566. *The Association of n-Tetra-alkoxy- and n-Alkoxy-chloro-derivatives of Titanium.*

By R. L. MARTIN and G. WINTER.

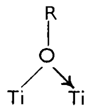
The temperature and concentration-dependence of the molecular association of tetrabutoxytitanium(IV) has been measured in benzene solution by cryoscopic and calorimetric methods. Although the association follows a reaction of the third order it probably proceeds through an unstable dimer, $Ti_2(OBu)_8$. The energy of the intermolecular bonding between pairs of titanium atoms is 9·8 kcal. $mole^{-1}$. The chlorine derivatives $TiCl(OBu)_3$, $TiCl_2(OBu)_2$, and $TiCl_3{\cdot}OBu$ are trimeric, dimeric, and monomeric, respectively.

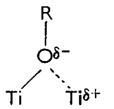
A structural hypothesis is postulated which differs from previous models in that a triangular rather than a linear arrangement of titanium atoms is envisaged.

A new and sensitive cryoscopic technique is described.

ALTHOUGH the tendency of n-alkyl titanates $Ti(OR)_4$ to associate is now well established,[1-5] the constitution of the resulting polymer remains open to speculation. It is generally believed [4-6] that association results from the ability of titanium to expand its co-ordination number when in an environment of donor atoms, but conclusive structural evidence is lacking to show whether quadrivalent titanium is five- or six-covalent in its alkoxides. No attempt has been made to measure directly the strength of the intermolecular bond which is believed to link pairs of metal atoms through alkoxide bridges as was first suggested for thallium(I) methoxide in 1930 by Sidgwick and Sutton;[7] whether the bond is predominantly covalent (Ia) or electrostatic (Ib) is still unknown. While it is generally accepted that n-alkyl titanates associate to form trimers, the experimental evidence on

(Ia)





(Ib)

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[1] Bradley, Mehrota, Swanwick, and Wardlaw, *J.*, 1953, 2025.

[2] Winter, *J. Oil Colour Chemists' Assoc.*, 1953, **36**, 689; M.Sc. Thesis, University of N.S.W., 1956.

[3] Bradley, Gaze, and Wardlaw, *J.*, 1957, 469.

[4] Coughlan, Smith, Katz, Hodgson, and Crowe, *J. Amer. Chem. Soc.*, 1951, **73**, 5652.

[5] Cullinane, Chard, Price, Millward, and Langlois, *J. Appl. Chem.*, 1951, **1**, 400.

[6] Bradley, *Nature*, 1958, **182**, 1211.

[7] Sidgwick and Sutton, *J.*, 1930, 1461.

which this conclusion is based is sometimes in conflict, as may be seen from Table 1 which summarises some data from the literature.

In the present investigation, an attempt has been made to ascertain the energy of intermolecular bonding by measuring cryoscopically and calorimetrically the variation with concentration of the degree of association in benzene solution. The n-butoxide was selected as a typical ester of medium chain length, and mixed chloro- and butoxy-derivatives were also studied.

Association of Tetrabutoxytitanium(IV) *and its Chloro-derivatives in Benzene*.—The association of tetra-alkyl titanates has been investigated cryoscopically in benzene in the concentration range 0—0·03 (molar fraction of solute) by Coughlan *et al.*[4] For the compounds $Ti(OEt)_4$, $Ti(OPr)_4$, $Ti(OBu)_4$, and $TiCl(OEt)_3$, the degree of association increased from one to a maximum value of three in the concentration range 0—0·01. At higher concentrations, the association number was found to decrease with increasing concentration, a result which is incompatible with any reasonable scheme envisaged for an association equilibrium dependent on concentration and temperature alone.

The present data for three independent series of molecular-weight determinations for tetrabutoxytitanium in benzene over the range 0—15 × 10^{-2}m are shown in Fig. 1. The curve represents the increase in average molecular weight with mass of tetrabutoxytitanium added, and becomes asymptotic towards the molecular weight of the trimer (1020) as the concentration is increased. No evidence for a maximum in the degree of association, observed by Coughlan *et al.*, was found in the present study. Thus, the limiting molecular complexity of three observed here is in line with the accepted view that the n-alkyl titanates are trimeric in the pure state.

TABLE 1. *Molecular complexity of n-alkyl titanates* $Ti(OR)_4$.

