti(OC_2H_5)_4}$ concn.			
g./100 g. of $\mathrm{C_6H_6}$	m × 10^2	Mol. wt.	Deg. of polymerization (n)
0.080	0.351	710	3.12
0.120	0.526	624	2.74
0.310	1.360	615	2.70
0.935	4.10	630	2.76
1.235	5.41	652	2.86
1.620	7.105	656	2.88
1.770	7.76	652	2.86

TABLE III

MOLECULAR WEIGHTS OF $\mathrm{Ti(OC_2H_5)_4}$ IN BENZENE (SERIES 3)

$\mathrm{Ti(OC_2H_5)_4}$ concn.			
g./100 g. of $\mathrm{C_6H_6}$	m × 10^2	Mol. wt.	Deg. of polymerization (n)
0.080	0.351	633	2.77
0.215	0.943	598	2.62
0.360	1.578	612	2.68
0.500	2.195	643	2.82

When a second series of experiments was conducted with a fresh batch of benzene, we found that at low concentrations the results differed significantly from those in series 1. In fact the data for series 2 in Table II suggest that there is no significant change in molecular weight with concentration. These results were confirmed in series 3 (reported in Table III) starting with another batch of freshly dried benzene. It was then found that the freezing point of the benzene used for series 1 was about 0.03° lower than the freezing points of samples 2 and 3, which were the same within experimental error. Actually the benzene for series 1 had been kept stoppered with an ungreased standard tapered stopper in a drybox for some days prior to use and may have picked up some moisture, and it seemed possible that the concentration dependence of the molecular weights in Table I was caused by hydrolysis. Assuming that titanium tetraethoxide and the titanium oxide ethoxides belong to the series $[\mathrm{Ti_{3(x+1)}O_{4x}(OC_2H_5)_{4(x+3)}}]$ (where $x = 0, 1, 2, 3 \ldots .$) suggested by Bradley, *et al.*,[6] and that the degree of polymerization of each species is independent of concentration, it is possible to calculate the concentration of water required in the benzene to give the observed apparent molecular weight of the added titanium ethoxide (*i.e.*, according to eq. 1). Thus the $(n + 4x)$ osmotic particles on the left-hand side of eq. 1 become $(n + 7x)$ osmotic particles due to hydrolysis. However, we must subtract the $4x$ particles from both sides because the depression of the freezing point was referred to "wet" benzene. Hence the original n moles of trimer behave after hydrolysis as if $(n + 3x)$ moles of particles were present. From the observed apparent molecular weight the values of $4x$ can then be calculated. From the apparent molecular weights and concentrations given in Table I values of $4x$ were deduced, and the results are given in Table IV. An average value of 4.4 × 10^{-3} m with a coefficient of variation of ±16% was derived for the initial concentration of water in benzene required to explain the molecular weight data. In order to check the validity of this

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(6) D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.*, 3977 (1955).