Alkyl	Method	Solvent	Concn. (10^{-3} mol. fraction)	Complexity	Authors
Ethyl	Ebull.	Benzene	1·3—8·0	2·4	Bradley *et al.*[1]
Butyl	,,	Butanol	5·9	1·14	Winter [2]
			6·7	1·17	
			10·3	1·28	
			11·7	1·29	
			16·1	1·40	
			18·1	1·41	
Butyl	,,	,,	5·0	1·0	Bradley *et al.*[1, 3]
Pentyl	,,	Benzene	1·1—7·0	1·4	
Octyl	,,	,,	2·5—8·1	1·4	
Propyl	Cryosc.	,,	3·7	1·0	Coughlan *et al.*[4]
			8·9	2·4	
			13·3	3·0	
			17·8	2·9	
			21·7	2·8	
			28·3	2·7	
			36·1	2·5	
Butyl	,,	,,	6·0	2·01	Cullinane *et al.*[5]
			11·4	2·04	
			14·5	2·05	
Butyl	,,	,,	3·1	1·0	Coughlan *et al.*[4]
			5·0	1·3	
			8·3	3·0	
			12·2	3·0	
			22·0	2·8	
			23·0	2·8	

The existence of monomeric and trimeric entities in benzene solution is established by the present work and, since effective collisions between three monomer molecules are likely to be uncommon, the dissociation is here visualized as a two-step reaction:

$$M_3 \rightleftharpoons M_2 + M_1 \qquad (1)$$

$$M_2 \rightleftharpoons 2M_1 \qquad (2)$$

where M_3, M_2, and M_1 represent trimer, dimer, and monomer, respectively. The equilibrium constants K_1 and K_2 for reactions (1) and (2) can be written:

$$K_1 = [M_2][M_1]/[M_3] \tag{3}$$

and

$$K_2 = [M_1]^2/[M_2] \tag{4}$$

If M_0 represents the mass of tetrabutoxytitanium added to the benzene solution, then

$$[M_0] = 3[M_3] + 2[M_2] + [M_1], \tag{5}$$

or from equations (3) and (4), we have

$$[M_0] = \frac{3[M_1]^3}{K_1K_2} + \frac{2[M_1]^2}{K_2} + [M_1], \tag{6}$$

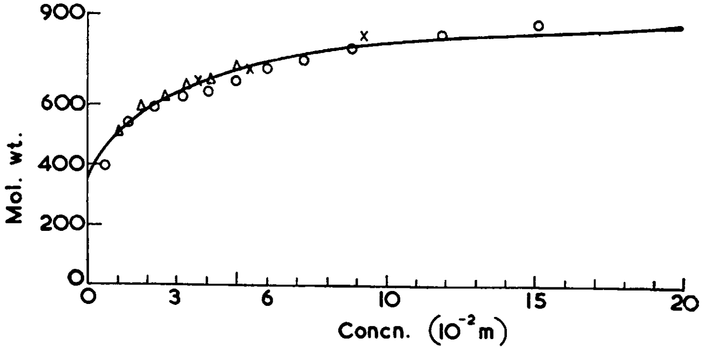
from which the relative concentrations of M_1, M_2, and M_3 can be calculated if K_1 and K_2 are known.

The experimental results can be fitted by trial-and-error selection of values for K_1 and K_2; it is found that there is a good fit only when K_2 is increased to such a value that the concentration of M_2 becomes negligible; equation (6) then reduces to

$$[M_0] = 3[M_1]^3/K + [M_1]. \tag{7}$$

Selecting $K = 1 \times 10^{-4}$ gives a calculated curve (see Fig. 1) which fits the experimental results closely, and confirms the view that the maxima observed by Coughlan *et al.* are incompatible with a reasonable model for the system. The dissociation of tetrameric methoxythallium(I) in benzene was found by Sidgwick and Sutton [7] to give a similar curve.

FIG. 1. *Variation of molecular weight with concentration of tetrabutoxytitanium*(IV).



Curve, calc. for $K = 1 \times 10^{-4}$

While equation (7) represents a reaction of the third order, it is extremely unlikely that the association of M_1 to M_3 involves an effective three-bodied collision, and it is more reasonable to assume that the reactions involving M_1 are really bimolecular. Since K_2 is very large, the dimer M_2 is unstable with respect to the monomer M_1.

Successive replacement of butoxy-groups by the more electronegative chlorine has a profound influence on the association equilibrium. Replacement of one group so stabilizes the trimer that no dissociation is observed at concentrations where tetrabutoxytitanium is nearly completely dissociated (cf. Fig. 2). This suggests that the positive charge, and hence acceptor properties, of the central titanium atom have been increased, with concomitant increase in the strength of the alkoxy-bridge. Dichlorodibutoxytitanium, $TiCl_2(OBu)_2$, is dimeric and also does not dissociate in the concentration range examined (cf. Fig. 2). Butoxytrichlorotitanium, $TiCl_3 \cdot OBu$, like titanium tetrachloride, is monomeric and displays no tendency to associate. Coughlan *et al.* reported a limiting association number of three for chlorotriethoxytitanium, $TiCl(OEt)_3$, in benzene.

The Strength of the Intermolecular Butoxy-bridge.—Dissociation of tetrabutoxytitanium(IV) was also followed calorimetrically, by measuring the variation, with concentration, of its heat of solution in benzene at 30°. The reaction is endothermic since rupture of intermolecular butoxy-bridges is involved; the heat absorbed per mole of ester is plotted against concentration in Fig. 3.

FIG. 2. *Molecular weights of alkoxytitanium chlorides.*

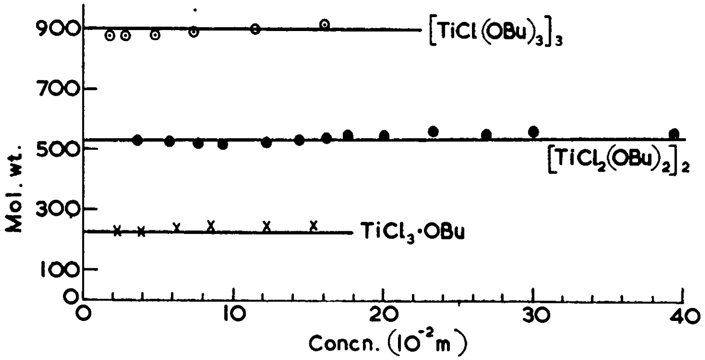
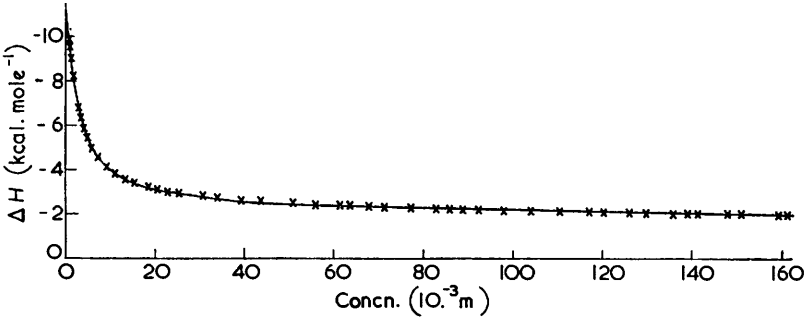


FIG. 3. *Variation of heats of solution (per mole of solute) with concentration of tetrabutoxytitanium*(IV).



The total energy change (ΔH), when the pure liquid trimer is completely dissociated and solvated in benzene solution, can be estimated by extrapolating the curve to zero concentration, giving a value *ca.* 11 kcal./mole. The major factors contributing to this are likely to be the heat of solution of the trimer in benzene, ΔH_S, M_3 (liquid) $\rightleftharpoons$ M_3 (solution), and the energy required to dissociate the trimer to the monomer, ΔH_B, M_3 (solution) $\rightleftharpoons$ $3M_1$ (solution), where ΔH_S and ΔH_B are expressed per titanium atom. For the present purpose, it is assumed that the interaction forces between titanium and benzene are small and independent of the state of aggregation. It follows that at a given concentration,

$$Q \approx [M_1]\Delta H_B + [M_0]\Delta H_S. \qquad (8)$$

The experimental results can again be closely fitted, by trial-and-error methods, by selecting $\Delta H_S = 1{\cdot}24$ kcal./mole and using 4×10^{-6} as the equilibrium constant defined by equation (7). The experimental result, Q, the values of $[M_1]\Delta H_B$ obtained from equation (8), and those calculated from equation (7) are compared in Fig. 4.

It is also possible to obtain an independent but approximate value for ΔH_B from the two equilibrium constants, $K_{5\cdot5^\circ}$ (cryoscopic), and K_{30° (calorimetric), and to compare this value with that obtained by extrapolation of the ΔH curve. Application of the integrated form the van't Hoff equation gives $-\Delta H_{\mathrm{B}} \approx 8$ kcal./mole, which may be compared with the value 9·8 kcal./mole (*i.e.*, 11 — ΔH_{S} kcal./mole) obtained by extrapolation of the experimental heats of solution to zero concentration. The agreement is satisfactory in view of the implicit assumptions, and in particular it is unlikely that solvent–solute interaction (ΔH_{S}) is the same for both the monomer and the trimer.

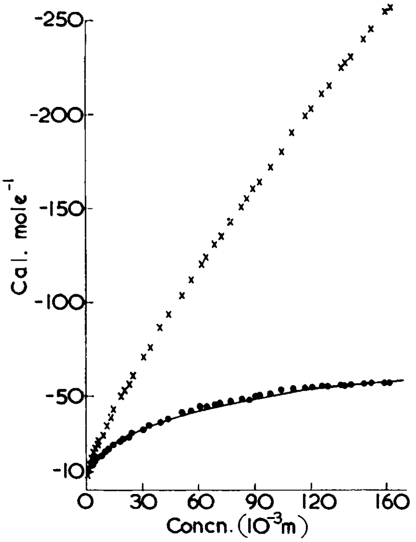


FIG. 4. *Q and* $[\mathrm{M_1}]\Delta H_{\mathrm{B}}$ *as a function of concentration of tetrabutoxytitanium*(IV).

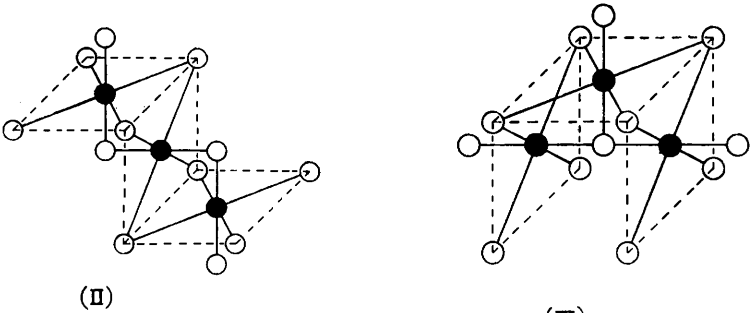
× Exptl. Q. ● Exptl. $Q - 1{\cdot}24[\mathrm{M_0}]$.

Curve: Calc. for $\mathrm{M_1} \times 9{\cdot}76$; $K = 4 \times 10^{-6}$.

The present value for the intermolecular-bridge energy, 9·8 kcal./mole, resembles the *ca.* 10 kcal./mole estimated by Bradley *et al.*[1] for tetraethoxytitanium. If the structure of the trimer involves two alkoxy-bridges per titanium atom, each alkoxide bridge will contribute 4·9 kcal./mole. This value is similar in magnitude to the energy of a hydrogen bond [8] and suggests that the intermolecular bonding in n-alkyl titanates is predominantly electrostatic (cf. formula 1b).

Structures.—The present work has confirmed the view that tetrabutyl titanate associates by means of weak intermolecular titanium–oxygen bonds and that polymerization ceases abruptly at the trimer. Coughlan *et al.* ascribed the association to the tendency of quadrivalent titanium to attain a six-covalent environment, as, for example, in rutile or anatase. They suggested that each pair of titanium atoms was supported by three-bridging alkoxy-groups, giving alternative structures (II) and (III), which are based on

Structures proposed by Coughlan et al.[4] *for* $\mathrm{Ti_3(OR)_{12}}$.



(II) (III)

● Ti. ○, O in OR.

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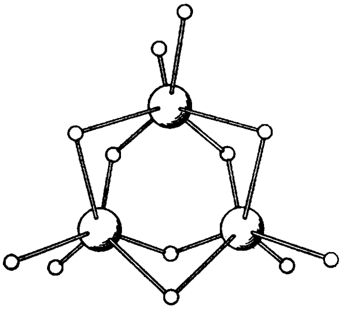
[8] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1948, p. 284.

the stacking of three TiO_6 octahedra face to face. Structure (III) necessitates a four co-ordinated square-planar oxygen atom attached to three titanium atoms and one alkyl group, and for this reason is considered here to be untenable. Structure (II) has been widely accepted and in particular, the group working at Birkbeck College [3,9] have stressed this arrangement when discussing the hydrolysis of n-alkyl titanates. This model is attractive as it is consistent with a co-ordination number of six for all the titanium atoms and limits the maximum association to three monomer units. However, a disadvantage is an inherent asymmetry which necessitates the central titanium atom being surrounded by six butoxy-bridges with the remaining titanium atoms each carrying three terminal and three butoxy-bridges. The need for high symmetry becomes apparent in the interpretation of the structure of trimeric tributoxychlorotitanium, $Ti_3Cl_3(OBu)_9$, where a triangular, rather than a linear, arrangement of the metal atoms would provide a higher natural symmetry and enable one chlorine atom to be bound to each titanium atom.



(IV)

Proposed cyclic structure for $Ti_3(OR)_{12}$ *based on* TiO_6 *trigonal prisms.*

Two stereochemical arrangements incorporating this concept have been proposed by the present authors.[10] One is based on a six-covalent oxygen environment for titanium, but a trigonal prismatic, rather than an octahedral, arrangement of the TiO_6 group is envisaged. This leads to structure (IV) in which two " bridge " and two " terminal " alkoxy-groups per titanium atom are present. A scale model reveals that twelve n-alkyl groups can be nicely accommodated about the three titanium atoms; it can accommodate either one or two terminal chlorine atoms per titanium atom and retain a high degree of symmetry.

The higher stability of $Ti_3Cl_3(OBu)_9$ than of $Ti_3(OBu)_{12}$ probably arises from the greater induced positive charge ($\delta+$) on the metal leading to stronger intermolecular bonding $(\overset{\delta+}{Ti}-\overset{\delta-}{O}\cdots\overset{\delta+}{Ti})$. From this point of view the stabilities of dibutoxydichlorotitanium and butoxytrichlorotitanium might be expected to increase with increasing chlorine content, if no steric interactions occur. In fact, neither ester is trimeric, but dibutoxydichlorotitanium is dimeric, $Ti_2Cl_4(OBu)_4$, and displays no tendency to dissociate (or associate), while the trichloro-compound $TiCl_3{\cdot}OBu$, like titanium tetrachloride, remains monomeric at all concentrations studied.

The monomeric nature of butoxytrichlorotitanium may well be evidence that a minimum number of two alkoxy-groups per titanium is a prerequisite for association, in harmony with both the structures (II) and (IV). If so, then titanium must exhibit six-covalency in its alkoxychloro-derivatives but their structure cannot be based on an octahedral stereochemistry for titanium. However, the above evidence is not unambiguous, for the inability of butoxytrichlorotitanium to associate may be a further manifestation of redistribution in electron density due to introduction of chlorine. Thus, the presence of three chlorine atoms may exert a cumulative inductive effect on titanium sufficiently large

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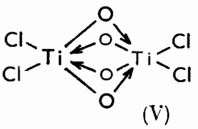
[9] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.
[10] Martin and Winter, *Nature*, 1960, **188**, 313.

to induce appreciable p_π–d_π bonding between the oxygen and titanium atoms and under these conditions association would not be expected. It seems unlikely that the steric effect of three chlorine atoms would be sufficient to hinder association, for titanium tetrachloride is known to form adducts with a large number of donor molecules.

The structure of the dimeric species, $Ti_2Cl_4(OBu)_4$, is open to speculation, but the high stability is consistent with a structure such as (V) which is based on a minimum requirement of two alkoxy-bridges per titanium atom. This requires a two-bodied collision of tetrahedral monomers and only a small rearrangement of bond angles. Further association to a trimer (IV) by collision with a third monomer would necessitate rupture of two bridges already stabilized by the high positive charge on the titanium. In this structure each titanium atom is involved in a six-covalent environment based on $TiCl_2O_4$ trigonal prisms sharing a common face.

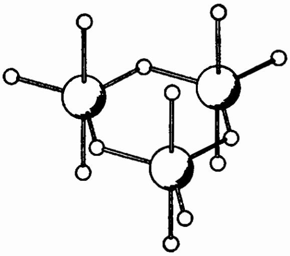


(V)

The cryoscopic and calorimetric results show that the dimer of tetrabutoxytitanium is relatively unstable; electronegative chlorine substituents are apparently necessary to stabilize structure (V). The positive charge induced on titanium by only one chlorine atom seems, however, insufficient to stabilize the dimer, and a further collision with monomer leads to the trimer in which the bond angles are somewhat more favourable for a strain-free structure.

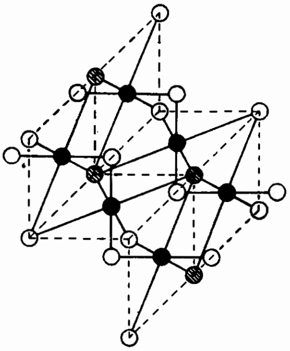
This interpretation is based on the concept that titanium achieves covalent saturation with a co-ordination number of six. Andersson and Wadsley[11] recently established by *X*-ray methods that quadrivalent titanium is five-covalent in the mixed oxide $K_2Ti_2O_5$. The TiO_5 grouping is trigonal bipyramidal, and on this basis they have suggested to us that structure (VI) provides an alternative stereochemical arrangement for $Ti_3(OBu)_{12}$ and $Ti_3Cl_3(OBu)_9$. This differs from structure (IV), not only in the five-covalency of titanium, but also in that only one alkoxy-bridge per titanium is present.

Alternative cyclic structure for $Ti_3(OR)_{12}$ *based on* TiO_5 *trigonal bipyramids.*



(VI)

Structure proposed by Bradley et al.[9] *for* $Ti_6O_4(OR)_{16}$.



(VII)

● Ti. ○ O in OR. ▨ O in Ti–O–Ti.

Hydrolysis of Titanium Alkoxides.—Bradley and his co-workers[3,9] studied the hydrolysis of the alkoxides in boiling butanol, a strong donor solvent, and established that the titanium oxide alkoxides, $TiO_n(OR)_{4-2n}$, formed are low polymers such as $Ti_6O_4(OR)_{16}$ and $Ti_{12}O_{12}(OR)_{24}$. These products were explained in terms of interaction of water with structure (II) to give a structure such as (VII) for $Ti_6O_4(OR)_{16}$. A polymerization of this kind would require a statistically unfavourable mutual orientation of two partly hydrolysed $Ti_3(OH)_4(OR)_8$ units before effective collision and expulsion of four water molecules could occur, and would require also the preferential hydrolysis of two terminal and two bridging

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[11] Andersson and Wadsley, *Nature*, 1960, **187**, 499.

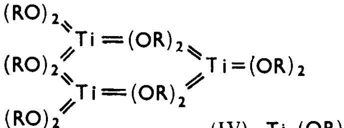
alkoxide groups from only one edge of the parent trimer. Further, it involves an unknown four-covalent bonding arrangement between oxygen and its nearest four titanium neighbours.

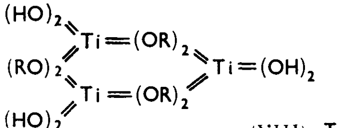
A hydrolysis mechanism based on the cyclic model (IV) can still logically lead to titanium oxide alkoxide polymers $TiO_n(OR)_{4-2n}$, yet is more amenable to kinetic interpretation. Hydrolysis of terminal alkoxy-groups, intermolecular elimination of alcohol, and intramolecular elimination of water are suggested as likely successive stages. Such a mechanism involves a kinetically simple two-point collision, and a possible scheme would be as follows (b = bridge; t = terminal group):

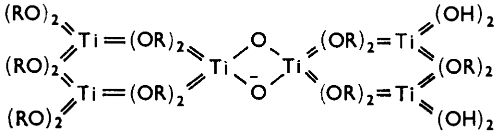
(i) $Ti_3(OR)_6{}^b(OR)_6{}^t + 6H_2O \longrightarrow Ti_3(OR)_6{}^b(OH)_6{}^t + 6ROH$
(see structure VIII)

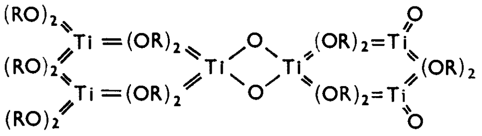
(ii) $Ti_3(OR)_6{}^b(OH)_6{}^t + Ti_3(OR)_6{}^b(OR)_6{}^t \longrightarrow (RO)_4{}^t(RO)_6{}^bTi_3(O)_2{}^bTi_3(OR)_6{}^b(OH)_4{}^t + 2ROH$
(see structure IX)

(iii) $(RO)_4{}^t(RO)_6{}^bTi_3(O)_2{}^bTi_3(OR)_6{}^b(OH)_4{}^t \longrightarrow (RO)_4{}^t(RO)_6{}^bTi_3(O)_2{}^bTi_3(OR)_6{}^b(O)_2{}^t + 2H_2O$
(see structure X)


(IV) $Ti_3(OR)_{12}$


(VIII) $Ti_3(OR)_6(OH)_6$


(IX) $Ti_6O_2(OR)_{16}(OH)_4$


(X) $Ti_6O_4(OR)_{16}$

The structures of the participating entities are represented diagrammatically by (IV), (VIII), (IX), and (X). Further hydrolysis of $Ti_6O_4(OR)_{16}$ by this mechanism could lead to polymers such as $Ti_9O_8(OR)_{20}$ and $Ti_{12}O_{12}(OR)_{24}$ as observed by Bradley and his colleagues.*

Whether the titanium is five- or six-covalent, octahedral or trigonal prismatic, must rest on a complete structure analysis. However, it is suggested that a structure based on a triangular rather than a linear arrangement of the titanium atoms is more consistent with the known chemistry of n-alkyl titanates.

EXPERIMENTAL

Tetrabutoxytitanium(IV).—This compound was prepared as described by Kraitzer, McTaggart, and Winter.[12] It was always freshly distilled before use (Found: TiO_2, 23·5. Calc. for $C_{16}H_{36}O_4Ti$: TiO_2, 23·5%).

Chlorotributoxytitanium(IV).—This was prepared by treatment of 1·0 equiv. of tetrabutoxytitanium with 0·9 equiv. of acetyl chloride, followed by distillation and fractionation of the crude ester at 1 mm. (Found: TiO_2, 26·9; Cl, 11·7. Calc. for $C_{12}H_{27}ClO_3Ti$: TiO_2, 26·4; Cl, 11·7%).

Dichlorodibutoxytitanium(IV).—Titanium tetrachloride (1·0 equiv.) was added slowly to butan-1-ol (2·0 equiv.) with cooling. Hydrogen chloride formed was removed under reduced pressure, and the crude ester distilled and fractionated at 1 mm. (Found: TiO_2, 29·9; Cl, 26·8. Calc. for $C_8H_{18}Cl_2O_2Ti$: TiO_2, 30·2; Cl, 26·8%).

Trichlorobutoxytitanium(IV).—The ester, prepared from titanium tetrachloride (1·0

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* For a further discussion concerning the structures of tetra-alkyl titanates and their hydrolysis products, see Bradley and Westlake, and Martin and Winter (*Nature*, 1961, in the press).

[12] Kraitzer, McTaggart, and Winter, *J. Council Sci. Ind. Res. Australia*, 1948, **21**, 328.

equiv.) in hexane with butan-1-ol (1·0 equiv.), was twice washed with hexane and twice crystallized from benzene (Found: TiO_2, 35·6; Cl, 46·3. Calc. for $C_4H_9Cl_3OTi$: TiO_2, 35·6; Cl, 46·8%).

Benzene.—Benzene used for the cryoscopic and calorimetric work was purified by treating it five times with concentrated sulphuric acid, washing it until neutral, and drying it (Na_2SO_4, then CaH_2). It was distilled through a column (*ca.* 80 theor. plates), and the fractions freezing at 5·48° (or better) were combined and fractionally crystallized.

Cryoscopy.—The classical Beckmann procedure was found to be too insensitive for the present measurements, since dissociation of alkyl titanates in benzene commences at very low concentrations. A more sensitive apparatus was developed which permitted exclusion of moisture and minimized errors due to irregular supercooling. The apparatus (Fig. 5) consisted of a ring shaped cell (A) to which were attached four B/10 sockets (B) and one B/7 socket (C). Accurately shaped and drilled Teflon cones, each holding one thermistor (Stantel F2311), were inserted at B in such a way that the tips of the thermistors were approximately 5 mm. below the liquid level. The opening (C) which served for filling and for the addition of the samples was stoppered with a sealed B/7 male cone. To avoid ingress of moisture the joints were protected with serum caps. Mixing was by a glass-covered steel ball moved by a magnet (D) (100 r.p.m.). Supercooling was minimized by provision of finely powdered glass sintered along the path of the ball. Cooling was by water at 1·5° ± 0·05° passed through the jacket (E). Rubber spacer-rings prevented direct contact of the cell with the jacket. During operation the top of the cell and jacket was covered with cotton wool. The whole assembly was surrounded by a shield (F) made from 1/8 in. steel plate, to eliminate magnetic interference with the electrical circuit.

FIG. 5a. *Cryoscope.*

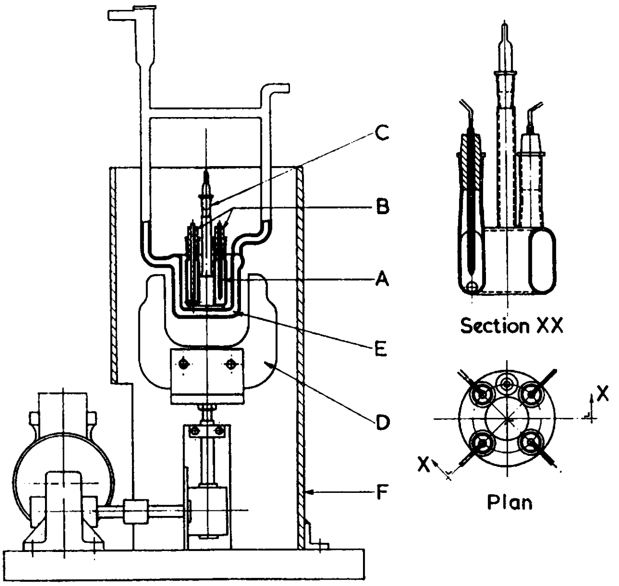
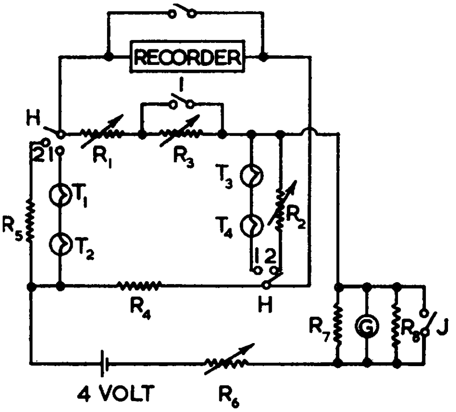
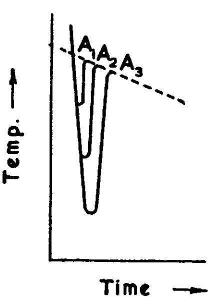


FIG. 5b. *Bridge circuit for cryoscope.*



T_1, T_2, T_3, T_4, Thermistors type F2311. R_1, R_2, 0—10^4 Ω Decade box. R_3, 0—10^3 Ω Decade box. R_4, R_5, 7·5 × 10^3 Ω Wire wound resistance. R_6, 2 × 10^3 Ω Potentiometer. R_7, 20·8 Ω Wire wound resistance. R_8, 1 × 10^3 Ω Resistance. G, Spot galvanometer. H, Double pole, double-throw switch. I, J, Single pole switch.

FIG. 6.

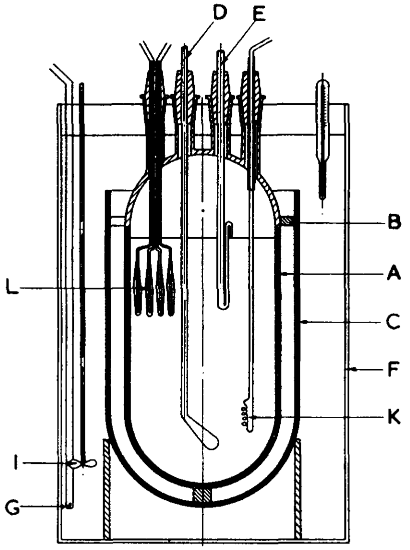


The variation in resistance of the thermistors with change in temperature was measured by means of a Wheatstone bridge and recorded automatically on a Varian recorder. The applied current (0·5 milliamp.) was measured by a damped galvanometer (G). Adjustments could be made with the potentiometer (R_6). Drifts in the circuit could be observed and allowed for by disconnecting the thermistors through switch (H) and replacing them by the two resistances R_2 and R_5. The degree of supercooling was measured by operating the decade box (R_3)

which could be short-circuited by means of switch (I) immediately after crystallization had commenced.

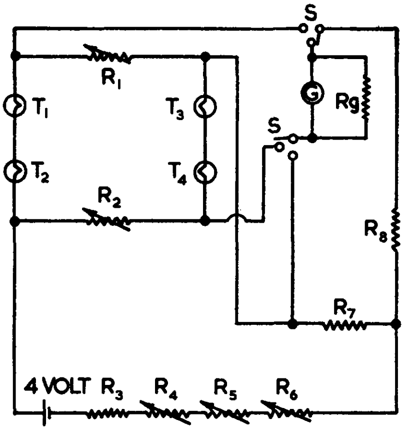
In the classical cooling-curve method, the true freezing point is determined by extrapolating the freezing-point curve to zero supercooling. Provided the concentration of the solute is not very large and the freezing is not allowed to proceed for too long, very little difficulty is met owing to the non-linearity of this curve. If, however, the sensitivity of the temperature-measuring device is increased, as with the present instrument, the non-linearity is accentuated to such a degree that extrapolation becomes impossible. To overcome this a different approach was chosen to determine the true freezing point at zero supercooling. The maximum temperature reached by the system (A_1, A_2, A_3 in Fig. 6) was found to be a linear function of the degree of supercooling. When this relationship had been established for each solute concentration, no difficulty in extrapolation was encountered provided the degree of supercooling was not too great.

FIG. 7a. *Calorimeter.*



A, 1-l. vacuum-jacketted vessel. B, Cork ring. C, 3-l. open-mouthed Dewar flask. D, Stirrer (*ca.* 100 r.p.m.). E, Pipette for addition of sample. F, Oil-bath. G, Heater. I, Stirrer. K, Calibration coil (*ca.* 50 ohms). L, Thermistors (Stantel F2311).

FIG. 7*b*. *Bridge circuit for calorimeter.*



T_1, T_2, T_3, T_4, Thermistors type F2311. R_3, R_9, 10,000 Ω Resistance. R_1, R_2, 10,000 Ω Decade box. R_4, 10,000 Ω Potentiometer. R_5, 1000 Ω Potentiometer. R_6, 100 Ω Potentiometer. R_7, 2·4 Ω Resistance. R_8, 4000 Ω Resistance. S, Double pole, double-throw switch. G, Cambridge galvanometer; 450 Ω resistance.

The method was evaluated by molecular-weight determinations on a number of pure organic compounds, with azobenzene as a calibrant. The results are shown in Table 2.

TABLE 2. *Accuracy of cryoscopic technique*

Compound	Concn. range (10^{-2} m)	Mol. wt. found	Mol. wt. calc.	No. of detns.
Biphenyl	1·03—11·69	158·5	154·2	8
Me stearate	1·08—8·09	296·2	298·5	5
1-Chloro-2,4-dinitrobenzene	3·50—8·84	209·4	202·5	3
Ph benzoate	1·31—12·98	200·0	198·5	7
Naphthalene	1·35—15·92	131·9	128·2	10

Heats of Solutions.—The heats of solution were measured in a calorimeter of 1-l. capacity as shown in Fig. 7. Variations in the resistance of the thermistors were measured with a Wheatstone bridge which incorporated a circuit for checking accurately the stability of the current applied. The optical arm of the galvanometer was 3·6 m. A galvanometer deflection of 1 mm. corresponded to approximately 1 × 10^{-4} °. Calibration was effected by applying an accurately measured current to the heating coil.

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